

**CHAPTER V**  
**SELECTIVE NO<sub>x</sub> REDUCTION OVER SOL-GEL PT/ALUMINA**  
**CATALYST BY AQUEOUS UREA SOLUTION**

**5.1 Abstract**

The activity of NO<sub>x</sub> reduction was investigated over 2% Pt on alumina under various oxidizing reaction conditions from 200-450 °C. This catalyst was synthesized from single step sol-gel technique. The NO<sub>x</sub> conversion was studied under different urea and water concentrations. The results showed that the temperature of maximum NO<sub>x</sub> conversion was shifted towards lower temperature when used higher amount of water. This condition accelerated the hydrolysis process that produced more reducing agent used for NO<sub>x</sub> reduction. When there was an adequate amount of urea for reducing NO<sub>x</sub> with the sufficient water content present in the feed stream, almost 100% NO<sub>x</sub> conversion was obtained as low as 200 °C. The oxidation of nitrogen-containing compounds which were produced from the decomposition/hydrolysis of urea resulted in the formation of N<sub>2</sub>, N<sub>2</sub>O, NO and NO<sub>2</sub>. The additional formation of NO and NO<sub>2</sub> at high temperatures via this oxidation caused the negative reduction activity.

*Keywords:* NO<sub>x</sub> reduction, Urea-SCR, Platinum/alumina, Sol-gel, Urea hydrolysis, Urea decomposition

**5.2 Introduction**

Selective catalytic reduction of NO<sub>x</sub> with ammonia (NH<sub>3</sub>-SCR) is a highly selective to reduce NO<sub>x</sub> emissions from stationary sources [1,2]. For mobile sources such as vehicles, NH<sub>3</sub> slip and manipulation of NH<sub>3</sub> together with NH<sub>3</sub> corrosion remain the major obstacles to the use of this technology. The use of gaseous NH<sub>3</sub> requires elaborate safety precautions for handling and storage. One of the first articles describing a SCR system to be applied in a vehicle was published by Held et al. [3] They suggested using non-toxic urea as a reducing agent. Urea as ammonia

source may be the best choice for such applications because urea is not toxic, much easier to handle and also can be easily transported on board of an automobile as a high concentration aqueous solution. Currently, it is considered as the most promising technique to reduce NO<sub>x</sub> emissions from heavy-duty diesel engines [4-6]. It is also developed for light-duty diesel vehicles.

Urea is usually applied as an aqueous solution. The conversion of the aqueous urea solution to ammonia consists of two steps. After evaporation of H<sub>2</sub>O, the remaining urea decomposes thermally into ammonia and isocyanic acid according to reaction (1).



The first step is so called thermolysis of urea. It occurs at temperature above 133 °C which is the melting point of urea. Equimolar amounts of ammonia and isocyanic acid are thus formed. This endothermic process can be accelerated by catalysts. Investigations of the selective non-catalytic reduction showed that the mixture of ammonia and isocyanic acid in gas phase is stable up to 850 °C [7]. However, reliable urea thermolysis is very difficult to achieve below 200 °C.

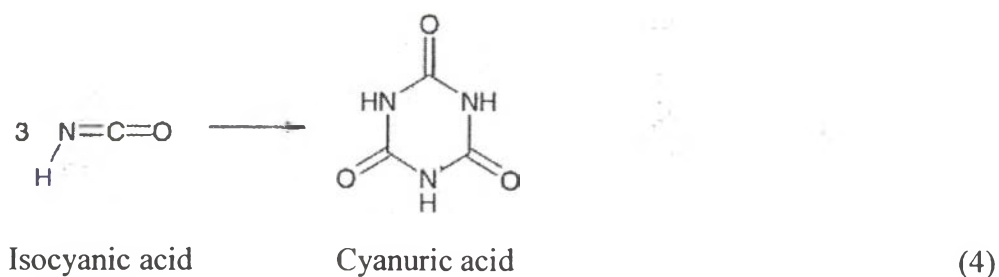
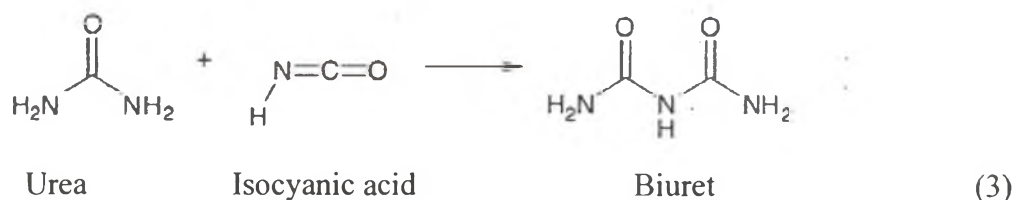
In the second step, the isocyanic acid is hydrolyzed over a catalyst giving ammonia and carbon dioxide according to reaction (2).



