Activation of key exhaust components from advanced combustion of future fuels

Master's Thesis in Nanoscale Science and Technology

Samuel Antonio Rosas Melendez

Department of Chemical and Biological Engineering
Competence Center for Catalysis - KCK
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2010

Activation of key exhaust components from advanced combustion of future fuels

Samuel Antonio Rosas Melendez

Master's Thesis in Nanoscale Science and Technology
Department of Chemical and Biological Engineering
Division of Competence Center for Catalysis - KCK
CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden, 2010

Supervisor: Assitant Professor Per-Anders Carlsson, Competence Center for catalysis
Examiner: Professor Magnus Skoglundh, Competence Center for catalysis

Activation of key exhaust components from advanced combustion of future fuels
Master's Thesis in Nanoscale Science and Technology
SAMUEL ANTONIO ROSAS MELENDEZ
Department of Chemical and Biological Engineering
Competence Center for Catalysis - KCK
Chalmers University of Technology

Abstract

The transportation sector is the second largest contributor of CO_2 emissions to the atmosphere. In order to reduce CO_2 emissions produced by the combustion of conventional, fossil-based, fuels such as gasoline and diesel. The use of hydrogen and electricity as the energy source in the transportation sector is promising. However, these two technologies are still too expensive to replace conventional fossil-based fuels, so much interest has been shown to the use of alternative fuels as bridging technologies. This includes reformulated gasoline, compressed natural gas, liquefied petroleum gas, dimethyl ether, alcohols and biodiesel.

Although CO_2 emissions are reduced using such alternative fuels, other types of emissions are produced. These emissions are usually unburned fuels and products from partial oxidation. These emissions not only cause health problems, but also are a main factor for the production of photochemical smog. In order to avoid the release of these emissions to the atmosphere, a total oxidation towards CO_2 should be performed. For vehicles, this is achieved by after-treatment using catalytic converters.

For this project two catalytic systems were prepared: Pt/Al_2O_3 and Pt/CeO_2. The oxidation of different hydrocarbons and oxygenates over the two catalysts were studied by temperature-programmed, step-response and pulse-response experiments for a total of nine representative compounds of alternative fuels, namely, methane, ethane, propane, ethylene, acetylene, propylene, allene, dimethyl ether and acetaldehyde.

Experimental data demonstrate that saturated hydrocarbons are more difficult to oxidize than non-saturated hydrocarbons or compounds in a higher state of oxidation. It was also concluded that the most efficient system to catalytically oxidize saturated hydrocarbons was Pt/Al_2O_3 under net-reducing (rich) conditions. For non-saturated hydrocarbons and the aldehyde, the oxidation was more efficient with Pt/CeO_2 under net-oxidizing (lean) conditions. The ether was oxidized in a more efficient way with the Pt/CeO_2, however, under rich conditions.

Keywords: Environmental catalysis, emissions, alternative fuels, catalytic oxidation, hydrocarbons, platinum, alumina, ceria

Acknowledgements

First of all, I want to thank Magnus Skoglundh, my examiner, for giving me the opportunity to do this project in the KCK and be involved in the world of catalysis.

I will give thanks specially to my supervisor, Per-Anders Carlsson. He gave me not only the chance to be involved in this world of environmental catalysis, but also gave me the freedom to work in this project at my rhythm and make my own decisions in order to give form this project.

Special thanks to the people working and making their thesis in the KCK. They made a very friendly environment and were very open to work by my side. In particular, I would like to thank Lisa Kylhammar, who provided a lot of help during the preparation of my samples. And last, but not least, to Lars Lindström, who also helped me very much during the experimental sessions.

Contents

To Santiago, Paulina and the ones to come

For them to know I wanted them to breathe a better air

1 Introduction

Ever since the discovery of fire, mankind has been dependent on combustion of various fuels. In the beginning combustion of wood provided a source of energy for heat and cooking. Today, combustion of petroleum and its derivatives provides a series of products and services worldwide. However, apart from giving the necessary energy for industrial, household and transportation sectors, the combustion of fuels is also a source of organic byproducts that impact both air quality and climate. Besides the principal products, i.e., carbon dioxide (CO_2) and water vapor, trace gasses and particulate emissions are also produced.

Carbon dioxide is a gas that naturally appears in the Earth's atmosphere in low concentrations (i.e. 390 ppm) [1]. Plants use CO_2 during photosynthesis for the production of carbohydrates. One of its main problems is that at higher concentrations, CO_2 can cause health effects. Probably more important is the fact that it is a greenhouse gas (GHG). The main problem is that GHG absorb and emit electromagnetic radiation that is claimed to contribute to an increase of the global temperature with climate changes, melting snow and ice caps and rising sea levels as results [2]. Combustion of fossil fuels has led to an increase of the CO_2 level in the atmosphere such that in 2005 its atmospheric concentration was increased by 35% as compared to the preindustrial level [3].

The transport sector is the second largest contributor of carbon dioxide emissions, after electricity generation [4]. Transports have contributed to 15% of the CO_2 emissions since pre-industrial times and grew by 25% between 1990 and 2000 [5]. The most significant emitters are light-duty and heavy-duty vehicles, accounting for 50% and 33%, respectively, of the global CO_2 emissions. The remaining part originates essentially from aircraft, sea transport and railway [6].

The transportation industry is a major source of pollution, which is estimated to produce 500,000 deaths per year [7]. Apart from CO_2, combustion of fossil fuels emits other pollutants to the environment, such as carbon monoxide (CO), nitrogen oxides (NO_x) and volatile organic compounds (VOC). The VOC are composed by aliphatic hydrocarbons, aromatic hydrocarbons and carbonyl-containing oxygenates. These compounds have the ability to react with sunlight and form ozone. The aliphatic and aromatic hydrocarbons are emitted as unburned fuels. Carbonyl-containing oxygenates, such as aldehydes and ketones, are produced by a partial oxidation of the fuels.

In order to decrease emissions generated by vehicles, people can change their way of transporting and use more public transportation. Another option is to change the fuel to a cleaner one, such as hydrogen or electricity. While the first option deals with people's way of living and their consumption trend, the latter deals with technological advances. Both of them take time, so a more immediate solution is needed [8].

In order to improve urban air quality, in 1970 US legislated the control of emissions from vehicles [7]. Regulated pollutants include carbon monoxide (CO) and nitrogen oxides (NO_x) [9]. To comply with the regulations in practice, technical solutions are often based on catalytic concepts, i.e. by including a three-way catalytic converter in the exhaust system. Today there is no single car that circulates without a catalytic converter [8]. Carbon monoxide has been treated by catalytic converters, but they require high operating temperatures. When the engines are cold there is still a substantial rate of emissions.

In order to reduce emissions in the transportation sector, the adoption of technologies and measures has to be done. Technology options include improvement in the efficiency of the systems, usage of alternative fuels and changes in urban infrastructures and transportation systems [6]. The usage of alternative fuels, or future fuels, is of our concern here.

1.1 Alternative fuels

In the course towards more energy efficient transport solutions, alternative fuels have been proposed. These include hydrogen and electricity. Hydrogen might be used in internal combustion engines or fuel cells. The resulting emissions contain mainly water vapor, in the case of combustion, also nitrogen oxides. Vehicles might also be powered by electricity that can be stored in batteries. Electricity can be produced from renewable energy sources such as solar panels, wind, hydroelectric plants or nuclear power. The emissions are more or less eliminated with these approaches. However, the main problem is that currently these technologies are too expensive for fuel production for transportations and in order to substantially decrease the prices for them to compete with fossil fuels, Research and Development has to be done [10]. In the meanwhile, bridging technologies should be adopted.

The increase in environmental pollution and global warming has lead to a change of the compositions of gasoline and diesel. In order to increase the oxidation of the compounds in the gasoline, an oxygenated additive is mixed into the fuel. These additives can be methyl tert-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE) or tertiary-amyl methyl ether (TAME). The mixture is known as reformulated gasoline (RFG) [9]. The use of RFG is legislated in the United States in the 1990 Clean Air Act Amendments, but while showing a decrease in CO emissions, the use of additives such as MTBE lead to the production of carbonyl-containing oxygenates such as formaldehyde, acetaldehyde and acetone [11].

Alcohols, such as methanol and ethanol, have also been considered as alternative fuels and oxygenated additives. These alcohols are renewable energy sources produced by fermentation of hydrocarbons in feedstock such as sugarcane, grain or corn. Countries like Brazil and Sweden already use blends such as E85 (85% ethanol + gasoline). The combustion of alcohols produces aldehydes. In the case of ethanol and ethanol blended fuels acetaldehyde is dominating the exhaust and increases while increasing the ethanol percent [12]. Methanol would produce formaldehyde instead. An increase of aldehyde and acetaldehyde emissions has been reported in Rio de Janeiro, Brazil, where ethanol is used as fuel or blended with gasoline and diesel [13]. The use of ethanol as an additive also showed an increase of carbonyl-containing oxygenates when compared to traditional fuels [14], but a decrease when compared to MTBE [15].

Another promising alternative is the use of ethers. Dimethyl Ether (DME) has a low autoignition-temperature and high oxygen content, which makes it ideal for combustion with low emissions. Compared to diesel, emissions of CO_2, NO_x and particulate matter are decreased, while the formation of aldehydes and aromatics are seen [16]. Although Diethyl Ether (DEE) is another candidate, DEE is presently not well studied. Some studies show that blending diesel with DEE reduces emissions of NO_x while increasing CO and hydrocarbons [17].

The use of other blends includes biodiesel-diesel and ethanol-biodiesel-diesel. Biodiesel is manufactured from vegetable oils such as soy, palm or rapeseed. The addition of palm or rapeseed biodiesel to diesel showed a decrease in CO emissions, but an increase in carbonyl-containing oxygenate emissions [18]. The ethanol-biodiesel-diesel blend seems to increase CO_2 and carbonyl-containing oxygenates such as acetaldehyde and acetone [19].

Biodiesel has also been tested as a fuel. The use of palm-biodiesel as a fuel showed an increase in carbonyl-containing oxygenate emissions compared with diesel, but the blend of paraffinic fuel with biodiesel showed a decrease [20]. While reducing CO and benzene emissions, compared with diesel, biodiesel from waste-cooking oil increases the emissions of carbonyl-containing oxygenates and, if blended with methanol, unburned methanol [21].

Compressed natural gas (CNG) in another candidate proposed as an alternative fuel. It is a gas that is usually compressed and its primary component is methane. Other aliphatic hydrocarbons such as propane and butanes are candidates and come as liquefied petroleum gas (LPG). In general, LPG and CNG vehicles tend to reduce emissions of CO, benzene, aldehydes and VOC [9].

In order to avoid climate change, future fuels should be introduced. These include hydrogen and electricity, but in order to bridge technologies, the use of cleaner combustion fuels should be implemented. The combustion of fuels such as alcohols, ethers, biodiesel, blends of gasoline, natural gas or liquefied petroleum gas produce emissions that pollute the atmosphere. In order to avoid these emissions, the transportation sector has introduced the use of catalytic converters.

1.2 Purpose

The objective of this thesis is to study the catalytic conversion of representative hydrocarbons and oxygenates present in the exhaust of alternative fuel combustion. The main focus is on aliphatic hydrocarbons, alcohols, ethers, aldehydes and ketones. This thesis does not include carbon monoxide or nitrogen oxides and excludes fuels such as regular gasoline, diesel, electricity and hydrogen.

The main focus is on understanding some catalytic systems and under which conditions these systems can function efficiently. A total of nine compounds and two catalysts (i.e. Pt/Al_2O_3 and Pt/CeO_2) were analyzed. These compounds included alkanes, alkenes, alkynes, an ether and an aldehyde.

2 Heterogeneous catalysis for environmental protection

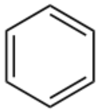
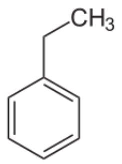
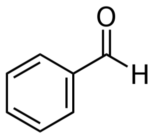
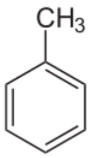
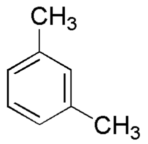
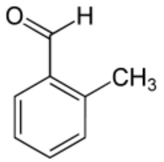
2.1 Emissions from the combustion of fuels

Fossil fuels are usually composed of alkanes and aromatics. When combusted, these hydrocarbons might undergo a series of reaction pathways. When the combustion is complete, the products are carbon dioxide and water. If the combustion is not complete, carbon monoxide and other partial oxidation compounds are produced [22]. Alkanes, alkenes and alkynes can be partially oxidized to alcohols or ethers. A further oxidation will produce aldehydes or ketones and eventually carboxylic acids.

Table 2.1 shows a series of emissions in order of its functional group and amount of carbons. These emissions will be analyzed in order to define its source, the fuel that emits it, and the main hazards involved.

Table 2.1: Series of emissions

Alkanes	Alkenes	Alkynes	Alcohols	Ethers	Aldehydes	Ketones	Carboxilic acids
Methane CH_4			Methanol CH_3-OH	Dimethyl ether CH_3-O-CH_3	Formaldehyde H-(C=O)-H		Formic Acid H-(C=O)-OH
Ethane CH_3-CH_3	Ethylene CH_2=CH_2	Acetylene $CH \equiv CH$	Ethanol CH_3-CH_2-OH	Diethyl ether C_2H_5-O-C_2H_5	Acetaldehyde CH_3-(C=O)-H	Acetone CH_3-(C=O)-CH_3	Acetic Acid CH_3-(C=O)-OH
Propane CH_3-CH_2-CH_3	Propylene CH_2=CH-CH_3 Allene CH_2=C=CH_2	Propyne $CH \equiv C$-CH_3	1-Propanol CH_3-CH_2-CH_2-OH 2-propanol CH_3-(CH-OH)-CH_3		Propionaldehyde CH_3-CH_2-(C=O)-H Acrolein CH_2=CH-(C=O)-H		Propionic Acid CH_3-CH_2-(C=O)-OH

Aromatics		Aromatic aldehydes
Benzene C_6H_6 	Ethylbenzene C_6H_5-CH_2-CH_3 	Benzaldehyde C_6H_6 
Toluene C_6H_5-CH_3 	$(o-,m-,p-)$ Xylene C_6H_4-$(CH_3)_2$ 	$(o-,m-,p-)$ Tolualdehyde C_6H_5-(C=O)-H 

2.2 Health hazards

The emissions listed in Table 2.1 are produced by the exhaust of cars either as unburned fuels or from the partial oxidation of the fuel. When these gases are emitted, the quality of the air we breathe is lowered. Breathing these gases may be harmful for human health.

The aliphatic hydrocarbons (methane, ethane, propane, ethylene, propylene, allene, acetylene and propyne) are flammable gases and explosive in some mixtures with air. Although they are proved not to be toxic, they can displace oxygen and become asphyxiant [23]. Methane in particular is a greenhouse gas that has a long lifetime. It has the capability of trapping 20 times more heat than carbon dioxide [24]. These compounds are mainly emitted as unburned fuels from reformulated gasolines, compressed natural gas or liquefied petroleum gas.

Further oxidation of the aliphatic hydrocarbons would produce an alcohol (methanol and ethanol). No reference is found for emissions of propan-1-ol and propan-2-ol. Alcohols are flammable and irritate eyes, skin and respiratory tract [23]. Methanol in particular is considered one Hazardous Air Pollutant according to The Clean Air Act Amendments of 1990 [25]. The main hazard involved with methanol is that it is toxic, causing blindness. These alcohols are emitted as unburned fuels when using them directly or as blended fuels.

Dimethyl ether (DME) and Diethyl ether are highly flammable compounds that are not considered toxic, but irritant to the respiratory system [23]. They are mainly emitted as an unburned fuels when using as a direct fuel or when blending other fuels with it.

The main products from a partial oxidation of fuels are aldehydes. Formaldehyde, acetaldehyde, acrolein and propionaldehyde are considered Hazardous Air Pollutants according to The Clean Air Act Amendments of 1990 [25]. The first three are highly toxic and potentially carcinogenic. The aldehydes are also irritants to the respiratory tract, eyes and skin. Acrolein in particular is extremely flammable, causes severe pulmonary irritation, and serious damage to skin [23].

Acetone is a highly flammable liquid that can form explosive mixtures. It is not considered a toxic compound, but may cause irritation at very high concentrations [23]. It is emitted by oxidation from fuels.

Benzene is considered one Hazardous Air Pollutant according to The Clean Air Act Amendments of 1990 [25]. It is highly flammable and toxic, causing nausea and dizziness. If the exposure is high, it may cause death. It also causes anemia when exposing chronically. It is considered a mutagenic and carcinogenic compound [23]. It is emitted as an unburned fuel and from dealkylation of aromatics when using fuels such as compressed natural gas, biodiesel and diesel blended with ethanol.

Toluene is considered one Hazardous Air Pollutant according to The Clean Air Act Amendments of 1990 [25]. It is flammable, toxic and a severe irritant for the eyes [23]. It is emitted from fuels such as compressed natural gas, biodiesel and diesel blended with ethanol.

Ethylbenzene is a colorless flammable liquid that is considered to be toxic and extremely irritant [23]. It is emitted from compressed natural gas and diesel blended with ethanol.

There are three types of Xylenes, depending on the position where the second methyl group is bounded in the aromatic ring, they are denominated ortho- (o-), metha- (m-) and para- (p-). The three of them are considered Hazardous Air Pollutants according to The Clean Air Act Amendments of 1990 [25]. They are very flammable liquids that are considered harmful. They cause irritation of skin, eyes and respiratory tract. At low levels they cause dizziness and headache, but increased levels may cause even death [23]. Their principal way of emission is in the use of compressed natural gas, biodiesel and diesel blended with ethanol.

Benzaldehyde is a colorless liquid that is harmful since it may be irritant and cause respiratory failure [23]. It is emitted when using biodiesel and reformulated gasolines.

Tolualdehyde also has three isomers, which can be also denominated ortho- (o-), metha- (m-) and para- (p-) depending on the position where the methyl group is bounded. They are considered harmful components, which may be irritant to the respiratory tract [23]. They are emitted when burning compressed natural gas, biodiesel and reformulated gasolines.

2.3 The role of hydrocarbons in photochemical smog formation

During the middle of the twentieth century a new type of smog was detected in the city of Los Angeles. The effects carried by this kind of smog were crop damages and deterioration of products made with rubber. The formation mechanism for the Los Angeles-type smog was explained by Arie Haagen-Smit. First he discovered that the damages produced to plants were similar to those when exposing them to ozone. After some years, he was able to prove that ozone is produced when reacting nitrogen oxides and hydrocarbons in presence of sunlight. The Los Angeles-type smog was then denominated photochemical smog and has been observed in huge cities like Mexico City or Baghdad [26].

The levels of ozone in the troposphere are determined by a series of reactions that involve nitrogen oxides. Nitrogen monoxide rapidly reacts with ozone to produce nitrogen dioxide and oxygen (reaction 2.1). The reaction does not exhaust the reactants. Nitrogen dioxide is photolyzed by photons with wavelengths less than 430 nm (reaction 2.2). The molecule of oxygen produced reacts with oxygen in presence of a third body (M) that is not consumed, but absorbs energy in order to stabilize the product (reaction 2.3) [27].