This hydrolysis reaction is exothermic and the Gibbs free energy of the reaction is strongly negative so that the equilibrium lies completely on the right side. But HNCO is quite stable in the gas phase even under humid conditions and hydrolysis only occurs in the presence of a catalyst [8]. Even its hydrolysis is kinetically hindered but proceeds rapidly on many single and mixed metal oxides as well as zeolites [5,8-10]. It should be noted that isocyanic acid can also undergo a series of condensation reactions leading to solid products ranging from cyanuric acid, biuret, ammelide, ammeline and melamine [6,11-13]. These high molecular weight compounds have been reported to deposit on the walls of the exhaust pipe and inside

the monolith channels [6]. They are only slowly decomposed under the typical reaction conditions. This leads to severe catalyst deactivation.

The formation of white to yellowish deposits was found when urea solution was injected at low temperature regimes. The analysis of the deposits showed that they mainly consisted of urea and some biuret at low temperatures and cyanuric acid and some biuret at higher temperatures around 350 °C [14]. For urea decomposition, it is known that biuret is easily formed from 150-190 °C [7,13] whereas the formation of cyanuric acid is predominant from 200-300 °C according to the following reactions [15]:



The key idea behind the development of urea-SCR for diesel powered vehicles was the necessity to have a catalyst to be active in the presence of O<sub>2</sub>, active at very high space velocities and low reaction temperatures as well as resistant to sulfur and phosphorus deactivation. To develop the catalysts for this application, there were many studies on vanadia based catalysts and ZSM-5 catalysts [8,16-19] whereas supported metal catalysts were rarely studied [20,21]. This work reported the experiments of the supported Pt catalyst. We studied the NO<sub>x</sub> reduction by aqueous urea solution over supported Pt on alumina catalyst. The catalytic activity under various urea and water concentrations was investigated. The effect of oxygen

on the decomposition and hydrolysis was also studied. The products formed under the reaction conditions were presented.

### 5.3 Experimental

#### 5.3.1 Catalyst Preparations and Activation

The platinum on alumina supported catalyst was prepared from single step sol-gel method. Aluminum tri-*sec*-butoxide and chloroplatinic acid of Pt were used as precursors to form sol-gel material. They were mixed in the same manner as reported by Seker et al. [22] Aluminum tri-*sec*-butoxide was first mixed with the water-ethanol solution. After sol was formed, the appropriate amount of chloroplatinic acid of Pt was added into the mixture to obtain 2% Pt loading. It was left to allow gel formation completely. Then, the resulting gel was dried at 100 °C for 12 h to remove the solvent followed by calcination at 600 °C for 24 h. Prior to the activity studies, the calcined catalyst was ground and sieved to 80-120 mesh size. The obtained 2% Pt supported on alumina sol-gel catalyst was designated as Pt-SG.

Before carried out the activity tests, the catalyst was activated with a gas mixture containing 750 ppm nitric oxide, 750 ppm propene, 7% oxygen, approximate 2% water and He as a balance. The gas stream was fed through 0.1 g of the catalyst bed at the total flow rate of 75 ml/min. The activation process performed at the temperature from 150 to 500 °C with a 50 °C increment. It was left at each step at least 1 h to reach a steady state reaction. After it reached 500 °C, it was kept overnight at this temperature. The activation procedure was repeated until the activity of catalyst reached its stable level.