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2.1}$$

$$NO_2 + hv \rightarrow NO + O \tag{2.2}$$

$$O + O_2 + M \rightarrow O_3 \tag{2.3}$$

For ozone levels to increase, there should be a decrease in the level of nitrogen dioxide. This happens during daytime by the formation of nitric acid due to the intervention of hydroxyl radicals (reaction 2.6). Hydroxyl radicals are formed when ozone is broken by photons with wavelengths less than 310 nm (reaction 2.4) and the presence of water vapor (reaction 2.5) [26].

$$O_3 + hv \rightarrow O_2 + O(^1D) \tag{2.4}$$

$$O(^1D) + H_2O \rightarrow 2OH^- \tag{2.5}$$

$$NO_2 + OH^- + M \rightarrow HNO_3 \tag{2.6}$$

Finally, ozone production is increased by adding carbon monoxide and hydrocarbons such as alkanes or aldehydes. For the case of alkanes (R-H; where R is the radical (e.g. methyl, ethyl, etc.)) the mechanism is initiated by an hydroxy radical (reaction 2.7) and follows the formation of peroxy radicals (reaction 2.8), and then oxy radicals with nitrogen dioxide (2.9). The formation of ozone is done as in reactions 2.2 and 2.3, previously discussed [26]:

$$R - H + OH^- \rightarrow R^- + H_2O \tag{2.7}$$

$$R^- + O_2 + M \rightarrow R - O_2^- \tag{2.8}$$

$$R - O_2^- + NO \rightarrow NO_2 + R - O^- \tag{2.9}$$

The production of an oxy radical in reaction 2.9 leads to the production of aldehydes and the hydroperoxy radical (which acts as the peroxy radical in reaction 2.9 and is reduced to the hydroxy radical for further production of ozone) [27]:

$$R - O^- + O_2 \rightarrow R - HO + HO_2^- \tag{2.10}$$

Aldehydes, formed by reaction 2.10 or directly emitted, further contribute to the formation of the photochemical smog in two ways. First, they may be oxidized after photolysis forming carbon monoxide and hydroperoxyl radicals [27]. Second, they also undergo a series of reactions that produce peroxyacyl nitrates. First they react with the hydroxyl radical to produce an acyl radical (reaction 2.11), which reacts with oxygen to produce a peroxyacyl radical (reaction 2.12). The last one reacts with nitrogen dioxide to produce the peroxyacyl radical (reaction 2.13) [26]:

$$R - HO + OH^- \rightarrow R = O^- + H_2O \tag{2.11}$$

$$R = O^- + O_2 + M \rightarrow R(= O) - O_2^- \tag{2.12}$$

$$R(= O) - O_2^- + NO_2 + M \rightarrow R(= O)O_2NO_2 \tag{2.13}$$

The problems associated with photochemical smog include human health problems, effects in plants and climate change. First of all, ozone and peroxyacetyl nitrate (a peroxyacyl nitrate produced from acetaldehyde) are respiratory irritants and lachrymators. The respiratory problems, such as asthma or infections, become aggravated when breathing photochemical smog. Plants may cut the rate of photosynthesis when exposed to photochemical smog, producing agricultural production losses. Finally, ozone is a greenhouse gas, which can contribute to climate change [27].

2.4 Heterogeneous catalysis

When a chemical reaction occurs, some bonds are broken giving place to the formation of new bonds. To break these bonds, energy, denominated activation energy, has to be supplied. For some reactions the activation energy is high, so their progress is very slow. We may increase the temperature to provide enough energy for the molecules to collide. Another problem we face is that sometimes the spontaneous reaction leads to the production of molecules that are easier to produce than the one we actually desire. In order to speed up the desired reactions we use a catalyst. A catalyst is a compound that changes the path of a reaction, but is not consumed and does not change the thermodynamics of the reaction. The catalyst finds a new route of reaction with lower activation barriers [7].

Catalysis can broadly be divided in homogeneous, heterogeneous and biocatalysis. The homogeneous catalysis is when the catalyst is in the same phase as the reactants. If the catalyst and the reactants are in different phases, then it is heterogeneous catalysis. Biocatalysis is a process carried out by enzymes [7]. Transportation industry uses heterogeneous catalysis for emissions treatment, since emissions are gases and the catalyst used is a solid.

In a gas/solid system, the reactants are fed to a reactor composed of a catalyst bed. It gives the impression that the reactants are fed to the reactor and the products leave it. The process is more complicated than that. The reactants diffuse through the catalyst, adsorb to its surface, react to form the products, which then desorb and diffuse to exit the reactor [8].

The two dominating mechanisms of surface reactions are Langmuir-Hinshelwood and Eley-Rideal mechanisms [8]. In order to explain these mechanisms, we consider the reaction A+B → C. In the Langmuir-Hinshelwood mechanism the reactants A and B are adsorbed to the catalyst where they meet in order to react and produce C. In the Eley-Rideal mechanism only one of the reactants, say A, adsorbs. B reacts directly with A to produce C.

Another complication arises from the fact that the solid catalyst has an irregular surface [8]. These irregularities are characterized by steps, kinks and vacancies, where the molecules are able to interact with the substrate. These were denominated active sites by Hugh Taylor. He suggested that the amount of atoms in the surface that are active for catalysis depends on the reaction that is catalyzed [28]. The active site should obey Sabatier's principle, reactants should be adsorbed easily, but products should be able to desorb.

Heterogeneous catalysis plays an important role in the control of emissions for the transportation sector. Today it is impossible to acquire a car without a catalytic converter. In the next section a brief discussion on catalytic converter will be presented.

2.5 Catalytic converter

The catalytic converter consists of a monolith support in the form of a honeycomb. The channels of the structure have typically an area of 1 mm^2. This structure is often made of a ceramic called cordierite (calcium/magnesium aluminosilicate), but aluminium-doped stainless steel is also used. The monolith is then wash-coated with a support material made mainly of silica (SiO_2) and alumina (Al_2O_3) to provide an irregular surface or porous volume increasing the surface area. The support is impregnated with precious metals, such as platinum (Pt), palladium (Pd) and rhodium (Rh). The first two are used for oxidation, the third one is used for catalyzing the reduction of nitrogen oxide with carbon monoxide and hydrogen. An oxygen reservoir, such as ceria (CeO_2), is often added [8].

When working with gasoline engines, the efficiency of the catalytic converter depends on the air-to-fuel ratio (A/F or λ). If the A/F ratio is low (rich conditions) there is an oxygen deficiency so CO and HCs cannot be completely oxidized and hence are emitted. Increasing the air (A/F ratio is high, lean conditions) increases the conversion of CO and HCs, but at the same time the conversion of NO_x is decreased. A control system for the air/fuel ratio has been adapted to maintain the A/F ratio near the stoichiometric level [8].

2.6 Selection of the catalyst

When the selection of the catalyst is done, one has to take into account the properties of the catalyst and the desired result. As an example, we take into consideration the oxidation of an alcohol. Two major groups of catalysts can be identified: the ones that oxidize the alcohol to carbon dioxide and aldehyde and the ones that dehydrate the alcohol to ether and alkene. The former group contains strong base sites (O_2^-, O_2^-, HOO^-) and promotes an acid reaction to dehydrogenate alcohols to aldehydes. The latter contains strong acid sites (Lewis or Bronsted) promoting the dehydration to ether or alkene by a base reaction [29].

The use of noble metals for catalysis of emissions has been studied widely. Platinum is broadly used due to its high activity for the oxidation of hydrocarbons. The main exception is methane, which has been reported to be catalyzed more efficiently by palladium or nickel [30]. Methane oxidation is difficult with platinum, it requires usually high temperatures. This is because at low temperatures methane is not able to dissociate in platinum surface due to a deactivation generated by adsorbed oxygen [31].

A support is added in order to provide optimal dispersion, good accessibility, and stability against sintering. Silica and alumina are typical examples of rather inactive supports [8]. Ceria is an active support, which acts as oxygen exchanger, storing oxygen excess during lean periods and releasing it during rich conditions [31].

McCabe and Mitchell presented a study of oxidation of ethanol and acetaldehyde, reaching to the conclusion that the most active catalysts were hopcalite (CuO-MnO_2) and Pt/Al_2O_3. Both catalysts were able to oxidize ethanol to CO_2 with low yields of acetaldehyde production and low maximum temperatures on acetaldehyde production. When oxidizing acetaldehyde, these catalysts were also the most active, producing CO_2 with small traces of CH_4 and CO. The hopcalite was more active than the Pt/Al_2O_3, but loose activity when oxidizing the ethanol. They also claimed that when ethanol is oxidized over Pt/Al_2O_3 some of it reacts to CO_2 directly and some of it reacts to CO_2 via the formation of an acetaldehyde intermediate [29].

Pettersson *et al.* presented a study on catalysts for the control of unregulated emissions for diesel engines fuelled with ethanol. They tested Pt and Pd in supports of alumina, titania, ceria and silica. They show that the most active catalyst in their experiment is the one supported with titania, but catalysts supported by alumina and ceria are also active. Pd and Pt have similar activities when supported by ceria [32].

3 Experimental Procedure

3.1 Preparation of samples

Two supported catalysts were prepared by impregnating either alumina (Al_2O_3) or ceria (CeO_2) with a platinum precursor. The precursor for active component was Tetraamine-platinum(II) nitrate solution (3.977% w/w Pt). The supports were alumina, thermally treated at 1023 K for 2 h 15 min, with a surface area of 180 m^2/g, and ceria, thermally treated at 873 K for 2 h, with a surface area of 140 m^2/g. The two samples were prepared in an alkaline media with ammonia. The samples were prepared so the moles of noble metal per surface area were 1.7×10^{-6}. This corresponds to the next weight percentage of noble metal per support: 2% for Pt/Al_2O_3, and 1.56% for Pt/CeO_2, as seen in Appendix A. To reach these percentages the sample of Pt/Al_2O_3 was done in one impregnation, but for Pt/CeO_2 two impregnations had to be done. The slurries were frozen in liquid nitrogen and freeze-dried for 12 h. The resulting powders were heat-treated with a 2 h ramp from room temperature to 823 K and 2 h at the same temperature.

Monolith samples (L = 15 mm, Ø= 12 mm, 69 channels) were cut from a commercial honeycomb structure of cordierite with 400 cpsi. The samples were immersed in water slurries containing the catalyst powders and a binder. The binders were a colloidal alumina solution (Disperal sol P2, Condea) for alumina-supported catalyst and a colloidal ceria solution (CeO_2(Ac), Nyacol) for the ceria-supported catalyst. The samples were dried at 363 K in air until water was evaporated and then calcined at 873 K for 5 min. The procedure was repeated in all samples until 200 mg of washcoat were attached to the samples. The samples were then heat-treated with a 2 h ramp from room temperature to 823 K and 2 h at the same temperature.

3.2 Flow-Reactor Experiments

The experiments were performed in a continuous gas flow-reactor that consists of a quartz tube (L = 500 mm, Ø= 14 mm) surrounded by a heating coil. The heating coil was connected to a power supply and insulated by quartz wool to avoid radiation losses. The catalyst was positioned in the middle of the tube, with two empty monoliths before and after it in order to decrease heat losses from radiation. Gases were introduced to the system by individual mass flow controllers (Bronkhorst Hi-Tech F-201C-FA/F-202D-FA). The temperature was measured by two thermocouples (Thermocoax TCI 10/25/A) placed 15 mm before the coated monolith and inside the coated monolith, respectively. The outlet gases were analyzed using a Mass Spectrometer (Balzers Quadstar 422).

The monoliths had a diameter of 12 mm and a length of 15 mm. The flow rate was 400 cm^2/min resulting in a space velocity of 14 150 h^{-1}, a residence time of 0.25 s and an average flow velocity of 0.06 m/s.

In experiments where the gas composition has to vary between oxidizing/reducing, the characteristics of the gas was quantified by the S-value (stoichiometric value) [33]. The S-value is the ratio of the oxidizing agents to the reducing agents in the reactant feedstream (mixture) [34]. The mixture is defined as lean (net-oxidizing) if $S > 1$, rich (net-reducing) if $S < 1$ and stoichiometric if $S = 1$.

The general reaction in our system for a complete oxidation is:

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O \tag{3.1}$$

If we take for example propylene, the reaction would be:

$$C_3H_6 + \frac{9}{2} O_2 \rightarrow 3CO_2 + 3H_2O \tag{3.2}$$

Hence the relationship would be:

$$S = \frac{2[O_2]}{9[C_3H_6]} \tag{3.3}$$

The tables of the flows used in the experiments and their corresponding concentrations and S-values may be found on Appendix B.

3.2.1 Characterization by CO chemisorption

The surface area of the Pt/Al_2O_3 catalyst was measured by CO chemisorption in a continuous flow-reactor system as described previously. The catalyst was pretreated with 15% O_2/Ar at 673 K for 10 min in order to oxidize it. Then the catalyst was reduced with 25% H_2/Ar for 30 min. During the 30 min of the H_2 pretreatment, 10 min were performed at 673 K and the rest were then cooled to room temperature.

After the pretreatment, the sample was subjected to two consecutive steps of 150 ppm CO/Ar, separated by a 2 h period of flushing in pure Ar. The steps were performed at room temperature. The difference in the outlet CO response between the two steps was taken as the CO chemisorbed.

3.2.2 Temperature-programmed experiments

In order to study the ignition and extinction temperatures and to map a suitable reaction temperature for the step and pulse response experiments, temperature-programmed (TP) experiments were done in a continuous flow-reactor system as described previously. The experiments were started at 823 K for 10 min, then exposed a temperature-ramp (5 K/min) to 323 K. The temperature was dwelled at 323 K for 20 min and then increased (5 K/min) to 823 K again. The temperature was dwelled at 823 K for 10 min. The hydrocarbon concentration was fixed at 1000 ppm and an O_2 excess was used. The S-value was fixed to 1.5. The conversion of the hydrocarbon versus temperature was measured and compared.

3.2.3 Step-response experiments

Step-response experiments were carried out in the continuous flow-reactor system as described previously. The system was kept in a suitable temperature based on the results of the TP experiments, discussed previously. The temperature was selected between the maximum temperature at which the compound burns (after which the conversion doesn't increase too much) and the minimum temperature (before which the conversion doesn't decrease too much). The concentration of hydrocarbon was fixed at 1000 ppm. Oxygen was introduced and the concentration was decreased step-wise starting with S = 3 for 10 min, then S = 1.50 (10 min), S = 1.25 (10 min), S = 1.05 (5 min), S = 0.95 (5 min), S = 0.75 (10 min), S = 0.50 (10 min) and finally S = 0.25 (10 min). Afterwards, the sequence was inverted increasing step-wise. The conversion of the hydrocarbon versus S-value was measured and compared.

3.2.4 Pulse-response experiments

Pulse-response experiments were done in a continuous flow-reactor system as described previously. The system was kept in a suitable temperature based on the results of the Temperature-programmed experiments, discussed previously. The concentration of hydrocarbon was fixed at 1000 ppm. Oxygen was introduced at a low S-value during 5 min and then switched to a higher S-value during 5 min. Five pulses of these type were performed per catalyst. For the saturated hydrocarbons another experiment was done with each catalyst by introducing oxygen at an S-value of 1.25 (lean conditions) for 5 minutes and pulsing four times for 1 minute with an S-value of 0.75. The results were measured and discussed.

4 Results

Experiments were done as described in Section 3. The flows used for different experiments varied according to the S-value used, and may be found in Appendix B. Figures not shown in this section may be found in Appendix C. For the experiments, a level on the carbon balance was measured, and should be around 1000 ppm (corresponding to the concentration of the hydrocarbon).

At the beginning of some experiments, the Carbon Balance is superior to the 1000 ppm expected. This is because the carbon monoxide concentration was measured for a m/z of 28, which is the same as nitrogen. Probably at the beginning of the experiment, there is a leakage of air in the flow of oxygen, and the mass being detected is not carbon monoxide, but nitrogen.

4.1 Temperature-programmed experiments

The temperature-programmed experiments were done for methane, ethane, propane, ethylene, acetylene, propylene, allene, dimethyl ether and acetaldehyde with Pt/Al_2O_3 and Pt/CeO_2 acting as catalysts, as described in Section 3.2.2. The results for each individual compound and catalyst may be found in Appendix C. The figures presented in this section show the comparison between the saturated hydrocarbons, the C_2 hydrocarbons and the C_3 hydrocarbons.

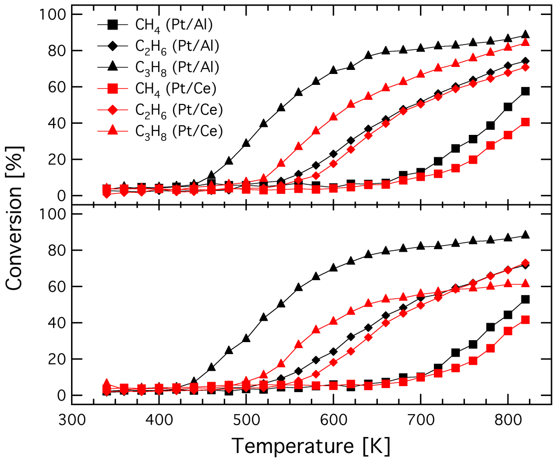


Figure 4.1: Temperature-programmed experiments for saturated hydrocarbons done with Pt/Al_2O_3 catalyst and Pt/CeO_2. Upper panel shows the experiment when ramping up the temperature from 323 K to 823 K. Lower panel shows the experiment when ramping down the temperature from 823 K to 323 K.

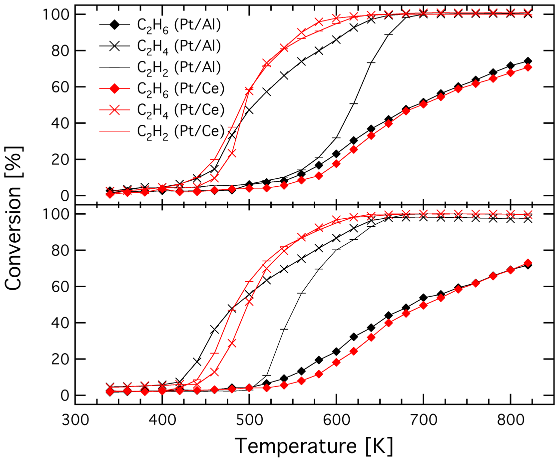


Figure 4.2: Temperature-programmed experiments for C_2-hydrocarbons done with Pt/Al_2O_3 catalyst and Pt/CeO_2. Upper panel shows the experiment when ramping up the temperature from 323 K to 823 K. Lower panel shows the experiment when ramping down the temperature from 823 K to 323 K.

Figure 4.1 shows the study of ignition and extinction temperatures for the saturated hydrocarbons. Methane starts to be oxidized at a temperature of 683 K for both catalysts and reaches more than 50% conversion at 823 K. Ethane starts to be oxidized at a temperature of 550 K for the alumina catalyst and 570 K for the ceria catalyst. After 690 K the conversion starts to increase slowly, reaching more than 70% at 823 K for both catalyst. Propane starts to be oxidized at 450 K with the alumina catalyst and 500 K with the ceria catalyst. After 630 K the conversion increases slowly for both cases, reaching almost 90%. In the ceria case, when the temperature is ramped-down, the maximum observed conversion is 60%. Under the experimental conditions used here, the Pt/Al_2O_3 catalyst shows higher activity than the Pt/CeO_2 catalyst in all three cases.

Figure 4.2 shows the study of the ignition and extinction temperatures for the C_2 hydrocarbons. Ethane is the most difficult hydrocarbon of the C_2 series to be oxidized, hardly reaching more than 70% conversion at very high temperatures. Ethylene starts to be oxidized at a temperature about 450 K, and reaches high conversions after the 600 K. Acetylene starts to be oxidized earlier with the ceria catalyst (450 K) than with the alumina catalyst (550 K), reaching also a maximum conversion earlier (580 K and 680 K, respectively). For the oxidation of ethane, Pt/Al_2O_3 is more active than Pt/CeO_2, while for the oxidation of acetylene, the latter is more active. The ceria supported Pt catalyst is more active for alkene oxidation at high temperatures, but at temperatures lower than 500K, the alumina catalyst is more efficient.

Figure 4.3 shows the study done for the C_3 hydrocarbons. Propane is the most difficult hydrocarbon to be oxidized. Propylene starts to be oxidized at a temperature about 450 K and reaches high conversions after 600 K. When allene is oxidized with the ceria catalyst, the oxidation starts at 450 K and shows a maximum at 580 K. If catalyzed with alumina, allene starts the oxidation at 550 K and shows a maximum conversion after the 680 K. The alumina shows more activity when oxidizing the alkane, but for the oxidation of the

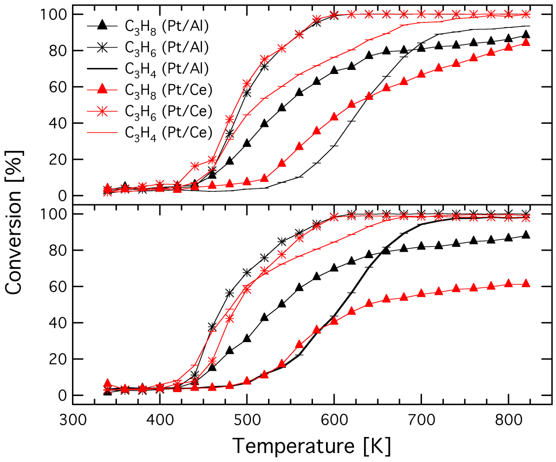


Figure 4.3: Temperature-programmed experiments for C_3-hydrocarbons done with Pt/Al_2O_3 catalyst and Pt/CeO_2. Upper panel shows the experiment when ramping up the temperature from 323 K to 823 K. Lower panel shows the experiment when ramping down the temperature from 823 K to 323 K.