#### 5.3.2 Catalyst Testing

The activity of catalyst was studied by using a quartz U-tube reactor (ID 3.5 mm). The amount of 0.1 g catalyst was packed between two quartz wool layers as a fixed bed. In the tests, reactant gases controlled by mass flow controllers were blended together resulting in 650 ppm NO with trace NO<sub>2</sub>, 0-6% O<sub>2</sub> balanced in He. It was sent to the reactor system with the total flow rate of 176 ml/min to give an approximate  $1 \times 10^5 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$  space velocity (SV). Before entering to the U-tube

reactor, the aqueous solution of urea was injected at a desired flow rate to system with a peristaltic tube pump. It was mixed with the feed gas stream in a port which was controlled the temperature at  $\sim 130$  °C. The feed line prior to the entrance section of reactor was further heated throughout to avoid the condensation of the solution.

During the activity tests, the reaction was kept at each temperature for 1 h to achieve a steady state. The outlet stream from the reactor was sent through a condenser and a water selective membrane dryer to remove water content before its composition was measured. Unreacted  $\text{NO}_x$  was determined by using a chemiluminescence  $\text{NO}_x$  analyzer, Thermo Environmental 42CHL. Prior to entering the analyzer, the outlet stream was eliminated  $\text{NH}_3$  and  $\text{HNCO}$  by passing through phosphoric acid trap. The amounts of forming  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{N}_2\text{O}$  were measured quantitatively by a Fourier-transform infrared (FTIR), Mattson galaxy 7020A, with a 10 cm path length gas cell. A gas chromatograph (GC), SRI 8610C, equipped with a helium ionization detector (HID) and thermal conductivity detector (TCD) was used to analyze  $\text{N}_2$  and  $\text{NH}_3$ . It was installed with a 36 ft long HayeSep DB column or a 6 ft long Porapak N column (Altech) to detect  $\text{N}_2$  or  $\text{NH}_3$ , respectively. The  $\text{NH}_3$  concentration in the outlet stream was also checked by using an ammonia analysis kit after absorbing it in water at 0 °C.

### 5.3.3 Catalyst Characterization

The Brunauer-Emmett-Teller (BET) method was applied to determine the surface area and pore size of the catalysts measured by a Micromeritics 2010 instrument. The sample was degassed under vacuum at 300 °C until it reached the steady state around  $5 \times 10^{-3}$  mmHg followed by  $\text{N}_2$  adsorption/desorption. Both BET surface area and BJH pore size distribution was calculated from a standard Micromeritics program.

Approximate crystallite size and phases present in the catalysts were determined by X-ray diffraction (Rigaku powder diffractometer, operated at 40 kV and 100 mA). The crystallite size distribution was obtained from JEOL 4000 HRTEM. The powder of catalyst was ground in *iso*-propyl alcohol, and then maintained in a sonic bath for 15 min. A drop of the alcohol power suspension was put on a holly carbon-coated copper screen and then alcohol was evaporated at room

temperature under vacuum before being transferred to the HRTEM column. About 200 crystallite pictures were collected spatially over the holly carbon coated copper screen to determine the crystallite size distribution for Pt.

## 5.4 Results and Discussion

### 5.4.1 Results

#### 5.4.1.1 Catalyst Characterization

The XRD pattern of the 2% Pt-SG catalyst showed Pt peaks at  $2\theta$  of ca. 40, 46, and  $67.5^\circ$  superimposed on alumina peaks ( $\gamma$  and  $\eta$ ) at  $2\theta$  of ca. 39, 45.5, and  $66.8^\circ$ . Approximate Pt crystallite size calculated from the Debye-Scherrer equation was  $16 \pm 1$  nm. HRTEM was also employed to determine the crystallite size distribution of the Pt-SG catalyst. It appeared two peaks in the distribution with 34% of  $13 \pm 2$  nm crystallites and 16% of  $20 \pm 7$  nm crystallites. The arithmetic average of these distributions was  $15.5 \pm 6$  nm in agreement with the XRD results.

The sol-gel synthesis and calcination treatment that we used produced the Pt-SG catalyst with BET surface area of ca.  $300 \text{ m}^2/\text{g}$  and a narrow pore size distribution centered at diameter ca. 68 Å. In contrast, when alumina was synthesized alone there was no change in surface area but the average pore size became ca. 77 Å. The dispersion of such a catalyst was about 10% based on CO chemisorption, and was in agreement with the estimated dispersion from the average crystallite size.

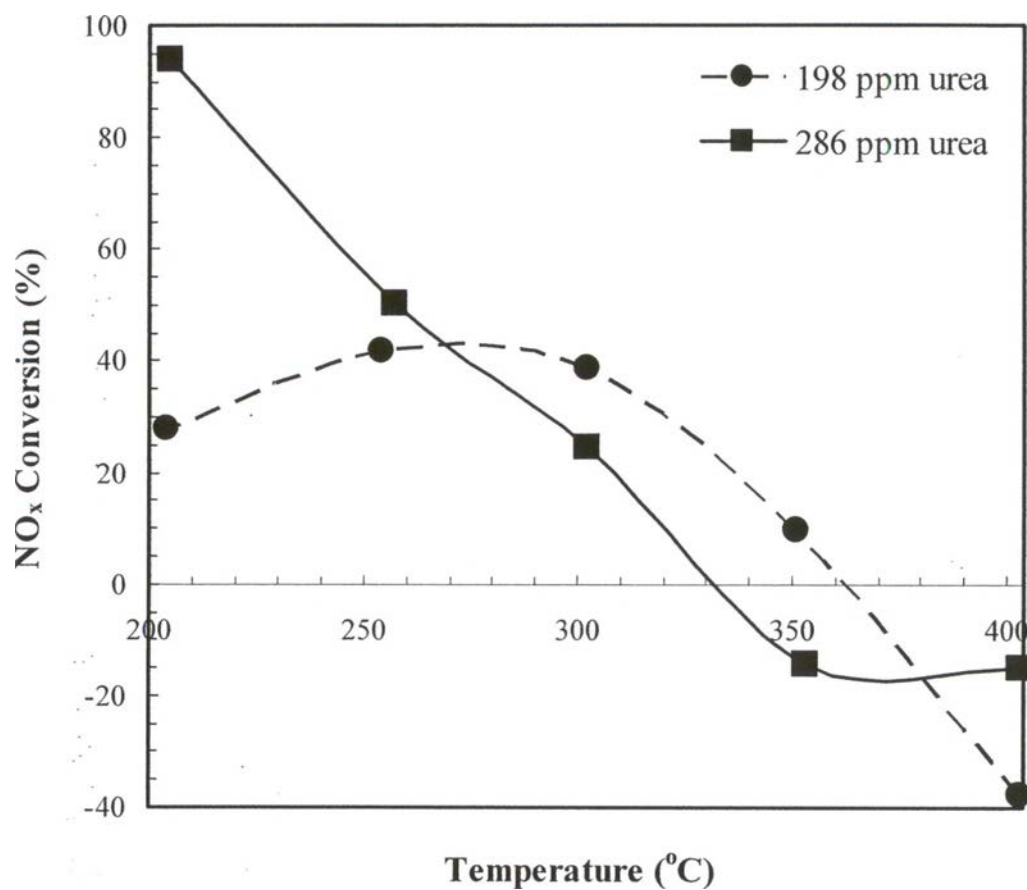
#### 5.4.1.2 Effect of Urea and Water Concentration on the $\text{NO}_x$ Reduction

The activity of Pt-SG catalyst in  $\text{NO}_x$  reduction was observed under the different urea concentrations. The reactant feed stream containing 650 ppm NO, 6%  $\text{O}_2$ , and ca. 17%  $\text{H}_2\text{O}$  balanced in He was employed in the tests. There was water condensation inside the catalyst bed at the temperature below  $200^\circ\text{C}$  for 15-17% water containing feed stream. So the experiments were carried out above this temperature. Figure 5.1 showed the activity of  $\text{NO}_x$  reduction with 198 and 286 ppm urea. When 198 ppm urea was used, the  $\text{NO}_x$  conversion increased with the