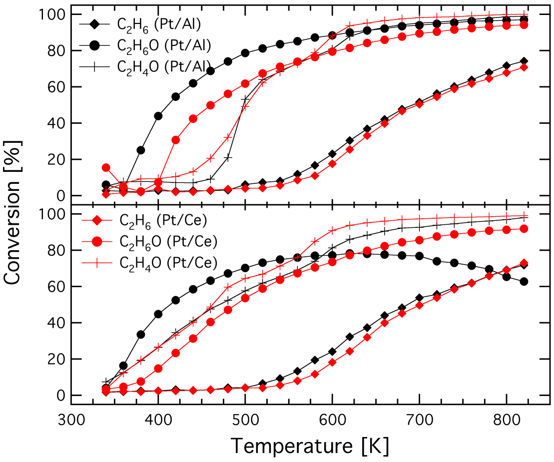


Figure 4.4: Temperature-programmed experiments for ethane, DME and acetaldehyde done with Pt/Al_2O_3 catalyst and Pt/CeO_2. Upper panel shows the experiment when ramping up the temperature from 323 K to 823 K. Lower panel shows the experiment when ramping down the temperature from 823 K to 323 K.

alkene and alkyne, the ceria is more efficient.

Figure 4.4 shows the study done with ethane, dimethyl ether and acetaldehyde. The alkane is more difficult to be oxidized than the ether and the aldehyde. If catalyzed with alumina, DME starts to be oxidized at 350 K and shows a maximum at 530 K. In the ramp-down experiment the conversion starts at 60% at 823 K, and then increases when decreasing the temperature, until it stabilizes to 80% at 700 K. If catalyzed with ceria, the oxidation starts at 400 K and reaches a maximum at 570 K. Acetaldehyde starts to be oxidized at 443 K if catalyzed with ceria and 473 K if catalyzed with alumina. In both cases the maximum is reached at 623 K. From these experiments we are able to see that the alumina is more active when catalyzing the oxidation of the alkane and the ether, while the ceria is more active when catalyzing the oxidation of the aldehyde.

From the results of these experiments, a suitable temperature to do the step-response and pulse-response experiments was selected. The temperature was selected in the region between the temperature where the hydrocarbon starts to be oxidized (named here as 'minimum') and the temperature where the hydrocarbon shows higher conversion (named here as 'maximum'). These temperatures are shown in Table 4.1, along with the maximum and minimum temperatures.

Table 4.1: Temperatures (K) at which the compounds burn. Top data is for Pt/Al_2O_3 catalyst. Bottom data is for Pt/CeO_2 catalyst.

	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_3H_4	C_2H_2	C_2H_6O	C_2H_4O
Maximum	823	690	630	650	600	700	680	530	623
Minimum	683	550	460	450	450	550	550	350	473
Suitable	723	623	573	523	543	668	633	473	573
Maximum	823	690	630	590	600	670	580	570	623
Minimum	683	570	500	460	460	430	450	400	443
Suitable	723	623	573	523	543	623	533	473	573

4.2 Step-response experiments

Based on the results of Section 4.1, step-response experiments were carried out for each compound with Pt/Al_2O_3 and Pt/CeO_2 acting as catalysts. The experiments were done as described in Section 3.2.3. The temperature at which these experiments were done is shown as 'Suitable' in Table 4.1. The results for each individual compound and catalyst may be found in Appendix C. The figures presented in this section show the comparison between the saturated hydrocarbons, the C_2 hydrocarbons and the C_3 hydrocarbons. Although the experiments were carried out at different temperatures, depending in the compound and catalyst, the results are combined in the figures below as to compare the behavior of the compounds as a function of the stoichiometry.

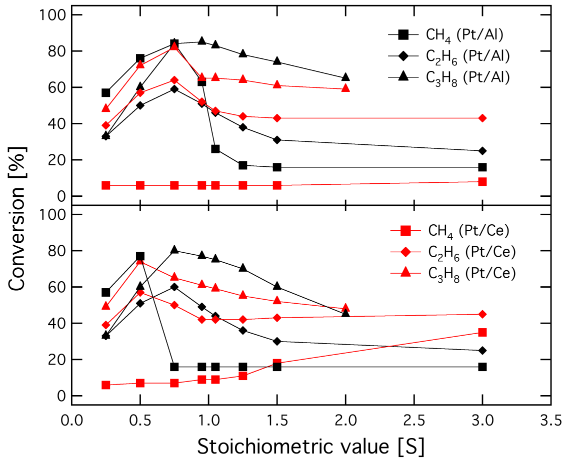


Figure 4.5: Step-response experiments for saturated hydrocarbons done with Pt/Al_2O_3 catalyst and Pt/CeO_2. Upper panel shows the experiment when stepping up the S-value from 0.25 to a high level. Lower panel shows the experiment when stepping down the S-value from a high level K to 0.25.

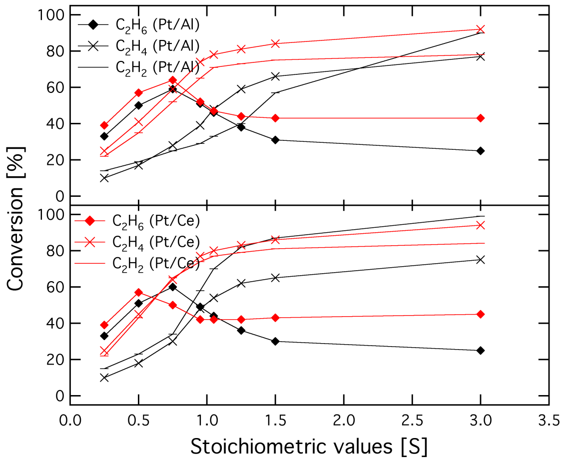


Figure 4.6: Step-response experiments for C_2-hydrocarbons done with Pt/Al_2O_3 catalyst and Pt/CeO_2. Upper panel shows the experiment when stepping up the S-value from 0.25 to a high level. Lower panel shows the experiment when stepping down the S-value from a high level K to 0.25.

Figure 4.5 shows the SR experiments for the saturated hydrocarbons. When catalyzed with Pt/Al_2O_3, methane starts with a conversion of 16%, which increases to 77% for S=0.50. The maximum conversion seen is 84% for S=0.75 when stepping up the oxygen concentration. If catalyzed with Pt/CeO_2 catalyst, methane shows a higher conversion at the beginning of the experiment (this is, high S-values and stepping-down the oxygen concentration), but decays rapidly and there is no activity seen during the rest of the experiment.

Ethane is oxidized more efficiently with Pt/CeO_2 during the whole experiment, compared to Pt/Al_2O_3. When catalyzed with Pt/Al_2O_3, the conversion shows a maximum of 60% for S=0.75 both, when stepping up and down the oxygen concentration. If catalyzed with Pt/CeO_2, the conversion reaches a maximum of 57% for S=0.50 when stepping down the oxygen concentration. Nevertheless, the conversion observed is 64% for S=0.75 when stepping up the oxygen concentration.

Propane oxidation is better catalyzed with Pt/Al_2O_3. When catalyzing with Pt/Al_2O_3 and stepping down the oxygen concentration, the maximum conversion observed is 80% reached when S=0.75. When stepping up the oxygen concentration, the maximum conversion observed is 85% reached when S=0.95. If catalyzed with Pt/CeO_2 and stepping down the oxygen concentration, the maximum conversion observed is 74% reached when S=0.50. When stepping up the oxygen concentration, the maximum conversion observed is 82% reached when S=0.75.

Figure 4.6 shows the SR experiments for the C_2 hydrocarbons. For both catalysts, ethylene oxidation shows a maximum conversion at the highest S-value, decreasing as the value decreases. When catalyzing with Pt/Al_2O_3, the conversion starts at 75%, decreasing slowly until it reaches S=1.25, where the decrease is faster. If catalyzed by Pt/CeO_2, the initial conversion observed is above 90% and decreases slowly until it reaches the S-value around the stoichiometric conditions, where the conversion decreases faster.

Acetylene oxidation also shows a maximum conversion at the highest S-value, and decreases then with decreasing S-value. If catalyzed with Pt/Al_2O_3, the conversion starts at 99% when stepping down the oxygen concentration and decreases slowly until S=1.25. Afterwards, the conversion falls faster. When stepping up the oxygen concentration the conversions rises fast when increasing the S-value until a maximum conversion of 90% is reached. When catalyzed with Pt/CeO_2 the maximum conversion observed is around 80%, and the decrease is slow while decreasing the S-value until stoichiometric conditions are reached, where the conversion decreases faster.

Figure 4.7 shows the SR experiments for the C_3 hydrocarbons. For both catalysts, propylene oxidation reaches a maximum conversion at the highest S-value, decreasing as the oxygen concentration decreases. When catalyzing with Pt/Al_2O_3, the conversion is 90%, decreasing slowly until it reaches an stoichiometric conditions, where the decrease is faster. If catalyzed by Pt/CeO_2, the initial conversion is 90% and decreases slowly until it reaches S=0.75, where the conversion decreases faster.

Allene oxidation also reaches a maximum conversion at the highest S-value, and decreases then with decreasing S-value. If it is catalyzed with Pt/Al_2O_3, the conversion starts at 85% when stepping down the oxygen concentration and decreases slowly while decreasing the S-value. When stepping up oxygen concentration, the conversion increases when increasing the S-value until it reached a maximum conversion of 96%. When catalyzed with Pt/CeO_2 the maximum conversion is 94% when stepping down the oxygen concentration. The decrease is slow while decreasing the S-value until an S-value of 1.25 is reached, where the conversion decreases faster. When stepping up the oxygen concentration, the conversion increases slowly until a maximum conversion of 80% is reached.

Figure 4.6 shows the SR experiments between ethane, dimethyl ether and acetaldehyde. Dimethyl ether conversion increases when decreasing the S-value, until a maximum is reached, after which the conversion falls drastically. If catalyzed with Pt/Al_2O_3, the maximum conversion observed is 58% reached when S=0.75 if stepping down the oxygen concentration and 59% when S=0.95 if stepping up the oxygen concentration. If we catalyze with Pt/CeO_2 the maximum conversion observed is 55% when S=0.75 for both

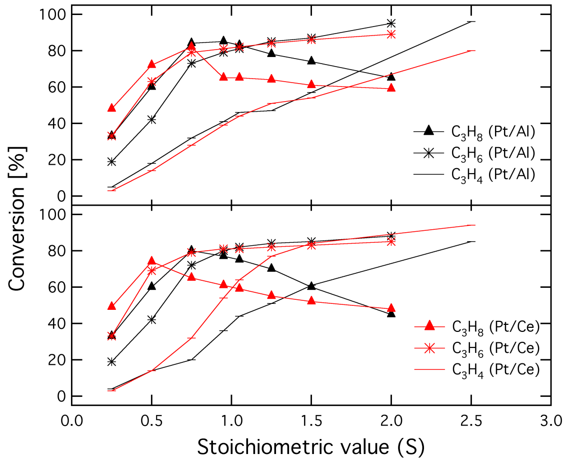


Figure 4.7: Step-response experiments for C_3-hydrocarbons done with Pt/Al_2O_3 catalyst and Pt/CeO_2. Upper panel shows the experiment when stepping up the S-value from 0.25 to a high level. Lower panel shows the experiment when stepping down the S-value from a high level to 0.25.

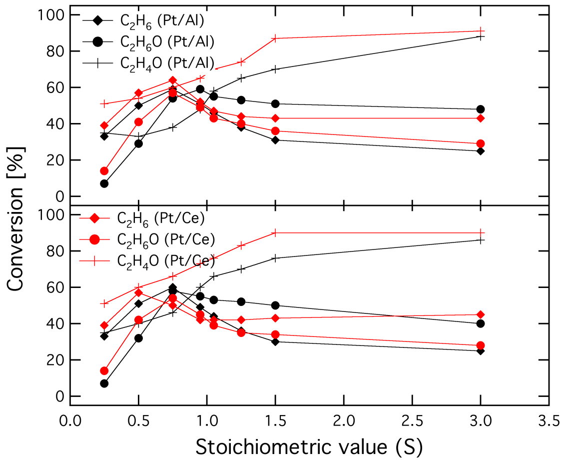


Figure 4.8: Step-response experiments for ethane, DME and acetaldehyde carbons done with Pt/Al_2O_3 catalyst and Pt/CeO_2. Upper panel shows the experiment when stepping up the S-value from 0.25 to a high level. Lower panel shows the experiment when stepping down the S-value from a high level to 0.25.

sequences. The Pt/Al_2O_3 catalyst for this compound is more active at lean conditions; for rich conditions, the Pt/CeO_2 is superior.

Acetaldehyde is more easily oxidized with an oxygen excess. The highest conversion is reached at the highest S-value, decreasing while this value is decreased. If catalyzed with Pt/Al_2O_3, the highest conversion is lower than 90%, and decreases slowly until an S-value around the stoichiometric value is reached, after which the conversion falls faster. If catalyzed with Pt/CeO_2, the maximum conversion is 90%. The conversion decreases slowly when decreasing the S-value.

4.3 Pulse-response experiments

Based on the results of Section 4.2, pulses were carried out for each compound with Pt/Al_2O_3 and Pt/CeO_2 acting as catalysts. The experiments were done as described in Section 3.2.4. The temperature at which these experiments were done is shown as 'Suitable' in Table 4.1. The results for each individual compound and catalyst may be found in Appendix C. In this section, results for methane, ethane and ethylene with Pt/CeO_2 are shown for comparison. The upper panel shows the variation of the S-value during time, the level of the hydrocarbon and the carbon balance. The lower level shows the CO_2 and CO levels.

Figure 4.9 and Figure 4.12 show the PR experiments done with methane and ethane respectively. One can see that after the first cycle, the following concentration responses are equal. In these experiments the concentration of the hydrocarbon, and more clearly the CO_2, hardly reach a steady state. When the S-value is increased, the conversion towards CO_2 peaks, and then slowly decreases. If the S-value is decreased, the conversion towards CO_2 drops and then slowly increases. Very low selectivity towards CO is seen in these experiments. The same behavior is seen in the experiments done for propane and DME.

Figure 4.11 shows the PR experiments carried out with ethylene. One can see that all the cycles show similar concentration responses. The concentration of the hydrocarbon and

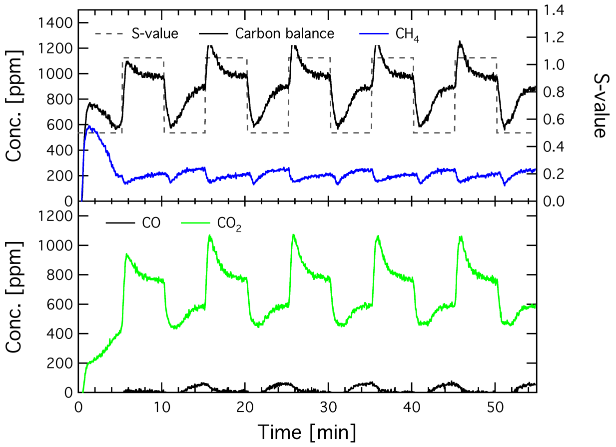


Figure 4.9: Pulse-response experiment for methane with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

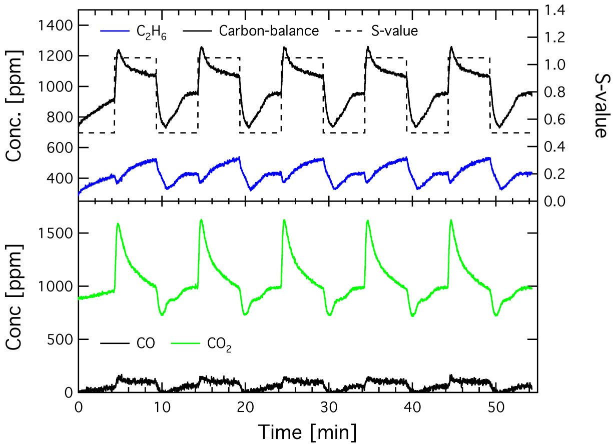


Figure 4.10: Pulse-response experiment for ethane with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

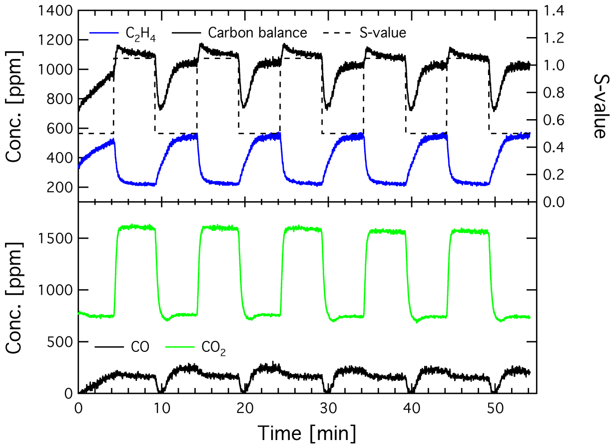


Figure 4.11: Pulse-response experiment for ethylene with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

the CO_2 easily reach steady state when pulsing. If the S-value increases, the conversion towards CO_2 is also increased. If the S-value decreases, the conversion towards CO_2 is decreased. There is a very low selectivity towards CO, which drops when the concentration of oxygen is decreased, but increases rapidly once again. The same behavior is seen in the experiments for the rest of the non-saturated hydrocarbons and the aldehyde.

In order to see the response of pulsing the S-value from lean conditions (S=1.25) to a rich conditions (S=0.75), experiments were done as described in Section 3.2.4. The temperature at which these experiments were done is shown as 'Suitable' in Table 4.1. In this section, results for ethane and propane with Pt/Al_2O_3 catalyst are shown. The upper panel shows the variation of the S-value during time, the level of the hydrocarbon and the carbon balance. The lower level shows the CO_2 and CO levels. The results for the rest of the compounds and catalyst may be found in Appendix C.

Figure 4.12 shows the lean to rich experiment carried out for ethane with Pt/Al_2O_3. After the first cycle is completed, the concentration responses are similar. When we switch from lean to rich conditions, the hydrocarbon concentration is decreased. When we switch back to lean conditions, the hydrocarbon level increases again. When we switch from lean

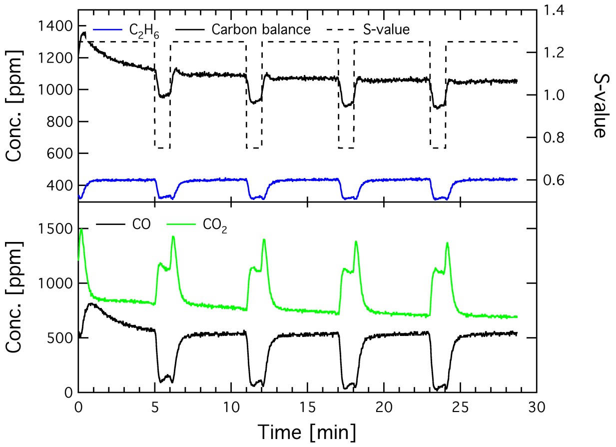


Figure 4.12: Pulse-response experiment for ethane with Pt/Al_2O_3 catalyst with S=1.25 (5 min) and S=0.75 (1 min)

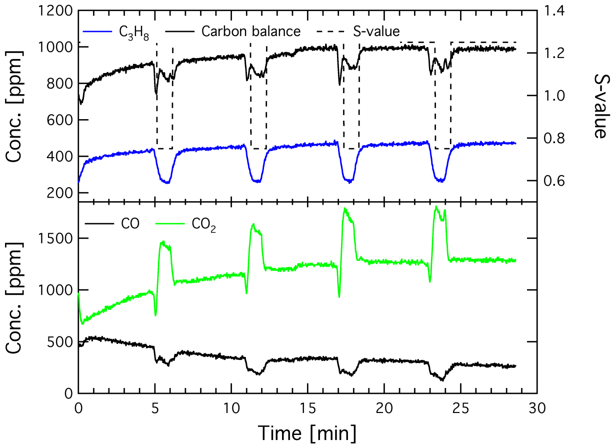


Figure 4.13: Pulse-response experiment for propane with Pt/Al_2O_3 catalyst with S=1.25 (5 min) and S=0.75 (1 min)

to rich conditions, the CO_2 increases at the beginning, and after few seconds, a peak is shown, where the excess of oxygen is consumed. This level is decreased once we switch back to lean conditions. Similar trends are shown in the experiment done with Pt/CeO_2.

Figure 4.13 shows the lean to rich experiment carried out for propane with Pt/Al_2O_3. After the first cycle is completed, the concentration responses are similar. When we switch from lean to rich conditions, the hydrocarbon concentration is decreased rapidly for some seconds. Then increases, corresponding to a complete consumption of the supplied oxygen, and decreases once again. When we switch back to lean conditions, the hydrocarbon level increases again. When we switch from lean to rich conditions, the CO_2 decreases at the beginning and then increases to a higher level while consuming the excess of oxygen. This level is decreased once we switch back to lean conditions. Similar trends are shown in the experiment done with Pt/CeO_2.

The methane experiment shows that for this hydrocarbon both catalysts are completely inactive for this type of experiment.

5 Discussion of results

The TP experiments show a correlation between the number of C-H and C-C bonds and the temperature at which the hydrocarbons start to be oxidized. When comparing methane, ethane and propane, we may see that the oxidation of the hydrocarbons is easier when increasing the number of carbons. If we compare ethane with ethylene and acetylene or propane with propylene and allene, we also see that the saturated hydrocarbons in most of the cases are more difficult to oxidize than the non-saturated hydrocarbons. We can explain this trends thinking of the number of C-H bonds in the hydrocarbons, which are more difficult to break than the C-C bonds. Larger chains give less C-H bonds to break. The same happens when adding double and triple bonds between the carbons. Dimethyl ether and acetaldehyde need lower temperatures of oxidation when compared to ethane. This may be explained since these two compounds are already in a superior state of oxidation.

The experiment carried out for propane with Pt/CeO_2 catalyst shows a very low conversion at high temperatures when the temperature is ramped-down, compared to the sequence where the temperature is ramped-up. It may be that at the beginning of the experiment, when we were working at high temperature and ramping down, the surface of catalyst was oxygen poisoned since we were working at high concentration of oxygen. Afterwards, when the temperature was low, the surface was not poisoned anymore and thus, when the ramp-up was carried out, the conversion could increase to a maximum level.

The experiment carried out for dimethyl ether with Pt/Al_2O_3 catalyst shows a lower conversion at 823 K than at 700 K during the ramp-down sequence. Since the ramp-down sequence is the first to happen, we suggest that during this experiment the system needed more time to reach a good conversion level at the beginning of the experiment.

The SR experiments were carried out in order to study the behavior of the hydrocarbons when changing the oxygen level. They were carried out in order to map the regions in which the compound has higher conversions. The sequence was carried out starting from a very high S-value, then stepping down the oxygen concentration until a very low S-value is reached. Afterwards, the oxygen concentration was stepped up until a high S-value was reached once again. All of the non-saturated hydrocarbons and the aldehyde showed a maximum conversion at the highest concentration of oxygen. The saturated hydrocarbons and dimethyl ether show a maximum conversion at rich conditions.

Some experiments show the maximum conversion of the hydrocarbon at a lower S-value when stepping down the oxygen concentration compared to the stepping up sequence. One example is seen when methane is catalyzed with Pt/Al_2O_3. When stepping down the oxygen concentration, the maximum conversion is observed when S=0.50, but with the stepping up sequence the maximum conversion is observed when S=0.75. We suggest that a higher conversion could not be reached during the step down sequence because the catalyst was still poisoned by the excess of oxygen from the previous steps.

The experiment carried out for methane with the Pt/CeO_2 catalyst shows very good activity at the beginning of the experiment. Afterwards, the conversion decays rapidly and no more activity is seen during the rest of the experiment. This suggests that the catalyst is saturated with oxygen during the whole experiment and is not able to recover a high conversion even at low S-values. The explanation could be that the ceria stores oxygen during lean periods, releasing it during rich periods, resulting in an oxygen poisoning of the catalyst during the whole experiment.

The results of the SR and PR experiments suggest that for the conversion of saturated hydrocarbons rich conditions are preferred. The most active catalyst for these compounds is shown to be the Pt/Al_2O_3. Since Pt/CeO_2 is a catalyst that acts as a reservoir of oxygen, the use of this catalyst for these compounds is not suggested. For the conversion of non-saturated hydrocarbons, lean conditions are preferred and the most active catalyst is shown to be Pt/CeO_2. For the ether, rich conditions seem more effective with Pt/CeO_2 as catalyst. The oxidation of the aldehyde is more effective at lean conditions with Pt/CeO_2 as catalyst.

These results make us think that for saturated hydrocarbons, the right amount of oxygen is very important in order to break the bonds. If the amount is not sufficiently high enough, the production of CO and CO_2 is very low. If the amount is too high, the catalyst is poisoned and the reaction is suppressed. If the catalyst is poisoned, the hydrocarbon does not find sites on the catalyst surface to be dissociated. Thus, it is recommended to use a catalyst that does not act as an oxygen reservoir (or the system will be poisoned by oxygen easily) and at rich conditions.

The carbon balance for the PR experiments carried out with Pt/CeO_2 is not constant. During rich conditions, the carbon balance is less than the 1000 ppm. We suggest that some of the carbon is accumulated on the catalyst surface and is released during lean conditions. When the pulse of oxygen is introduced, all the carbon that is accumulated on the catalyst is oxidized, producing the CO_2 peaks. During lean conditions the carbon balance slowly decreases towards 1000 ppm. We suggest that the accumulation of carbon in the catalyst is due to a partial oxidation, producing a state that binds with the catalyst.

The non-saturated hydrocarbons and acetaldehyde behave different. The oxidation of these compounds is better catalyzed with an oxygen excess. Reducing the levels of oxygen would produce less amount of products. The catalyst in this case should be poisoned as in the case before. This makes us think that these reactions are not so sensitive to oxygen poisoning, so the hydrocarbons may find sites on the catalyst surface where they can be dissociated. Thus, it is recommended to use a catalyst that acts as an oxygen reservoir and lean conditions.

The carbon balance for the PR experiments carried out with these compounds is also not constant, but in this case occurs for both catalysts. We suggest that in this case the carbon is accumulated by the oxygen in a partial oxidation that binds with the catalyst. When the pulse of oxygen increases, it displaces the other compound from the catalyst, which is finally released mostly as CO_2, but also as CO.

The excess of oxygen made the conversion of dimethyl ether fall. The difference with saturated hydrocarbons is that the carbons are not bonded with other carbons, but with an oxygen. That could be the reason why the active catalyst works better for this system. DME needs to find sites on the catalyst surface in order to dissociate, so an excess of oxygen is not recommended or the catalyst would be poisoned and DME will not find any site. After adsorbing onto the catalyst surface, one C-O bond would be broken, releasing the other C-O bond. Still another carbon needs another oxygen, which is given by the active catalyst. Thus, for this system is recommended to use a catalyst that acts as an oxygen reservoir, but with rich conditions.

The carbon balance for the PR experiments carried out with DME is not constant for either catalyst. We suggest that, as we need high levels of oxygen to release the carbon that is bound to the catalyst surface (since the other one would be released) pulsing to lean conditions would release this carbon from the catalyst surface. That is also the reason why pulsing to rich conditions makes the carbon balance to go down the 1000 ppm, since the carbon is being bound waiting for the oxygen to come.

6 Concluding remarks

Experimental results for the catalytic oxidation of characteristic hydrocarbons and oxygenates produced during the combustion of alternative fuels have been presented. In particular, Pt/Al_2O_3 and Pt/CeO_2 were investigated as catalytic systems. The oxidation of three alkanes (methane, ethane, and propane), two alkenes (ethylene and propylene), one diene (allene), one alkyne (acetylene), one ether (dimethyl ether) and one aldehyde (acetaldehyde) was studied.

The studies were carried out by observing the conversion of the hydrocarbon or oxygenate over the catalyst as a function of the temperature by temperature-programmed experiments. The experiments were performed with an oxygen excess (S=1.5), in order to facilitate complete oxidation and hence avoid the production of CO. The results mapped out the temperature in which the hydrocarbon or oxygenate started to be oxidized and the temperature in which the conversion of the hydrocarbon/oxygenate reached maximum. Based on these results, we were able to map a suitable reaction temperature to perform step and pulse response experiments. The results reveal that the oxidation of hydrocarbons with longer carbon chain is catalyzed at lower temperatures than the ones with shorter chain. Also, the oxidation of hydrocarbons with double and triple bonds is catalyzed at lower temperatures compared to the saturated ones. This demonstrates that there is a strong dependence of temperature to break C-H bonds, compared to C-C bonds.

After mapping a suitable temperature, step response experiments were carried out for the hydrocarbons and oxygenates. This study was performed in order to observe the oxygen concentration needed to have the highest conversion of the hydrocarbons and oxygenates. The results showed that for saturated hydrocarbons and for dimethyl ether rich conditions lead to higher conversions, while for non-saturated hydrocarbons and for acetaldehyde, lean conditions were more efficient.

Pulse response experiments were carried out in order to observe the concentration response of the hydrocarbons and oxygenates. From these experiments, and the previous ones, we are able to conclude that for the catalysis for the oxidation of saturated hydrocarbons rich conditions with Pt/Al_2O_3 lead to a higher conversion of the hydrocarbon. Maintaining the system at lean conditions and decreasing the oxygen concentration may work for ethane and propane, but does not work for methane. For the oxidation of the non-saturated hydrocarbons, acetaldehyde and dimethyl ether Pt/CeO_2 leads to a higher conversion. For the former two lean conditions lead to higher conversion, but for the latter rich conditions is more efficient.

7 Further perspectives

During this work, the study of the catalytic oxidation of nine hydrocarbons with two different catalytic systems was performed. However, the process rather than being completed, has just begun. More studies need to be done in order to fully understand these systems.

The first natural step would be doing mechanistic studies for the systems tested here. During this report, a probable mechanism was suggested for the compounds. These suggestions were based on the results obtained in a gas-flow reactor. The picture would be more complete by doing mechanistic studies with FTIR spectroscopy.

Another step suggested is to complete the series begun during this work by adding the study for ethanol and acetone. During this project these two compounds could not be included because they are liquids, and an evaporator is needed in order to do experiments with them. During the time when this project was done, a reactor that counts with this system could not be used. Other interesting compounds that could be studied are the aromatic compounds, which are not covered in this project.

Finally, the study of other catalytic systems could also be recommended. This includes the use of other metals such as Pd or other supports such as TiO_2, MnO_2 or SiO_2.

References

[1] Michael McGee. (2010, July 15). *CO2 Home.* Retrieved August 17, 2010, from CO2 Now: http://co2now.org/

[2] Cambridge University Press. (2007). *IPCC, 2007: Summary for Policymakers. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge, United Kingdom and New York, NY, USA: S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor, H.L. Miller.

[3] Environmental Protection Agency (2009, November 30). *Carbon Dioxide.* Retrieved February 17, 2010, from Climate Change - Greenhouse Gas Emissions: http://www.epa.gov/climatechange/emissions/co2.html

[4] Environmetal Protection Agency (2009, November 30). *Human-Related Sources and Sinks of Carbon Dioxide.* Retrieved February 17, 2010, from Climate Change - Greenhouse Gas Emissions: http://www.epa.gov/climatechange/emissions/co2_human.html

[5] Fuglestvedt, J.; Berntsen, T.; Myhre, G.; Rypdal, K.; Skeie, R. B. (2008). Climate forcing from the transport sectors. *Proceedings of the National Academy of Sciences 105*, 454-458.

[6] Intergovernmental Panel of Climate Change (1996). *Technologies, Policies and Measures for Mitigating Climate Change.* R. T. Watson, M. C. Zinyowera, R. H. Moss.

[7] Chorkendorff, I.; Niemantsverdriet, J. W. (2003). *Concepts of modern catalysis and kinetics.* Weinheim: Wiley-VCH.

[8] Rothenberg, G. (2008). *Catalysis.* Weinheim: Wiley-CVH.

[9] Gaffney, J. S.; Marley, N. A. (2009). The impacts of combustion emissions on air quality and climate - From coal to biofuels and beyond. *Atmospheric Environment 43*, 23-36.

[10] Azar, C. (2008). *Makten över klimatet.* Stockholm: Bonniers.

[11] Grosjean, D.; Grosjean, E.; Gertler, A. W. (2001). On-road emissions of carbonyls from light-duty and heavy-duty vehicles. *Environmental Science & Technology 35*, 45-53.

[12] Magnusson, R.; Nilsson, C.; Andersson, B. (2002). Emissions of aldehydes and ketones from a two-stroke engine using ethanol and ethanol-blended gasoline as fuel. *Environmental Science & Technology 36*, 1656-1664.

[13] Correa, S. M.; Martins, E. M.; Arbilla, G. (2003). Formaldehyde and acetaldehyde in a high traffic street of Rio de Janeiro, Brazil. *Atmospheric Environment 37*, 23-29.

[14] Tang, S. D.; Frank, B. P.; Lanni, T.; Rideout, G.; Meyer, N.; Beregzaszy, C. (2007). Unregulated emissions from a heavy-duty diesel engine with various fuels and emission control systems. *Environmental Science & Technology 41*, 5037–5043.

[15] Ban-Weiss, G. A.; McLaughlin, J. P.; Harley, R. A.; Kean, A. J.; Grosjean, E.; Grosjean, D. (2008). Carbonyl and nitrogen dioxide emissions from gasoline- and diesel-powered motor vehicles. *Environmental Science & Technology 42*, 3944–3950.

[16] Arcoumanis, C.; Bae, C.; Crookes, R.; Kinoshita, E. (2008). The potential of di-methyl ether (DME) as an alternative fuel for compression-ignition engines: A review. *Fuel 87*, 1014-1030.

[17] Anand, R.; Mahalakshmi, N. V. (2007). Simultaneous reduction of NOx and smoke from a direct-injection diesel engine with exhaust gas recirculation and diethyl ether. *Journal of Automobile Engineering 221*, 109-116.

[18] Karavalakis, G.; Stournas, S.; Bakeas, E. (2009). Light vehicle regulated and unregulated emissions from different biodiesels. *Science of the Total Environment 407*, 3338-3346.

[19] Shi, X., Pang, X.; Mu, Y.; He, H.; Shuai, S.; Wang, J.; Chen, H.; Li, R. (2006). Emission reduction potential of using ethanol–biodiesel–diesel fuel blend on a heavy-duty diesel engine. *Atmospheric Environment 40*, 2567–2574.

[20] Yuan, C. S.; Lin, Y. C.; Tsai, C. H.; Wu, C. C.; Lin, Y. S. (2009). Reducing carbonyl emissions from a heavy-duty diesel engine at US transient cycle test by use of paraffinic/biodiesel blends. *Atmospheric Environment 43*, 6175-6181.

[21] Cheung, C. S.; Zhu, L.; Huang, Z. (2009). Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol. *Atmospheric Environment 43*, 4865-4872.

[22] Solomons, T. W. G. (1997). *Fundamentals of organic chemistry.* New York: Wiley.

[23] National Library of Medicine (2009, July 5). *Hazardous Substances Data Bank.* Retrieved March 9, 2010 from Toxicology Data Network: http://toxnet.nlm.nih.gov/

[24] Environmetal Protection Agency (2010, March 5). *Methane.* Retrieved March 9, 2010, from Methane: http://www.epa.gov/methane/index.html

[25] Environmetal Protection Agency (2008, November 12). *The Clean Air Act Amendments of 1990 List of Hazardous Air Pollutants.* Retrieved March 9, 2010, from Technology Transfer Network, Air Toxics Web Site: http://www.epa.gov/ttn/atw/orig189.html

[26] Jacobson, M. Z. (2002). *Atmospheric pollution. History, science, and regulation.* United Kingdom: Cambridge University Press.

[27] Jackson, A. R. W.; Jackson, J. M. (2000) *Environmental Science. The natural environment and human impact.* Harlow: Pearson Education

[28] Taylor, H. S. (1925). A theory of the catalytic surface. *Proceedings of the Royal Society A105*, 105.

[29] McCabe, R. W.; Mitchell, P. J. (1984). Reactions of ethanol and acetaldehyde over noble metal and metal oxide catalysis. *Industrial & Engineering Chemistry Product Research and Development 23*, 196-202.

[30] Aryafar, M.; Zaera, F. (1997) Kinetic study of the catalytic oxidation of alkanes over nickel, palladium, and platinum foils. *Catalysis Letters 48*, 173-183.

[31] Becker, E.; Carlsson, P. A.; Skoglundh, M. (2009) Methane oxidation over alumina and ceria supported platinum. *Topics in Catalysis 52*, 1957-1961.

[32] Pettersson, L. J.; Järås, S. G.; Andersson, S.; Marsh, P. (1995) Control of unregulated emissions from ethanol-fuelled diesel engines - A study of the effect of catalyst support on the low temperature oxidation of ethanol and acetaldehyde using precious metals. In Frennet, A.; Bastin, J. M. *Catalysis and Automotive Pollution Control III.* Amsterdam: Elsevier Science. 855-869.

[33] Carlsson, P. A.; Mollner, S.; Arnby, K.; Skoglundh, M. (2004) Effect of periodic operation on the low-temperature activity for propane oxidation over Pt/Al_2O_3 catalysts. *Chemical Engineering Science 59.* 4313-4323.

[34] Summers, J. C.; Baron, K. (1979) The effects of SO_2 on the performance of noble metal catalysts in automobile exhaust. *Journal of Catalysis 57.* 380-389.

A Preparation of catalyst samples

The two catalysts were prepared so the number of moles per surface area was 1.7×10^{-6}. For each sample a total of 3 g was prepared. The weight percentage of noble metal per support was calculated as follows:

$$mol = \left(\frac{mol}{SA}\right)(SA) \tag{A.1}$$

$$\%w/w = \frac{(mol)\,(M)}{m_T}\,(100) \tag{A.2}$$

Where mol is the amount of moles of catalyst, SA is the surface area of the support, M is the molar mass of the catalyst and m_T is the total mass of the sample.