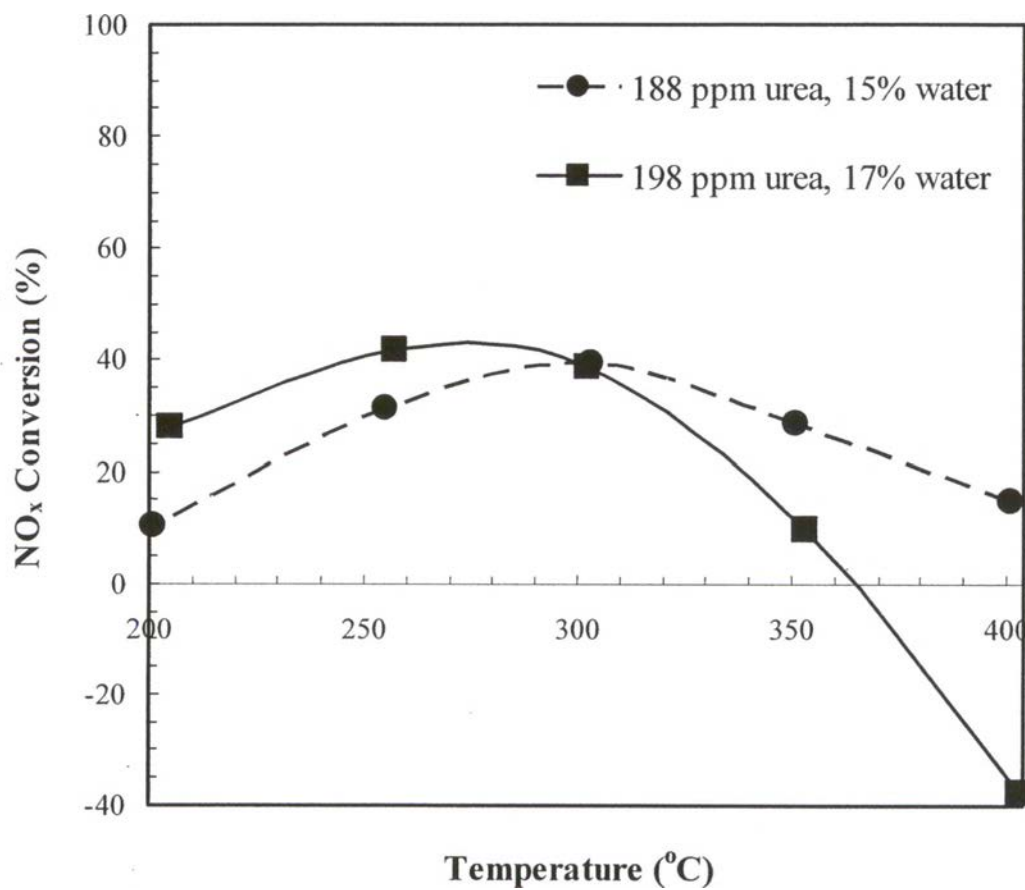
temperature profile and reached the maximum conversion around 40% at 250-300 °C. After that, it dropped down and became negative after approximate 350 °C. In comparison, when 286 ppm urea was used, the temperature of the maximum NO<sub>x</sub> conversion shifted to lower temperature. High NO<sub>x</sub> conversion ca. 94% was already obtained at 200 °C. When the reaction temperature was increased, the NO<sub>x</sub> conversion continuously decreased and dropped below 0% after 330 °C. Furthermore, the activity of this catalyst was observed under different concentrations of water. The same reaction condition of 650 ppm NO and 6% O<sub>2</sub> balanced in He was used. The results were shown in Figure 5.2. When 15% water with 188 ppm urea was used, the activity began from 10% conversion and increased along with the higher temperatures. It gave the maximum NO<sub>x</sub> conversion around 40% at 300 °C. After that the conversion slowly decreased with the temperature until it reached ca. 15% at 400 °C. Contrarily, when the higher amount of water around 17% with 198 ppm urea was employed, the maximum NO<sub>x</sub> conversion shifted towards lower temperature. Its maximum conversion around 40% took place at 250 °C and was maintained at this level until 300 °C. Then the catalytic activity was continuously dropped down with the temperature until it became negative at about 360 °C. Then, it further decreased to -40% conversion at 400 °C.

From the experiments to study the effect of urea and water contractions, the formation of N<sub>2</sub>O was observed. It increased with higher urea concentration in the reactant stream. For example, N<sub>2</sub>O formation was below 100 ppm for the feed stream containing 198 ppm urea with 17% water. While 286 ppm urea with 17% water containing feed stream gave the maximum N<sub>2</sub>O formation of 400 ppm around 200 °C. These results implied that at lower temperatures, urea decomposition/hydrolysis gave nitrogen-containing products which were used as reducing agents such as NH<sub>3</sub> and HNCO according to equation (1) and (2) in the reduction of NO<sub>x</sub>. Consequently, it formed N<sub>2</sub>O as by-product. Therefore further tests were carried out as described in the next section.