For Pt/Al_2O_3:

$mol = (1.7 \times 10^{-6})\,(180) = 3.08 \times 10^{-4}$

$\%w/w = \frac{(3.08\times10^{-4})(195.08)}{3}\,(100) = 2\%$

For Pt/CeO_2:

$mol = (1.7 \times 10^{-6})\,(140) = 2.39 \times 10^{-4}$

$\%w/w = \frac{(2.39\times10^{-4})(195.08)}{3}\,(100) = 1.56\%$

The next table shows the amount of substances mixed during the preparation of these catalysts:

Substance	Amount used in Pt/Al_2O_3 catalyst [g]	Amount used in Pt/CeO_2 catalyst [g]
$(NH_3)_4Pt(NO_3)_2$	1.5087	1.2594
NH_3	0.3	0.3
H_2O	0.5763	0.4515
Support	2.94	2.95

B Flows used by experiment

This section presents the flows used for each gas experiment at different S-values. The total flow was fixed at 400 ml/min. The mass flow controllers flow was calculated with a K-factor for each mixture as presented in the next table:

Component	Concentration (%)	K-factor (mix)
Ar	100	1.40
O_2/Ar	2	1.39
CH_4/Ar	2	1.38
C_2H_6/Ar	2	1.35
C_2H_4/Ar	2	1.36
C_2H_2/Ar	2	1.33
C_3H_8/Ar	10	1.07
C_3H_6/Ar	4	1.30
C_3H_2/Ar	2	0.94
C_2H_6O/Ar	10	1.11
C_2H_4O/Ar	2	1.35

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{B.1}$$

$$S = \frac{[O_2]}{2[CH_4]} \tag{B.2}$$

[CH_4] (ppm)	Flow CH_4 (ml/min)	Set Point (ml/min)	S	[O_2] (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	20	14.56	3.00	6000	120	86.45	260	185.71
1000	20	14.56	1.50	3000	60	43.22	320	228.57
1000	20	14.56	1.25	2500	50	36.02	330	235.71
1000	20	14.56	1.05	2100	42	30.26	338	241.43
1000	20	14.56	0.95	1900	38	27.38	342	244.29
1000	20	14.56	0.75	1500	30	21.61	350	250.00
1000	20	14.56	0.50	1000	20	14.41	360	257.14
1000	20	14.56	0.25	500	10	7.20	370	264.29

$$C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O \tag{B.3}$$

$$S = \frac{2[O_2]}{7[C_2H_6]} \tag{B.4}$$

[C_2H_6] (ppm)	Flow C_2H_6 (ml/min)	Set Point (ml/min)	S	[O_2] (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	20	14.82	3.00	10500	210	151.29	170	121.43
1000	20	14.82	1.50	5250	105	75.64	275	196.43
1000	20	14.82	1.25	4375	87.5	63.04	292.5	208.93
1000	20	14.82	1.05	3675	73.5	52.95	306.5	218.93
1000	20	14.82	0.95	3325	66.5	47.91	313.5	223.93
1000	20	14.82	0.75	2625	52.5	37.82	327.5	233.93
1000	20	14.82	0.50	1750	35	25.21	345	246.43
1000	20	14.82	0.25	875	17.5	12.61	362.5	258.93

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{B.5}$$

$$S = \frac{[O_2]}{3[C_2H_4]} \tag{B.6}$$

$[C_2H_4]$ (ppm)	Flow C_2H_4 (ml/min)	Set Point (ml/min)	S	$[O_2]$ (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	20	14.67	3.00	9000	180	129.67	200	142.86
1000	20	14.67	1.50	4500	90	64.84	290	207.14
1000	20	14.67	1.25	3750	75	54.03	305	217.86
1000	20	14.67	1.05	3150	63	45.39	317	226.43
1000	20	14.67	0.95	2850	57	41.06	323	230.71
1000	20	14.67	0.75	2250	45	32.42	335	239.29
1000	20	14.67	0.50	1500	30	21.61	350	250.00
1000	20	14.67	0.25	750	15	10.81	365	260.71

$$C_2H_2 + 5/2O_2 \rightarrow 2CO_2 + H_2O \tag{B.7}$$

$$S = \frac{2[O_2]}{5[C_2H_2]} \tag{B.8}$$

$[C_2H_2]$ (ppm)	Flow C_2H_2 (ml/min)	Set Point (ml/min)	S	$[O_2]$ (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	20	15.00	3.00	7500	150	108.06	230	164.29
1000	20	15.00	1.50	3750	75	54.03	305	217.86
1000	20	15.00	1.25	3125	62.5	45.03	317.5	226.79
1000	20	15.00	1.05	2625	52.5	37.82	327.5	233.93
1000	20	15.00	0.95	2375	47.5	34.22	332.5	237.50
1000	20	15.00	0.75	1875	37.5	27.02	342.5	244.64
1000	20	15.00	0.50	1250	25	18.01	355	253.57
1000	20	15.00	0.25	625	12.5	9.01	367.5	262.50

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{B.9}$$

$$S = \frac{[O_2]}{5[C_3H_8]} \tag{B.10}$$

$[C_3H_8]$ (ppm)	Flow C_3H_8 (ml/min)	Set Point (ml/min)	S	$[O_2]$ (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	4	3.75	2.00	10000	200	144.08	196	140.00
1000	4	3.75	1.50	7500	150	108.06	246	175.71
1000	4	3.75	1.25	6250	125	90.05	271	193.57
1000	4	3.75	1.05	5250	105	75.64	291	207.86
1000	4	3.75	0.95	4750	95	68.44	301	215.00
1000	4	3.75	0.75	3750	75	54.03	321	229.14
1000	4	3.75	0.50	2500	50	36.02	346	247.14
1000	4	3.75	0.25	1250	25	18.01	371	265.00

$$C_3H_6 + 9/2O_2 \rightarrow 3CO_2 + 3H_2O \tag{B.11}$$

$$S = \frac{2[O_2]}{9[C_3H_6]} \tag{B.12}$$

$[C_3H_6]$ (ppm)	Flow C_3H_6 (ml/min)	Set Point (ml/min)	S	$[O_2]$ (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	10	7.67	2.00	9000	180	129.67	210	150.00
1000	10	7.67	1.50	6750	135	97.26	255	182.14
1000	10	7.67	1.25	5625	112.5	81.05	277.5	198.21
1000	10	7.67	1.05	4725	94.5	68.08	295.5	211.07
1000	10	7.67	0.95	4275	85.5	61.59	304.5	217.50
1000	10	7.67	0.75	3375	67.5	48.63	322.5	230.36
1000	10	7.67	0.50	2250	45	32.42	345	246.43
1000	10	7.67	0.25	1125	22.5	16.21	367.5	262.50

$$C_3H_4 + 4O_2 \rightarrow 3CO_2 + 2H_2O \tag{B.13}$$

$$S = \frac{[O_2]}{4[C_3H_4]} \tag{B.14}$$

$[C_3H_4]$ (ppm)	Flow C_3H_4 (ml/min)	Set Point (ml/min)	S	$[O_2]$ (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	20	21.18	2.50	10000	200	144.08	180	128.57
1000	20	21.18	1.50	6000	120	86.45	260	185.71
1000	20	21.18	1.25	5000	100	72.04	280	200.00
1000	20	21.18	1.05	4200	84	60.51	296	211.43
1000	20	21.18	0.95	3800	76	54.75	304	217.14
1000	20	21.18	0.75	3000	60	43.22	320	228.57
1000	20	21.18	0.50	2000	20	28.82	340	242.86
1000	20	21.18	0.25	1000	20	14.41	360	257.14

$$C_2H_6O + 3O_2 \rightarrow 2CO_2 + 3H_2O \tag{B.15}$$

$$S = \frac{[O_2]}{3[C_2H_6O]} \tag{B.16}$$

$[C_2H_6O]$ (ppm)	Flow C_2H_6O (ml/min)	Set Point (ml/min)	S	$[O_2]$ (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	4	3.60	3.00	9000	180	129.67	216	154.29
1000	4	3.60	1.50	4500	90	64.84	306	218.57
1000	4	3.60	1.25	3750	75	54.03	321	229.29
1000	4	3.60	1.05	3150	63	45.39	333	237.86
1000	4	3.60	0.95	2850	57	41.06	339	242.14
1000	4	3.60	0.75	2250	45	32.42	351	250.71
1000	4	3.60	0.50	1500	30	21.61	366	261.43
1000	4	3.60	0.25	750	15	10.81	381	272.14

$$C_2H_4O + 5/2O_2 \rightarrow 2CO_2 + 2H_2O \tag{B.17}$$

$$S = \frac{2[O_2]}{5[C_2H_4O]} \tag{B.18}$$

$[C_2H_4O]$ (ppm)	Flow C_2H_4O (ml/min)	Set Point (ml/min)	S	$[O_2]$ (ppm)	Flow O_2 (ml/min)	Set Point (ml/min)	Flow Ar (ml/min)	Set Point (ml/min)
1000	20	14.77	3.00	7500	150	108.06	230	164.29
1000	20	14.77	1.50	3750	75	54.03	305	217.86
1000	20	14.77	1.25	3125	62.5	45.03	317.5	226.79
1000	20	14.77	1.05	2625	52.5	37.82	327.5	233.93
1000	20	14.77	0.95	2375	47.5	34.22	332.5	237.50
1000	20	14.77	0.75	1875	37.5	27.02	342.5	244.64
1000	20	14.77	0.50	1250	25	18.01	355	253.57
1000	20	14.77	0.25	625	12.5	9.01	367.5	262.50

C Additional results

C.1 Methane

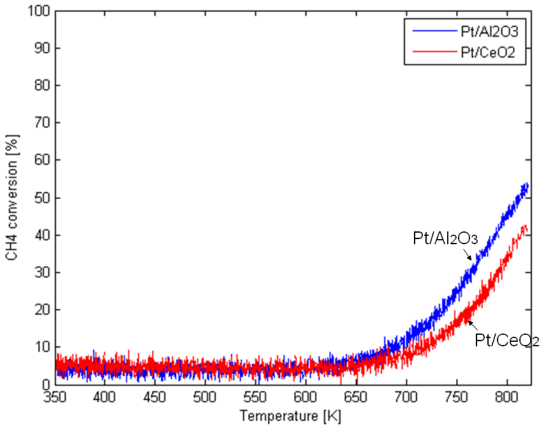


Figure C.1: Temperature-programmed experiment for methane ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

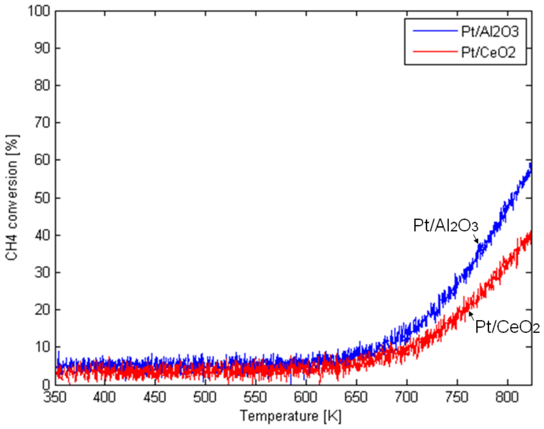


Figure C.2: Temperature-programmed experiment for methane ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

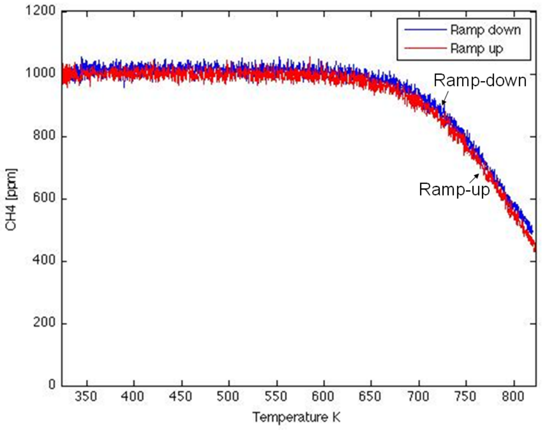


Figure C.3: Temperature-programmed experiment for methane with Pt/Al_2O_3 acting as the catalyst

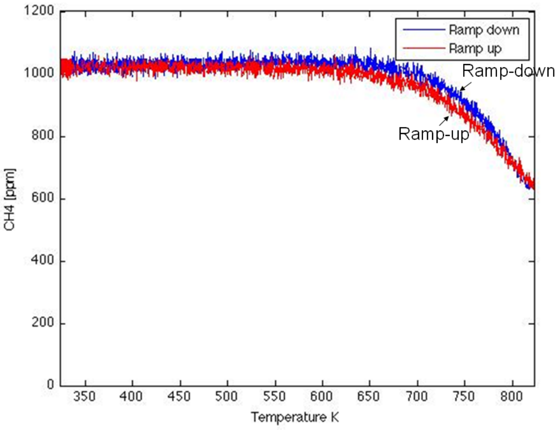


Figure C.4: Temperature-programmed experiment for methane with Pt/CeO_2 acting as the catalyst

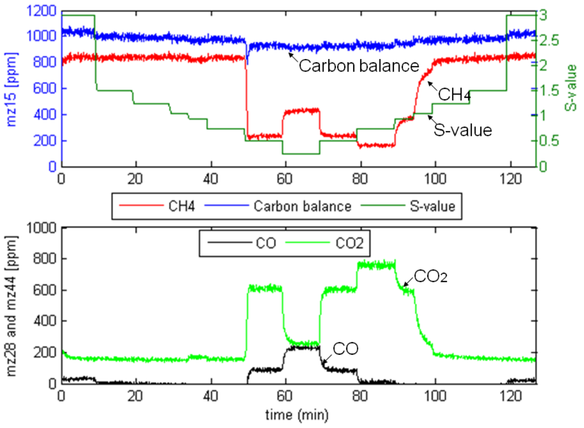


Figure C.5: Step-response experiment for methane with Pt/Al_2O_3 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

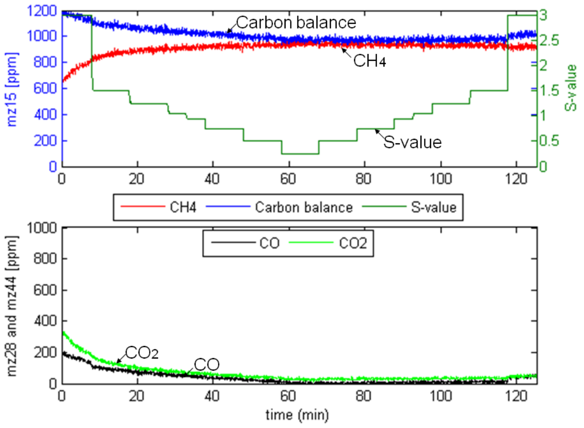


Figure C.6: Step-response experiment for methane with Pt/CeO_2 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

Table C.1: Methane conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
3.00	16	16	35-18	8
1.50	16	16	18-12	6
1.25	16	17	11	6
1.05	16	26	9	6
0.95	16	63	9	6
0.75	16	84	7	6
0.50	77	76	7	6
0.25	57	57	6	6

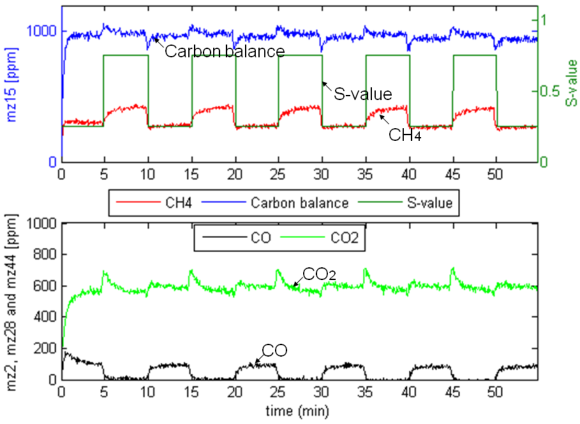


Figure C.7: Pulse-response experiment for methane with Pt/Al_2O_3 catalyst with S=0.25 (5 min) and S=0.75 (5 min)

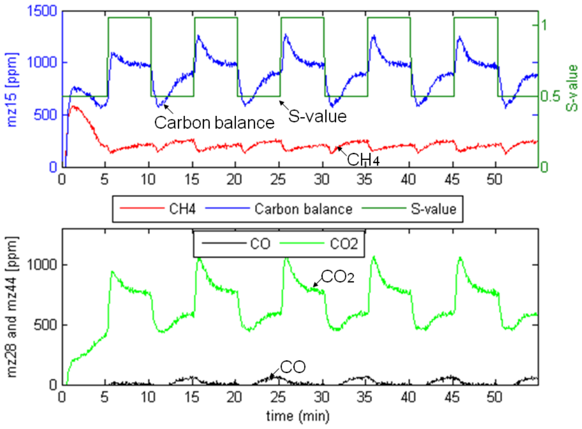


Figure C.8: Pulse-response experiment for methane with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

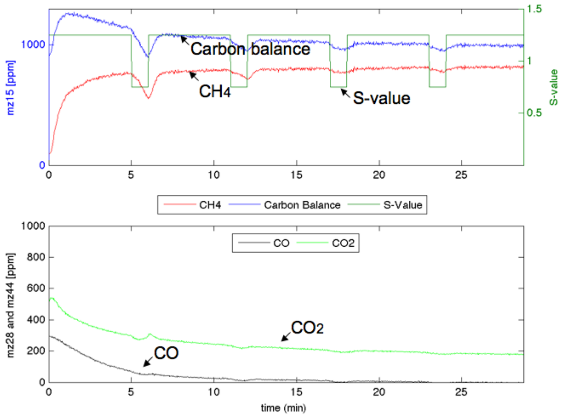


Figure C.9: Pulse-response experiment for methane with Pt/Al_2O_3 catalyst with S=1.25 (5 min) and S=0.75 (1 min)

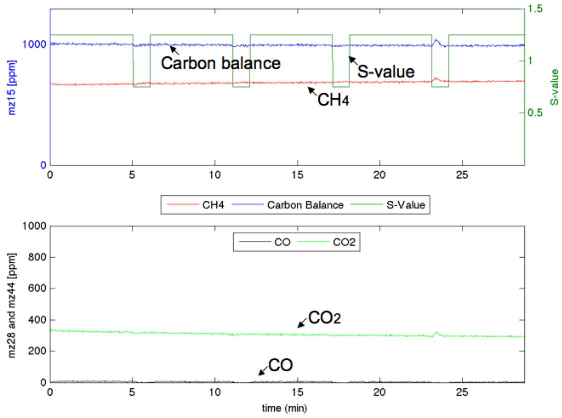


Figure C.10: Pulse-response experiment for methane with Pt/CeO_2 catalyst with S=1.25 (5 min) and S=0.75 (1 min)

C.2 Ethane

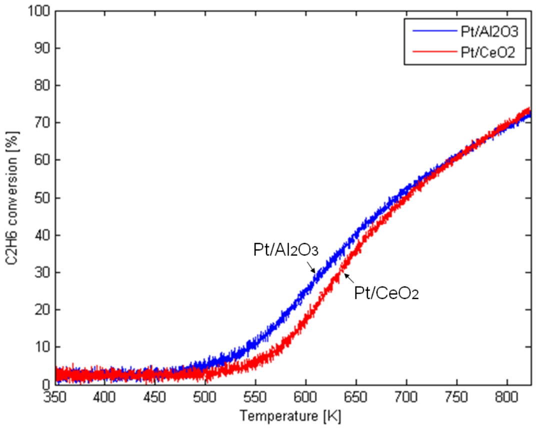


Figure C.11: Temperature-programmed experiment for ethane ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

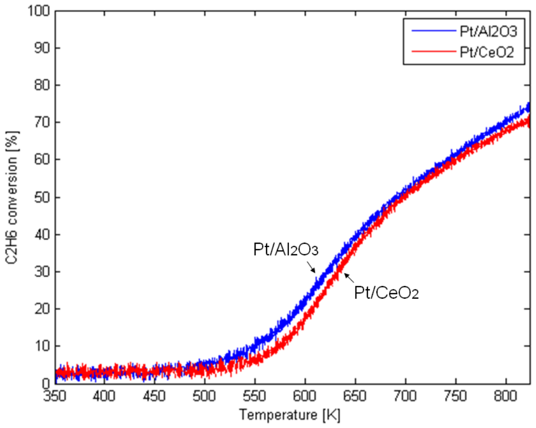


Figure C.12: Temperature-programmed experiment for ethane ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

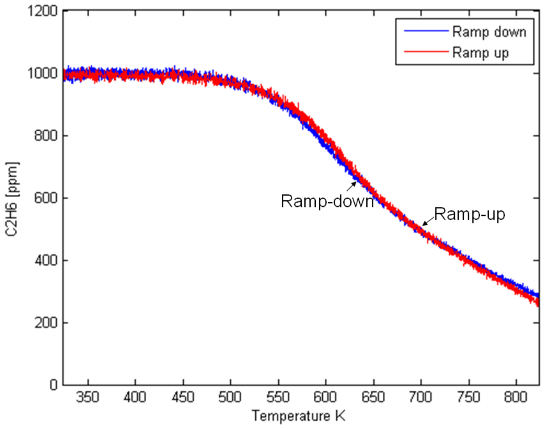


Figure C.13: Temperature-programmed experiment for ethane with Pt/Al_2O_3 acting as the catalyst

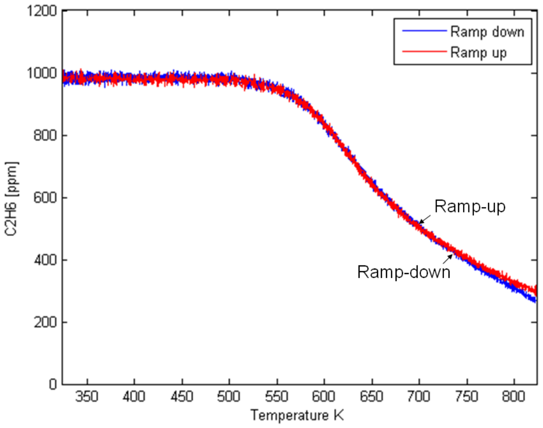


Figure C.14: Temperature-programmed experiment for ethane with Pt/CeO_2 acting as the catalyst

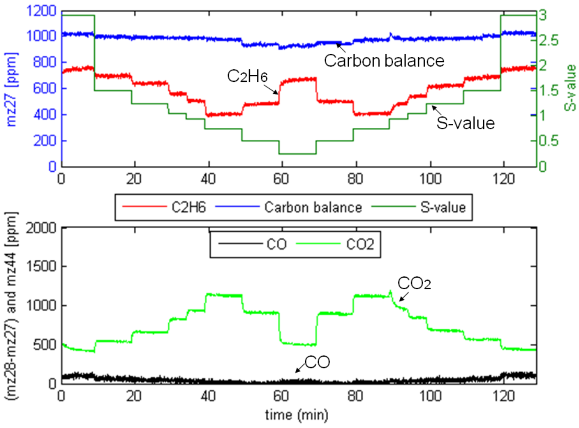


Figure C.15: Step-response experiment for ethane with Pt/Al_2O_3 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

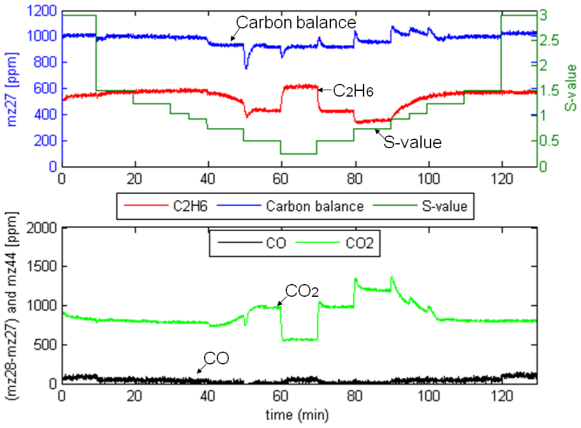


Figure C.16: Step-response experiment for ethane with Pt/CeO_2 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

Table C.2: Ethane conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
3.00	25	25	45	43
1.50	30	31	43	43
1.25	36	38	42	44
1.05	44	46	42	47
0.95	49	51	42	52
0.75	60	59	50	64
0.50	51	50	57	57
0.25	33	33	39	39

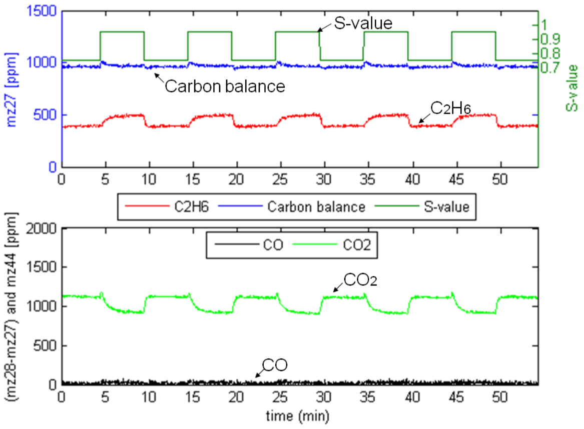


Figure C.17: Pulse-response experiment for ethane with Pt/Al_2O_3 catalyst with S=0.75 (5 min) and S=0.95 (5 min)

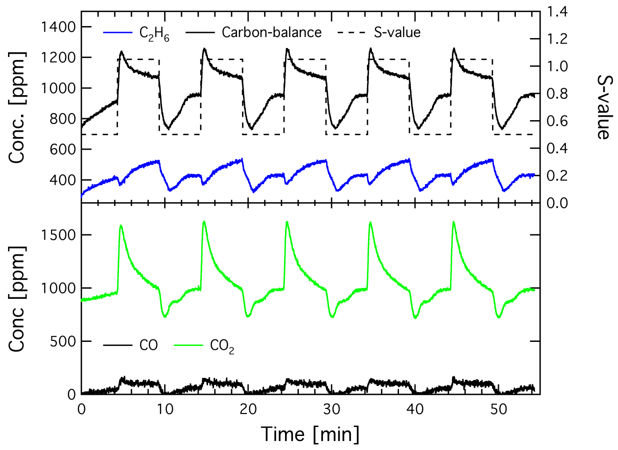


Figure C.18: Pulse-response experiment for ethane with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

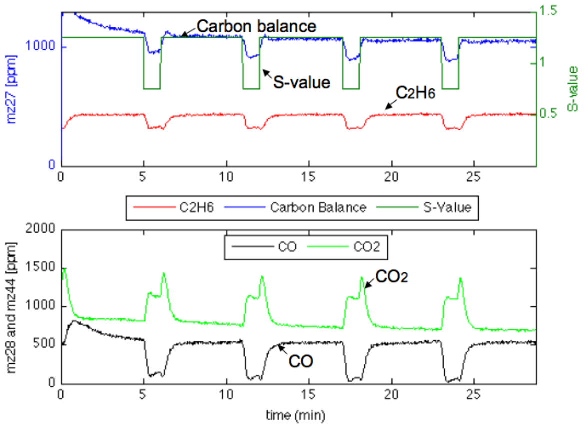


Figure C.19: Pulse-response experiment for ethane with Pt/Al_2O_3 catalyst with S=1.25 (5 min) and S=0.75 (1 min)

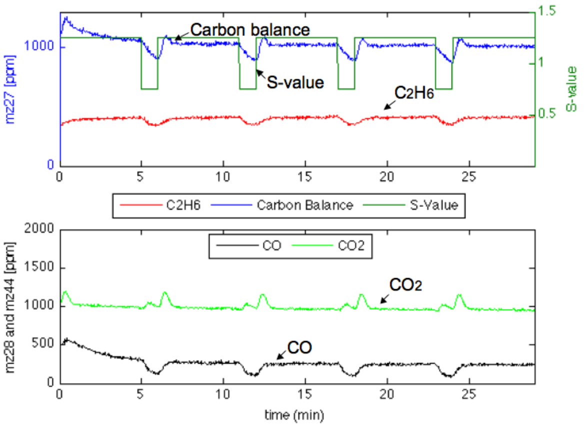


Figure C.20: Pulse-response experiment for ethane with Pt/CeO_2 catalyst with S=1.25 (5 min) and S=0.75 (1 min)

C.3 Propane

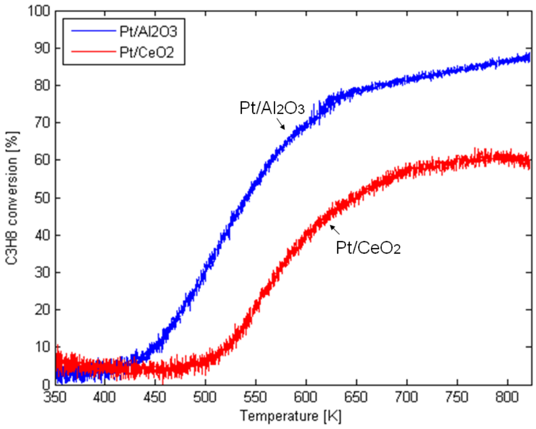


Figure C.21: Temperature-programmed experiment for propane ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

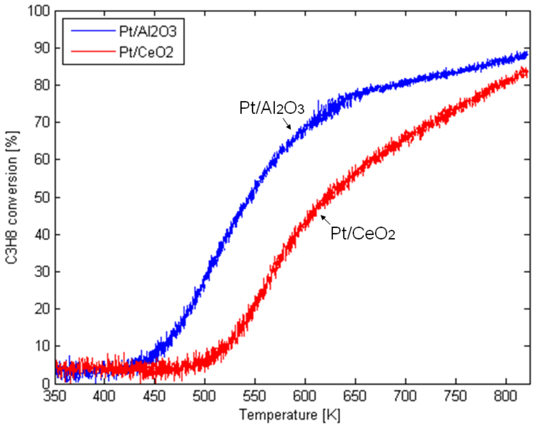


Figure C.22: Temperature-programmed experiment for propane ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

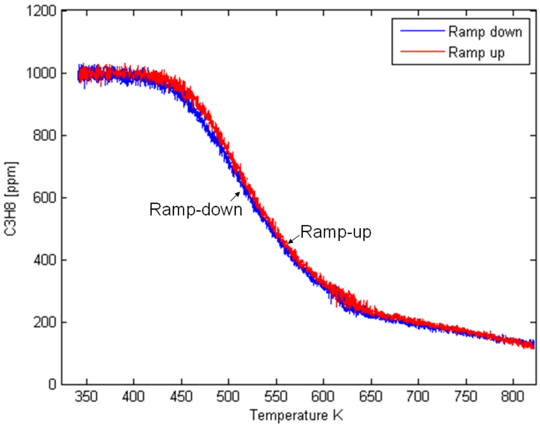


Figure C.23: Temperature-programmed experiment for propane with Pt/Al_2O_3 acting as the catalyst

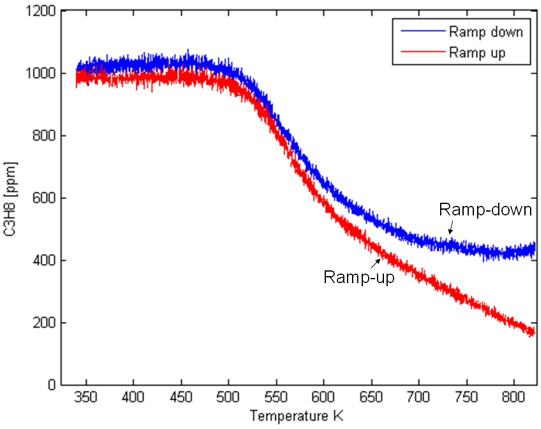


Figure C.24: Temperature-programmed experiment for propane with Pt/CeO_2 acting as the catalyst

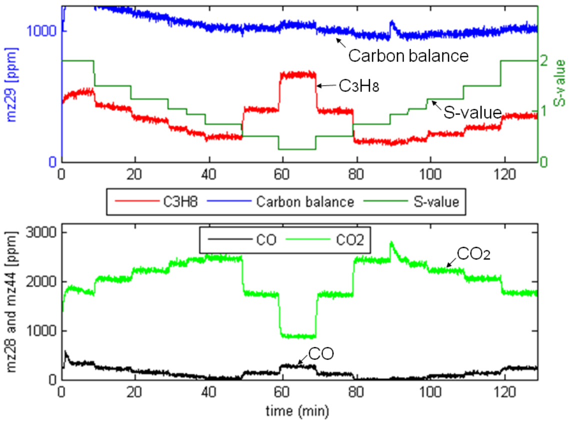


Figure C.25: Step-response experiment for propane with Pt/Al_2O_3 as the catalyst. Step-down from S=2 to S=0.25 and step-up from S=0.25 to S=2.

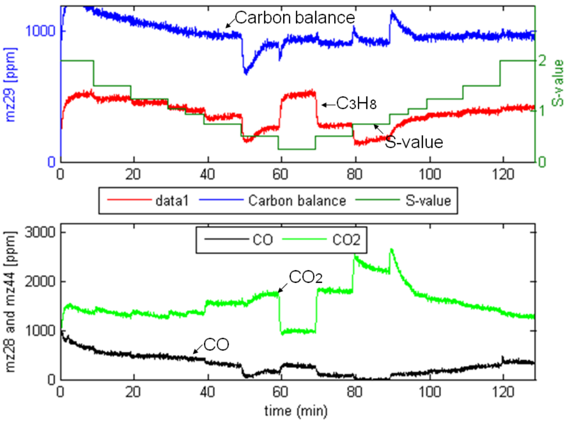


Figure C.26: Step-response experiment for propane with Pt/CeO_2 as the catalyst. Step-down from S=2 to S=0.25 and step-up from S=0.25 to S=2.

Table C.3: Propane conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
2.00	45	65	48	59
1.50	60	74	52	61
1.25	70	78	55	64
1.05	75	83	59	65
0.95	77	85	61	65
0.75	80	84	65	82
0.50	60	60	74	72
0.25	33	33	49	48

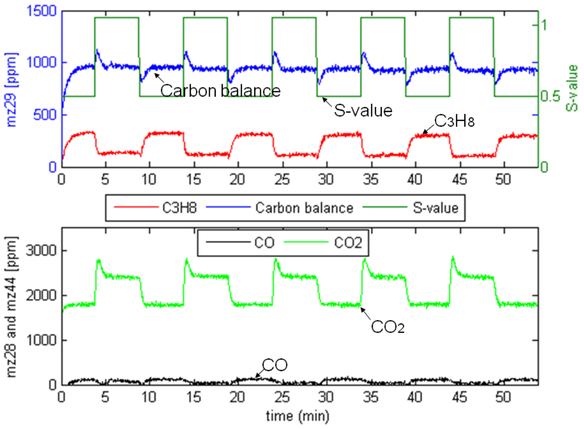


Figure C.27: Pulse-response experiment for propane with Pt/Al_2O_3 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

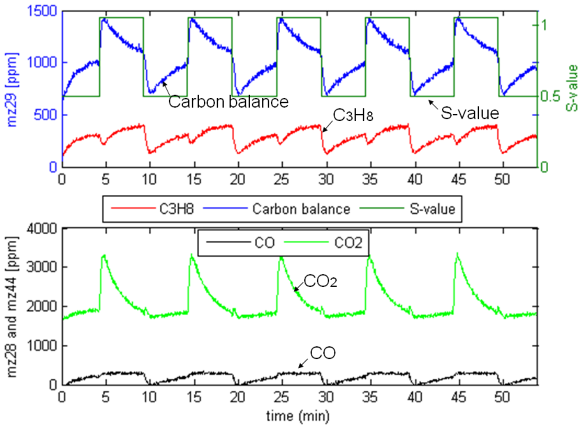


Figure C.28: Pulse-response experiment for propane with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

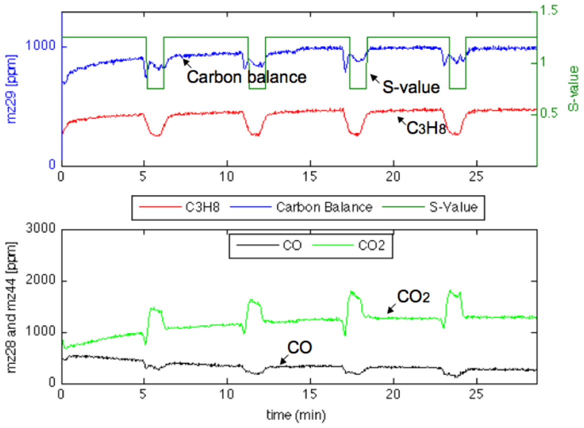


Figure C.29: Pulse-response experiment for propane with Pt/Al_2O_3 catalyst with S=1.25 (5 min) and S=0.75 (1 min)

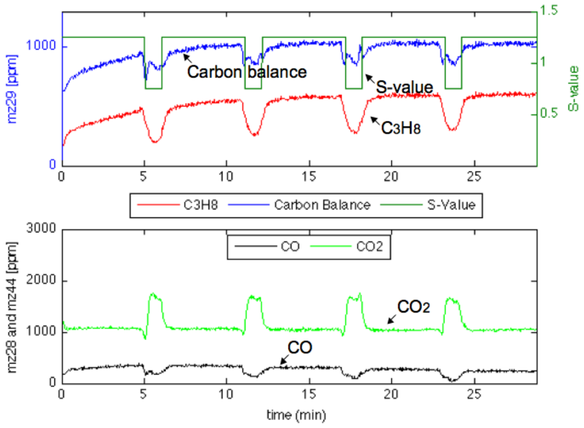


Figure C.30: Pulse-response experiment for propane with Pt/CeO_2 catalyst with S=1.25 (5 min) and S=0.75 (1 min)

C.4 Ethylene

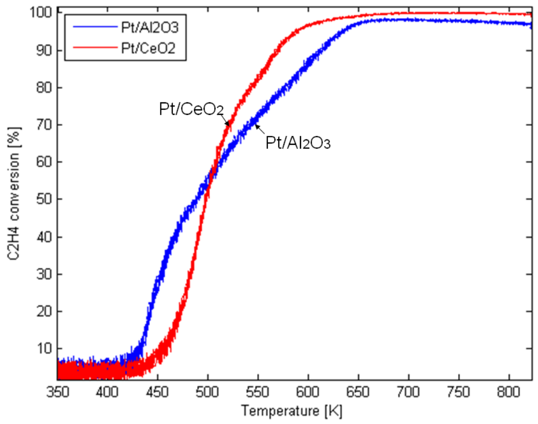


Figure C.31: Temperature-programmed experiment for ethylene ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

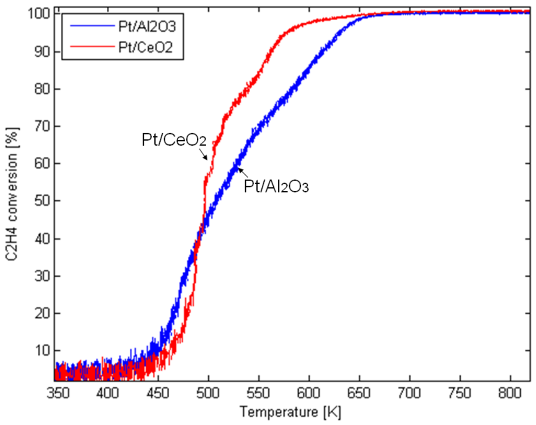


Figure C.32: Temperature-programmed experiment for ethylene ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

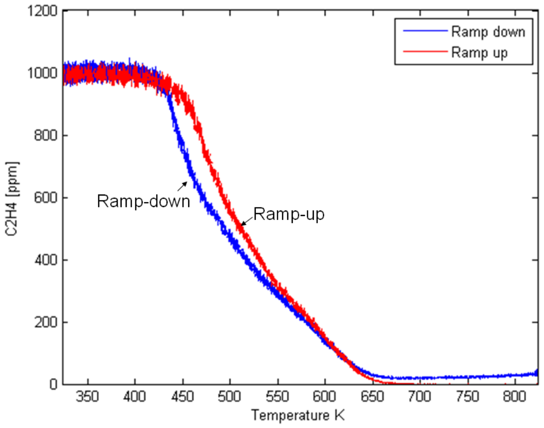


Figure C.33: Temperature-programmed experiment for ethylene with Pt/Al_2O_3 acting as the catalyst

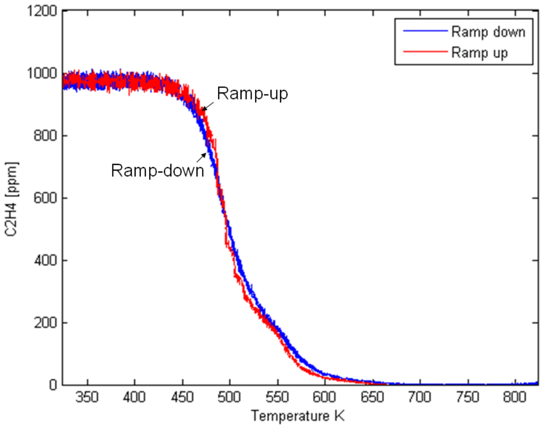


Figure C.34: Temperature-programmed experiment for ethylene with Pt/CeO_2 acting as the catalyst

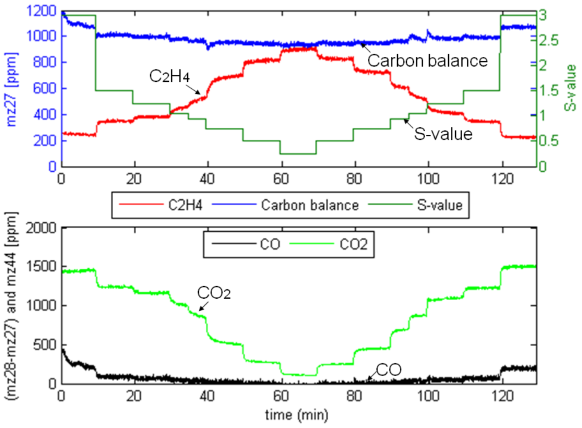


Figure C.35: Step-response experiment for ethylene with Pt/Al_2O_3 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