**Figure 5.1** The NO<sub>x</sub> reduction activity of 2% Pt-SG as a function of urea concentration. Reaction conditions: 650 ppm NO, 6% O<sub>2</sub>, ~17% H<sub>2</sub>O balanced in He, SV = 105,075 cm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>.



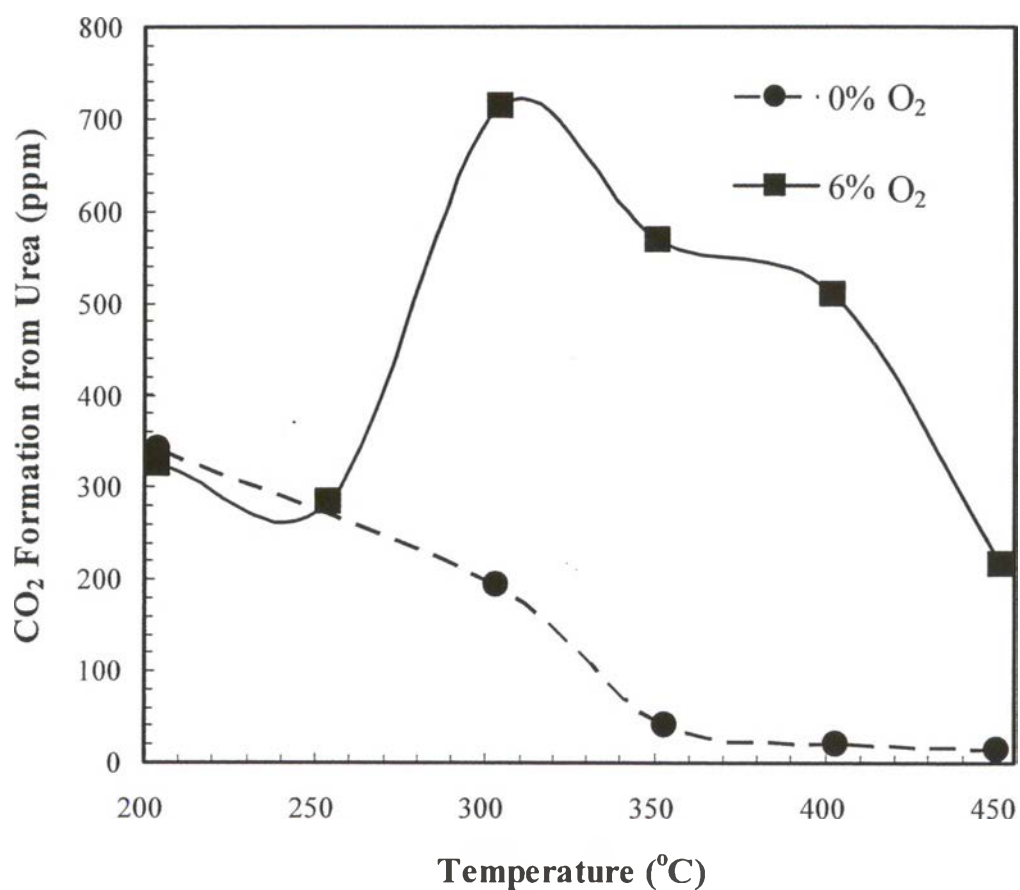


**Figure 5.2** The NO<sub>x</sub> reduction activity of 2% Pt-SG as a function of water concentration. Reaction conditions: 650 ppm NO, 188-198 ppm urea, 6% O<sub>2</sub>, balanced in He, SV = 105,075 cm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>.