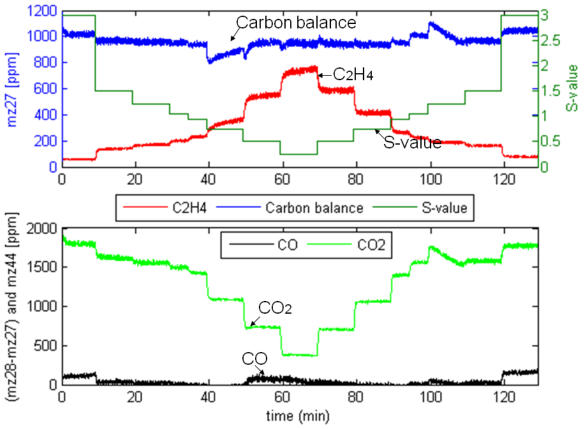


Figure C.36: Step-response experiment for ethylene with Pt/CeO_2 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

Table C.4: Ethylene conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
3.00	75	77	94	92
1.50	65	66	86	84
1.25	62	59	83	81
1.05	54	48	80	78
0.95	48	39	77	74
0.75	30	28	64	59
0.50	18	17	45	41
0.25	10	10	25	25

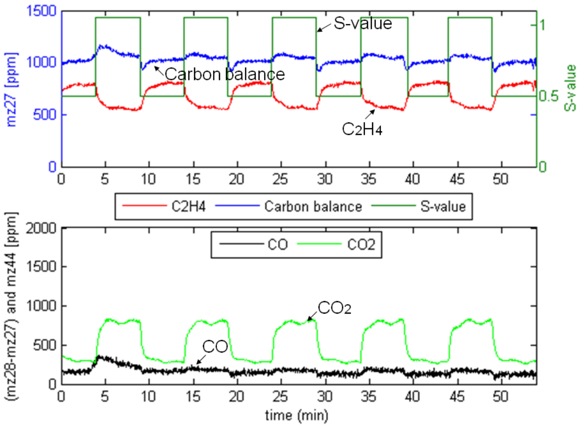


Figure C.37: Pulse-response experiment for ethylene with Pt/Al_2O_3 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

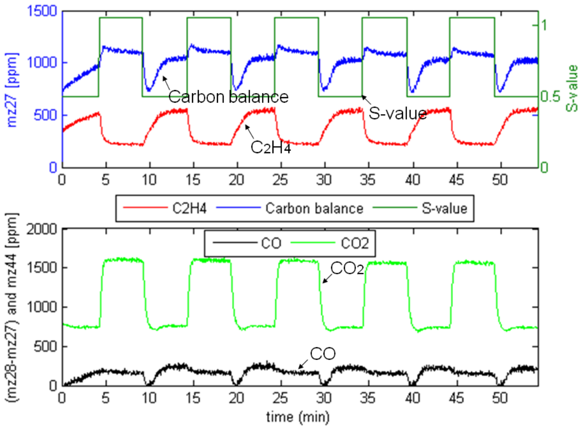


Figure C.38: Pulse-response experiment for ethylene with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

C.5 Propylene

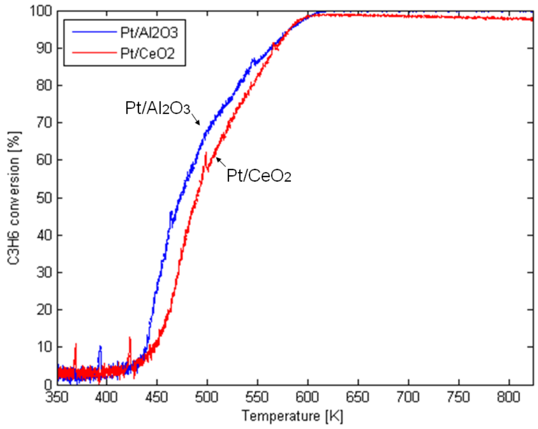


Figure C.39: Temperature-programmed experiment for propylene ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

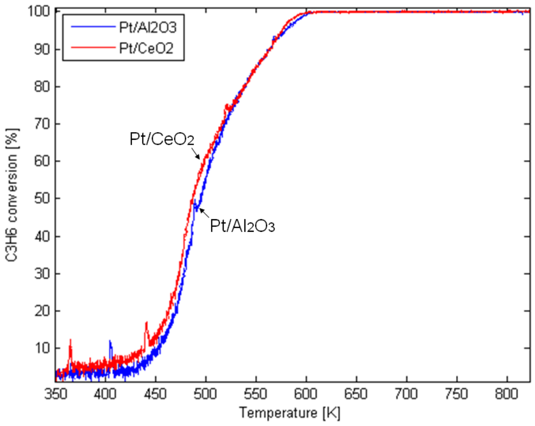


Figure C.40: Temperature-programmed experiment for propylene ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

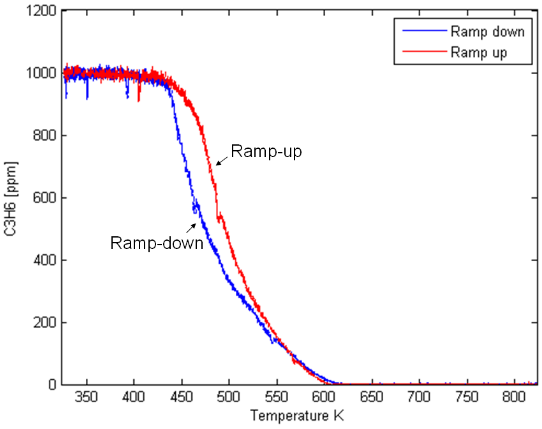


Figure C.41: Temperature-programmed experiment for propylene with Pt/Al_2O_3 acting as the catalyst

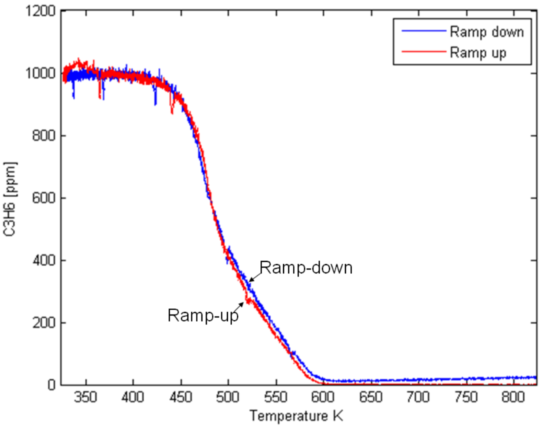


Figure C.42: Temperature-programmed experiment for propylene with Pt/CeO_2 acting as the catalyst

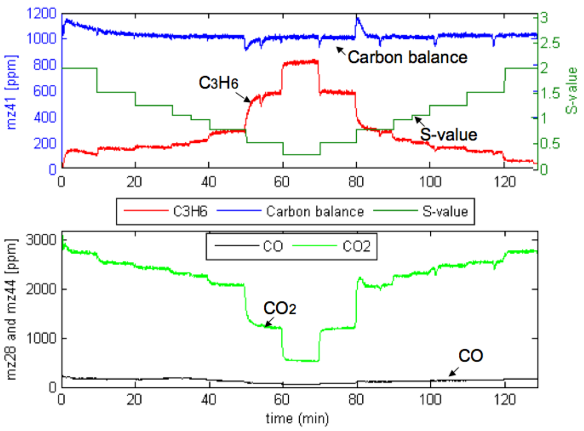


Figure C.43: Step-response experiment for propylene with Pt/Al_2O_3 as the catalyst. Step-down from S=2 to S=0.25 and step-up from S=0.25 to S=2.

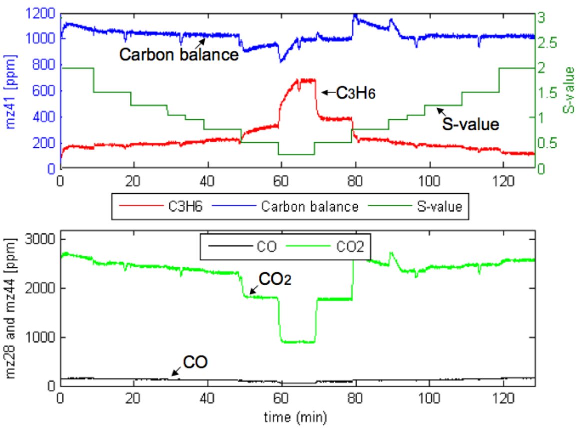


Figure C.44: Step-response experiment for propylene with Pt/CeO_2 as the catalyst. Step-down from S=2 to S=0.25 and step-up from S=0.25 to S=2.

Table C.5: Propylene conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
2.00	88	95	85	89
1.50	85	87	83	86
1.25	84	85	82	84
1.05	82	81	81	82
0.95	80	79	81	81
0.75	72	73	79	79
0.50	42	42	69	63
0.25	19	19	33	33

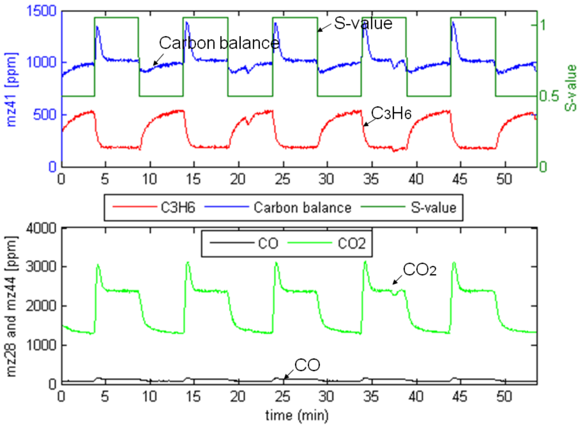


Figure C.45: Pulse-response experiment for propylene with Pt/Al_2O_3 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

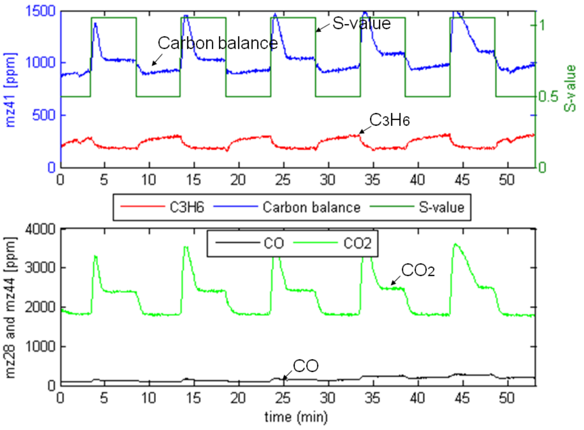


Figure C.46: Pulse-response experiment for propylene with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

C.6 Allene

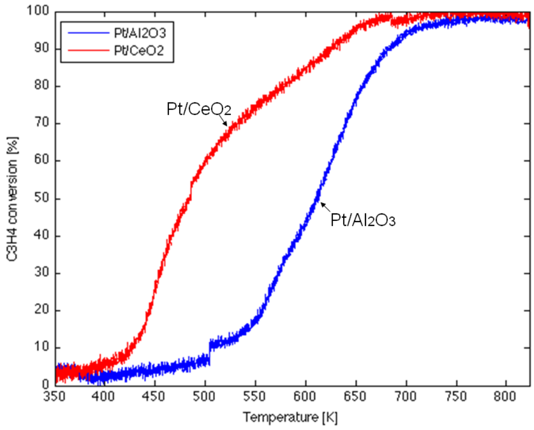


Figure C.47: Temperature-programmed experiment for allene ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

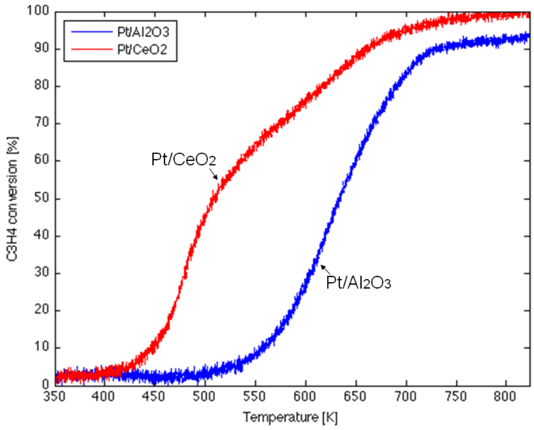


Figure C.48: Temperature-programmed experiment for allene ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

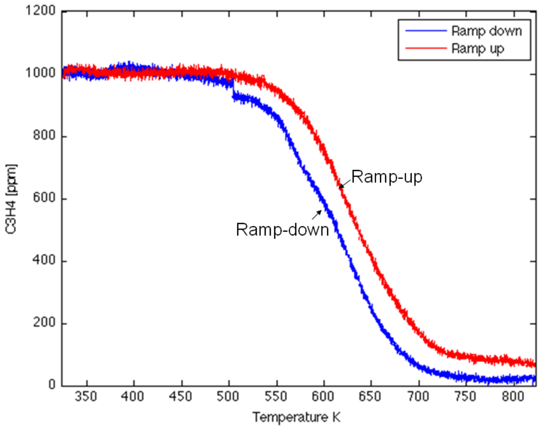


Figure C.49: Temperature-programmed experiment for allene with Pt/Al_2O_3 acting as the catalyst

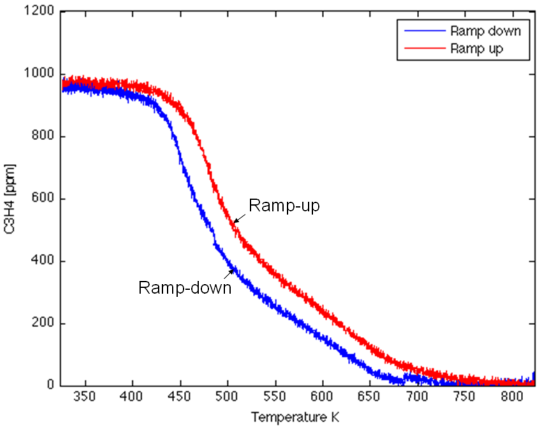


Figure C.50: Temperature-programmed experiment for allene with Pt/CeO_2 acting as the catalyst

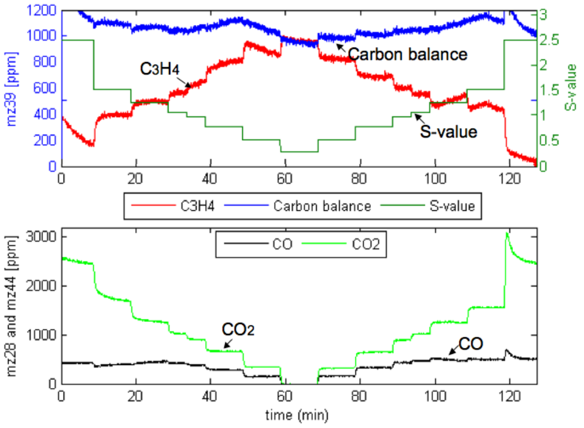


Figure C.51: Step-response experiment for allene with Pt/Al_2O_3 as the catalyst. Step-down from S=2.50 to S=0.25 and step-up from S=0.25 to S=2.50.

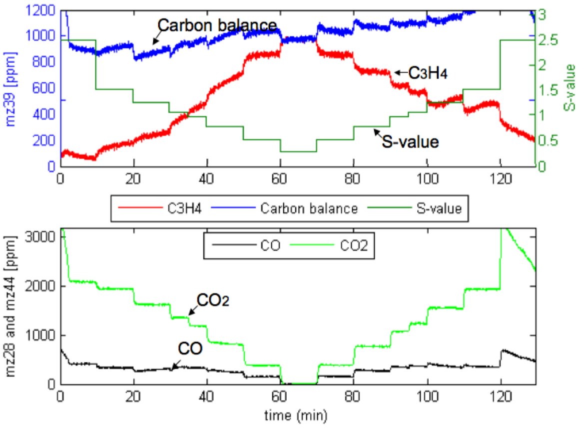


Figure C.52: Step-response experiment for allene with Pt/CeO_2 as the catalyst. Step-down from S=2.50 to S=0.25 and step-up from S=0.25 to S=2.50.

Table C.6: Allene conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
2.50	85	96	94	80
1.50	61	57	84	54
1.25	51	47	77	51
1.05	44	46	64	44
0.95	36	41	54	39
0.75	20	32	32	28
0.50	14	18	14	14
0.25	4	5	3	3

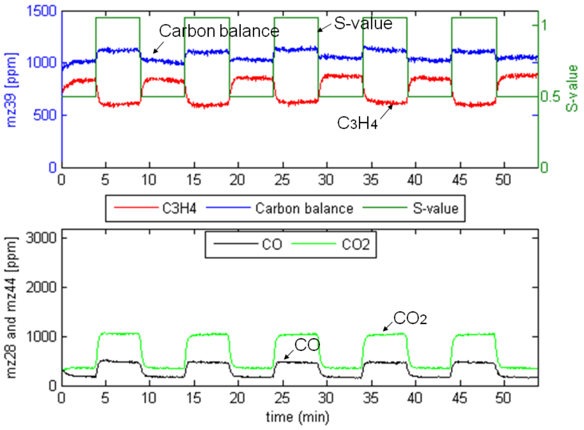


Figure C.53: Pulse-response experiment for allene with Pt/Al_2O_3 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

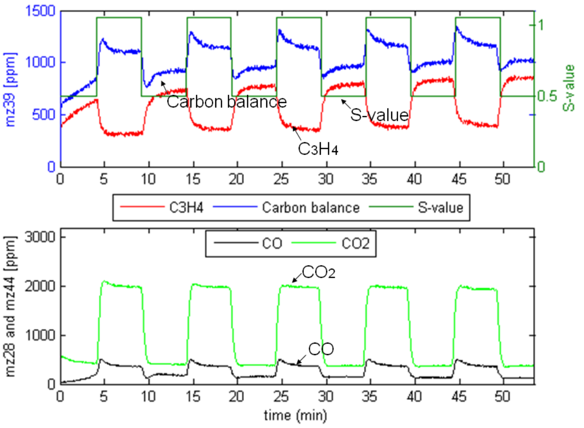


Figure C.54: Pulse-response experiment for allene with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

C.7 Acetylene

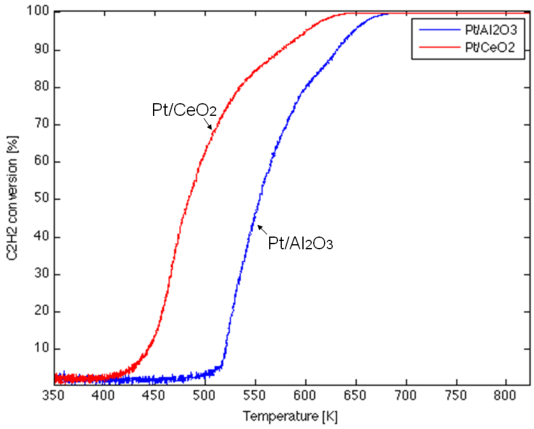


Figure C.55: Temperature-programmed experiment for acetylene ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

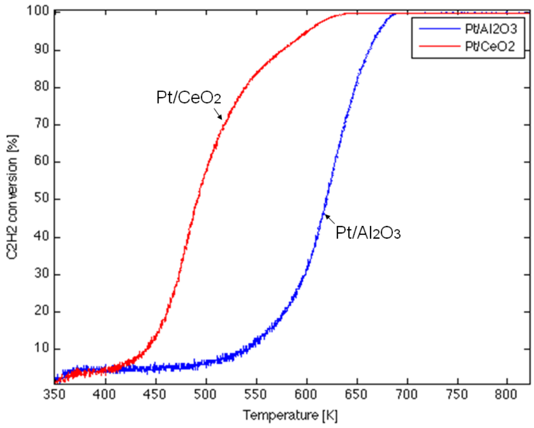


Figure C.56: Temperature-programmed experiment for acetylene ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

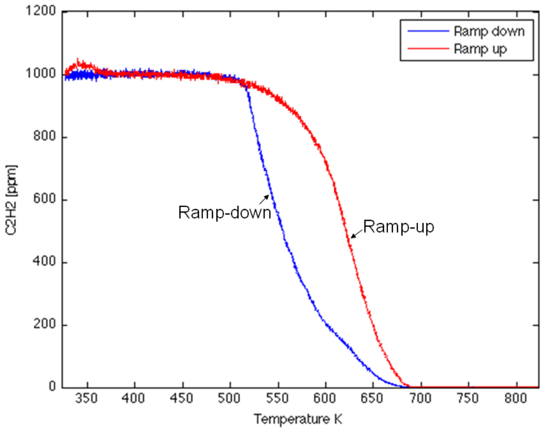


Figure C.57: Temperature-programmed experiment for acetylene with Pt/Al_2O_3 acting as the catalyst

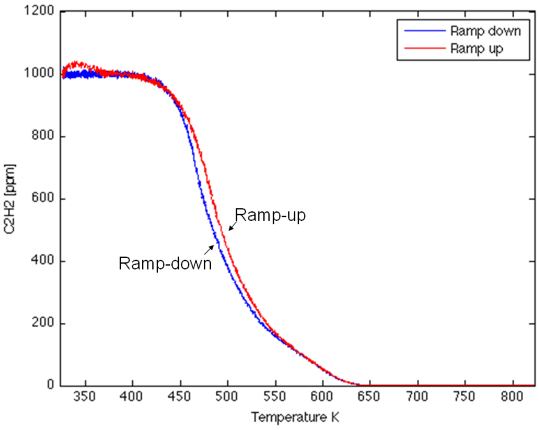


Figure C.58: Temperature-programmed experiment for acetylene with Pt/CeO_2 acting as the catalyst

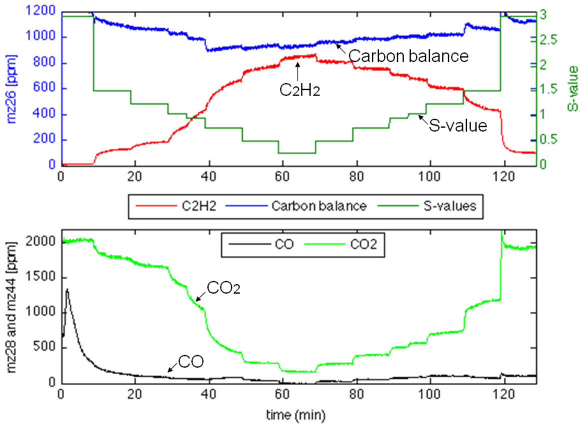


Figure C.59: Step-response experiment for acetylene with Pt/Al_2O_3 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

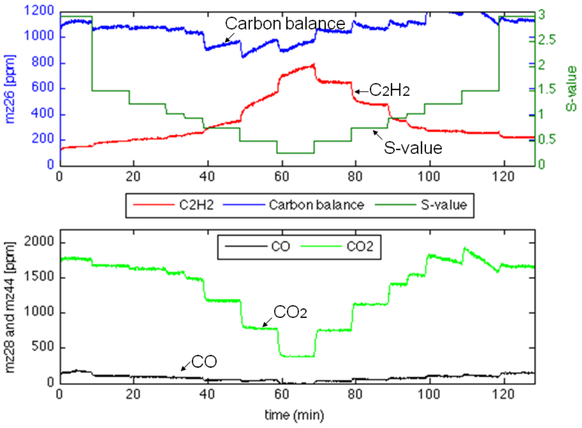


Figure C.60: Step-response experiment for acetylene with Pt/CeO_2 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

Table C.7: Acetylene conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
3.00	99	90	84	78
1.50	87	57	81	75
1.25	82	40	79	73
1.05	70	33	77	71
0.95	58	29	74	65
0.75	34	25	65	52
0.50	23	19	43	35
0.25	15	14	22	22

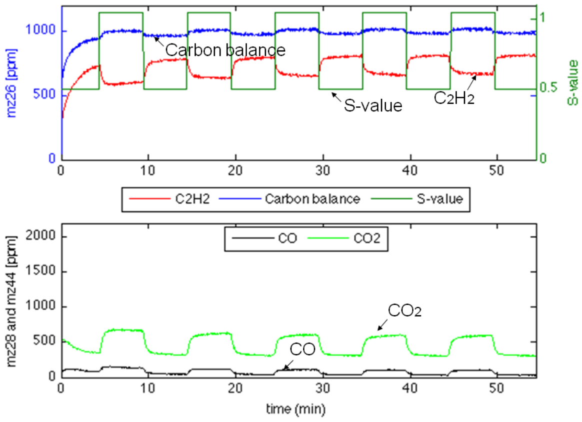


Figure C.61: Pulse-response experiment for acetylene with Pt/Al_2O_3 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

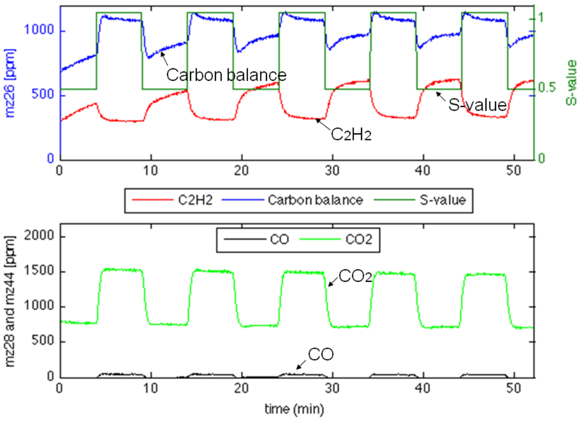


Figure C.62: Pulse-response experiment for acetylene with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

C.8 Dimethyl Ether

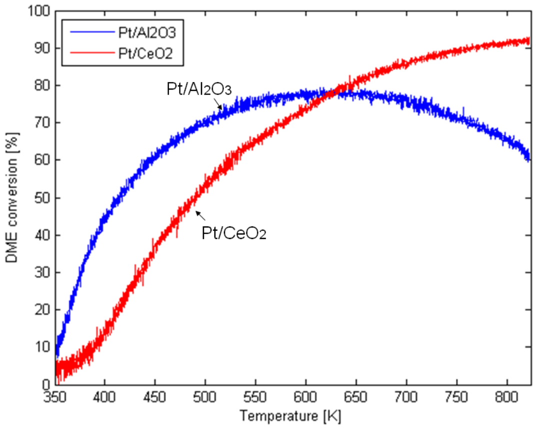


Figure C.63: Temperature-programmed experiment for DME ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

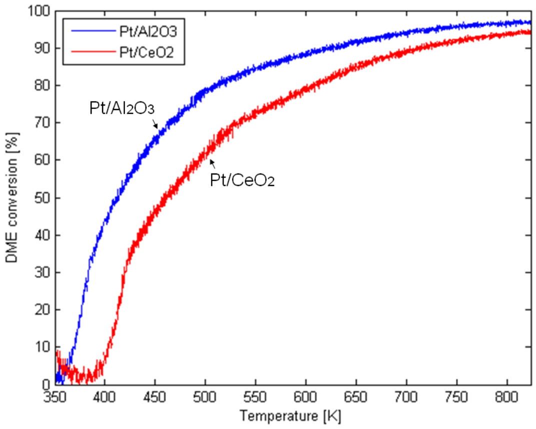


Figure C.64: Temperature-programmed experiment for DME ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

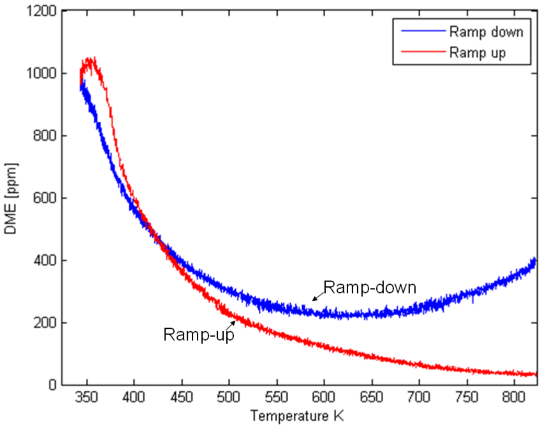


Figure C.65: Temperature-programmed experiment for DME with Pt/Al_2O_3 acting as the catalyst

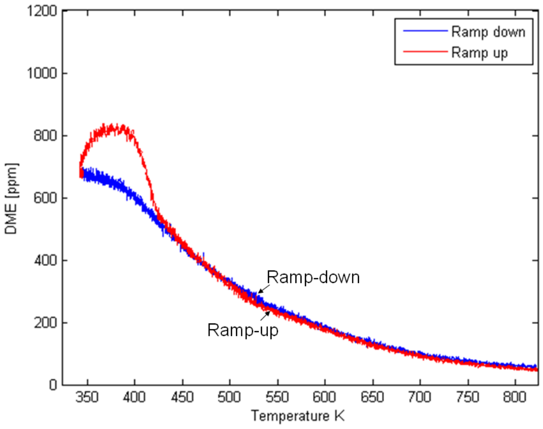


Figure C.66: Temperature-programmed experiment for DME with Pt/CeO_2 acting as the catalyst

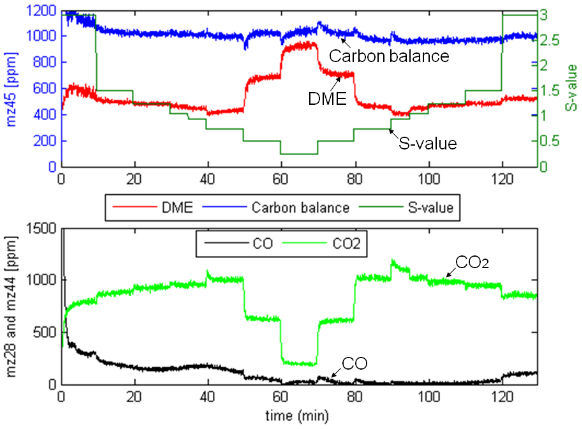


Figure C.67: Step-response experiment for DME with Pt/Al_2O_3 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

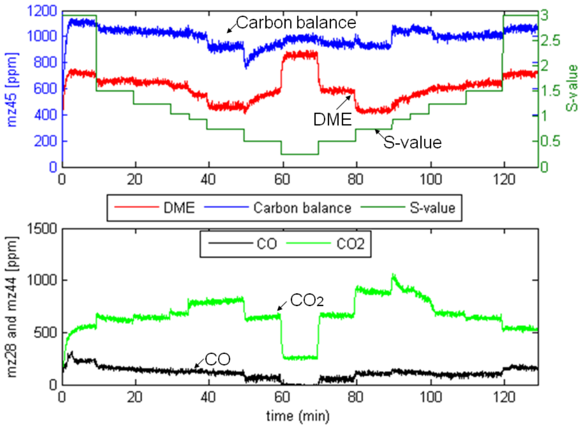


Figure C.68: Step-response experiment for DME with Pt/CeO_2 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

Table C.8: DME conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
3.00	40	48	28	29
1.50	50	51	34	36
1.25	52	53	35	40
1.05	53	55	39	43
0.95	55	59	45	49
0.75	58	54	54	57
0.50	32	29	42	41
0.25	7	7	14	14

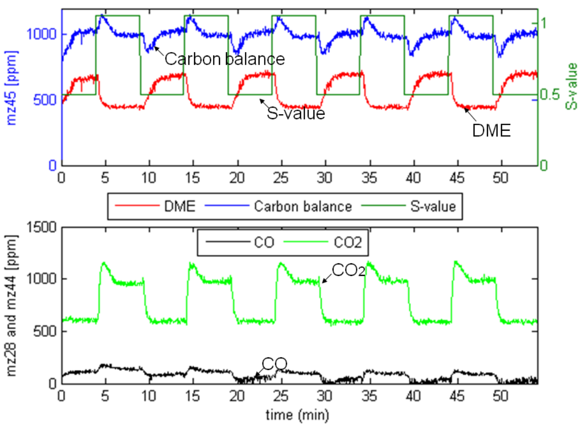


Figure C.69: Pulse-response experiment for DME with Pt/Al_2O_3 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

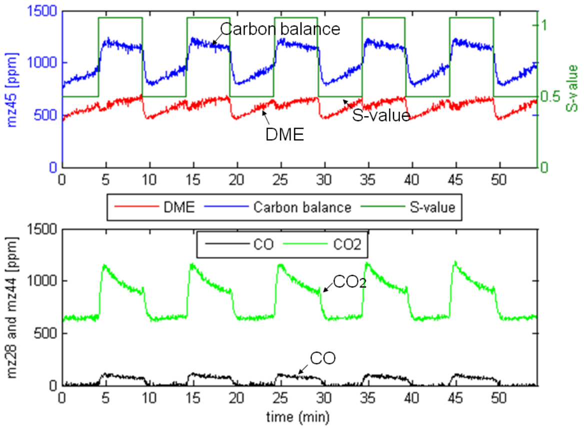


Figure C.70: Pulse-response experiment for DME with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

C.9 Acetaldehyde

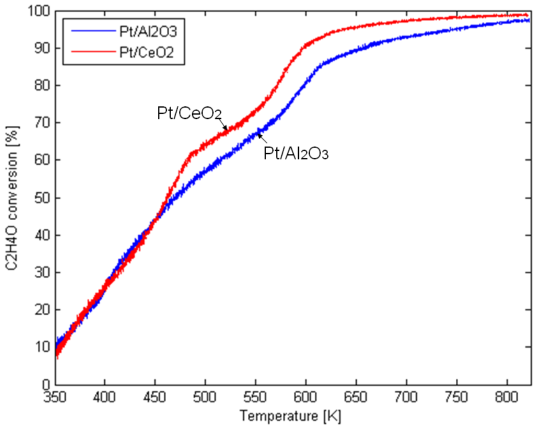


Figure C.71: Temperature-programmed experiment for acetaldehyde ramping-down from 823 K to 323 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

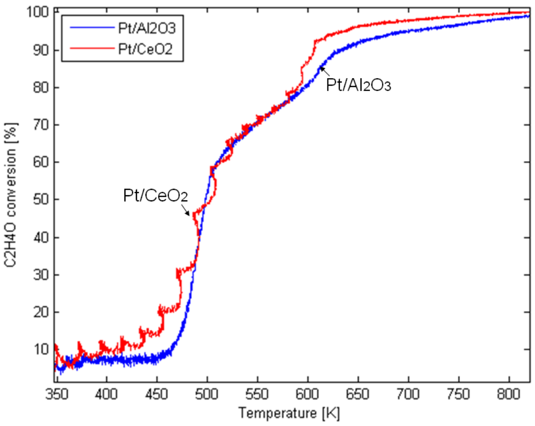


Figure C.72: Temperature-programmed experiment for acetaldehyde ramping-up from 323 K to 823 K with Pt/Al_2O_3 and Pt/CeO_2 acting as the catalyst

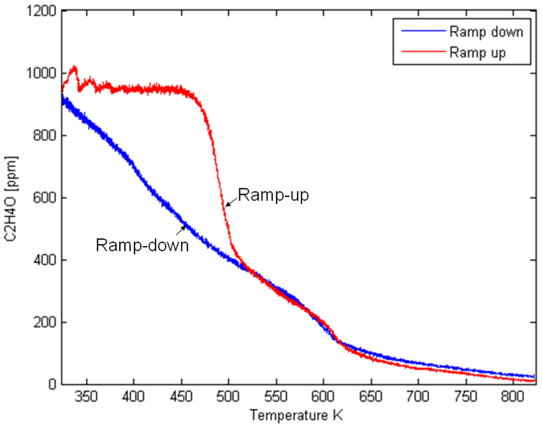


Figure C.73: Temperature-programmed experiment for acetaldehyde with Pt/Al_2O_3 acting as the catalyst

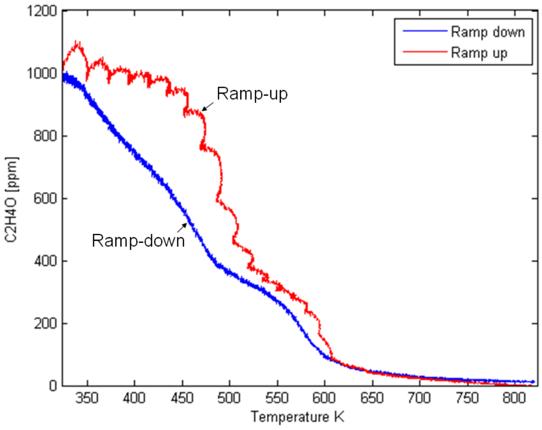


Figure C.74: Temperature-programmed experiment for acetaldehyde with Pt/CeO_2 acting as the catalyst

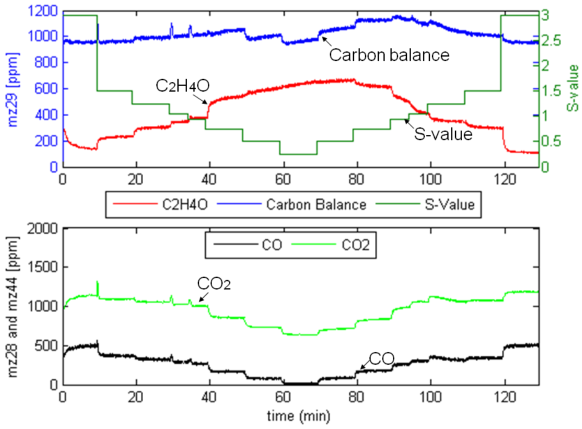


Figure C.75: Step-response experiment for acetaldehyde with Pt/Al_2O_3 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

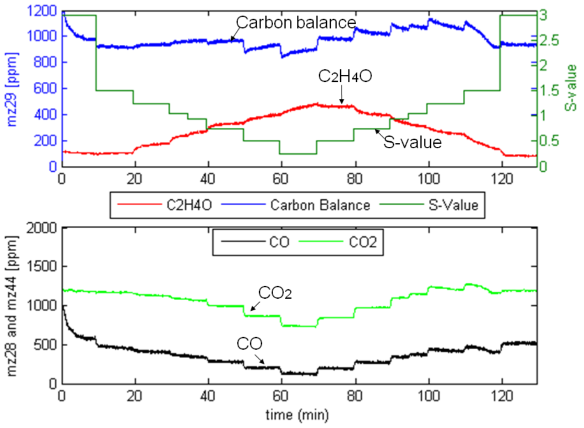


Figure C.76: Step-response experiment for acetaldehyde with Pt/CeO_2 as the catalyst. Step-down from S=3 to S=0.25 and step-up from S=0.25 to S=3.

Table C.9: Acetaldehyde conversion (%) for different S-values with different catalysts.

S-Value	Pt/Al_2O_3 Step-down	Pt/Al_2O_3 Step-up	Pt/CeO_2 Step-down	Pt/CeO_2 Step-up
3.00	86	88	90	91
1.50	76	70	90	87
1.25	70	65	83	74
1.05	66	58	76	70
0.95	60	48	73	65
0.75	46	38	66	60
0.50	40	33	60	54
0.25	35	35	51	51

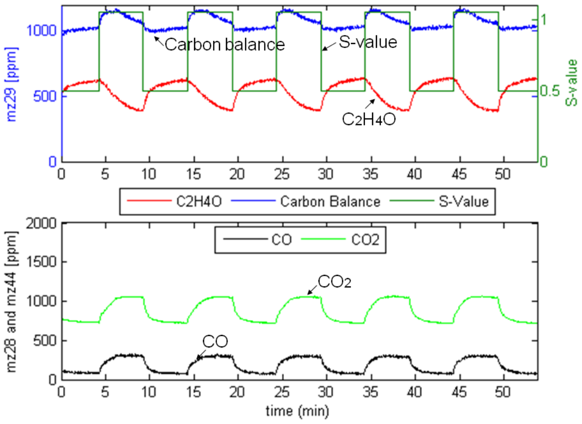


Figure C.77: Pulse-response experiment for acetaldehyde with Pt/Al_2O_3 catalyst with S=0.50 (5 min) and S=1.05 (5 min)

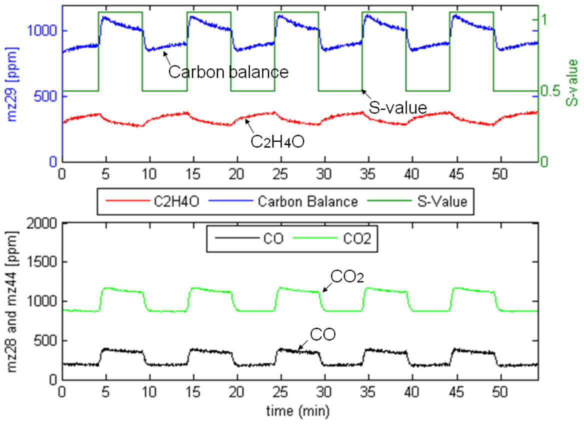


Figure C.78: Pulse-response experiment for acetaldehyde with Pt/CeO_2 catalyst with S=0.50 (5 min) and S=1.05 (5 min)