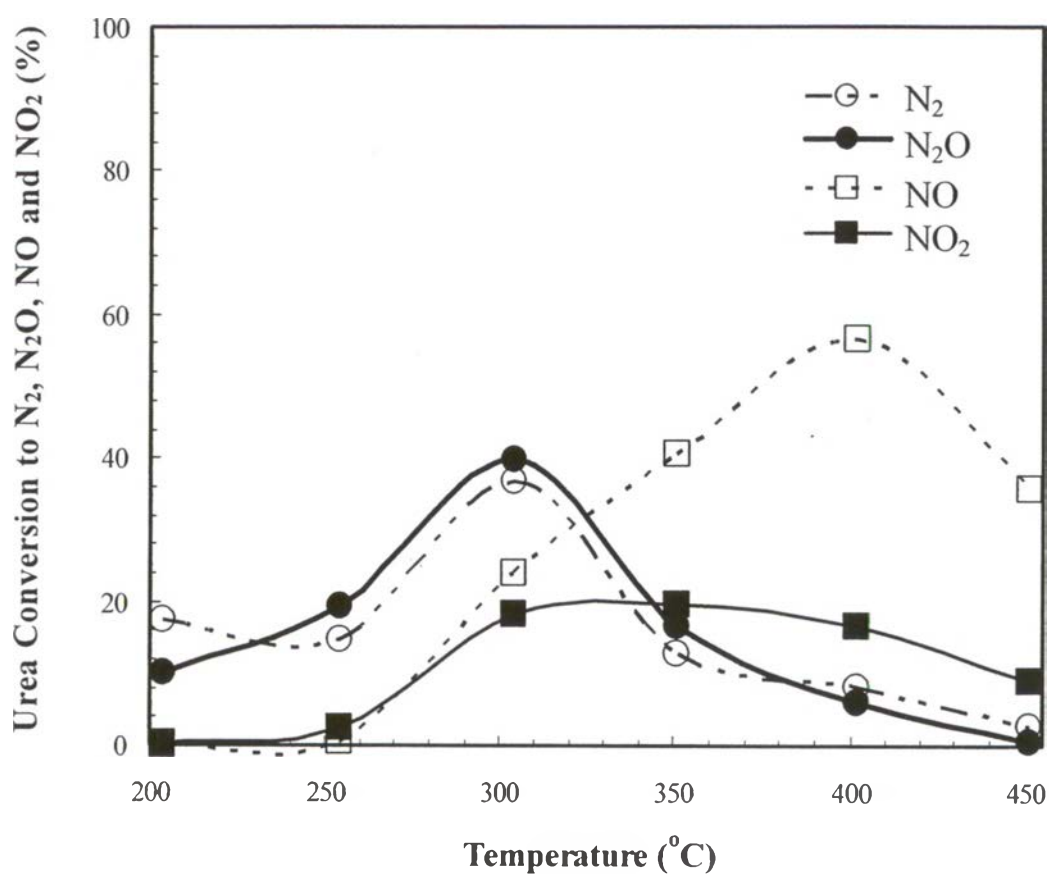
#### 5.4.1.3 *The Characteristic of Urea Decomposition/Hydrolysis and NO<sub>x</sub> Reduction*

The decomposition and hydrolysis of urea over 2% Pt-SG catalyst were investigated with the reactant stream consisting of 450 ppm urea, 15% H<sub>2</sub>O balanced in He. The activities observed under the reaction temperature of 200-450 °C were illustrated in Figure 5.3. The absence of oxygen in feed stream resulted in the CO<sub>2</sub> formation as low as 200 ppm at 200 °C. It was produced around 320 ppm at this temperature. When the temperature was increased, the amount of CO<sub>2</sub> formation was further reduced until it reached around 40 ppm at 350 °C. Its formation was insignificant ca. 20 ppm between this temperature and 450 °C. This implied that the hydrolysis of urea decreased along with the temperature profile. It was negligible after 350 °C. However, the decomposition of urea may still occur as the temperature increased. In contrast, the presence of oxygen in the reactant stream gave no change in the amount of CO<sub>2</sub> formation between 200-250 °C. After that, the forming CO<sub>2</sub> increased with the temperature and reached its maximum level about 700 ppm at 300 °C and subsequently decreased after this temperature. Its formation was rapidly dropped after 400 °C and reached around 200 ppm at 450 °C.

The decomposition and hydrolysis of urea gave nitrogen-containing compounds. They were subsequently converted to several nitrogen species when oxygen was present in the feed stream. Figure 5.4 showed the formation of these products as a function of temperature. Under the same reaction conditions as previously mentioned, N<sub>2</sub>, N<sub>2</sub>O, NO, and NO<sub>2</sub> were produced from the oxidation of nitrogen-containing compounds derived from urea. N<sub>2</sub> and N<sub>2</sub>O were already formed at 200 °C and increased with the temperature. They reached their maximum levels at around 300 °C. Then, their formations dropped continuously after this temperature. While NO and NO<sub>2</sub> were not formed at low temperatures until it reached the temperature of 250 °C. The formation of NO was higher according to the temperature. It was highest produced around 60% at 400 °C. Then, its formation subsequently dropped to 40% at 450 °C. The formation NO<sub>2</sub> began after 200 °C as well as NO formation. Its formation around 20% was obtained at 300 °C and seemed to be constant at this level until 400 °C. Then, it slightly decreased at 450 °C.



**Figure 5.3** The oxygen effect on the activity of urea decomposition/hydrolysis over 2% Pt-SG. Reaction conditions: 450 ppm urea, 15% H<sub>2</sub>O balanced in He, SV = 105,075 cm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>.



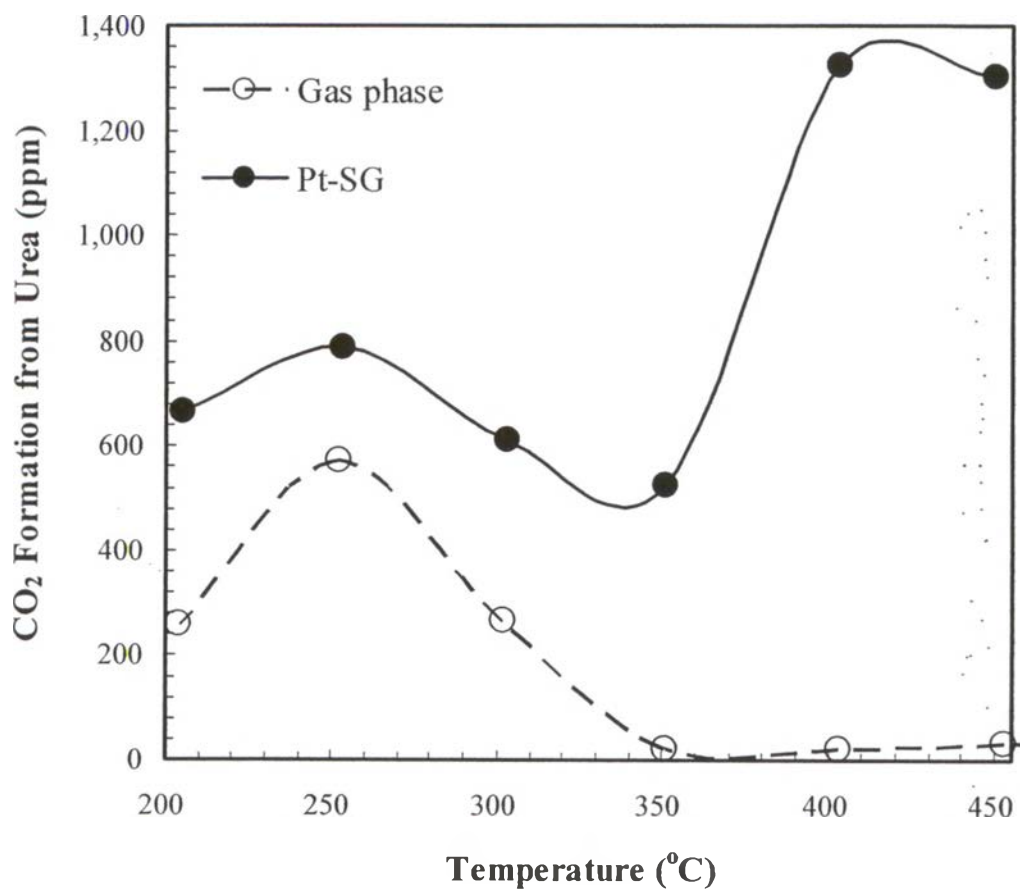
**Figure 5.4** The oxidation of N-containing compounds derived from urea over 2% Pt-SG. Reaction conditions: 450 ppm urea, 6% O<sub>2</sub>, 15% H<sub>2</sub>O balanced in He, SV = 105,075 cm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>.

Under the same reaction conditions as previously mentioned, NO was introduced to the feed stream in order to study the NO<sub>x</sub> reduction in gas phase and on 2% Pt-SG catalyst. Figure 5.5 showed the urea conversion to CO<sub>2</sub> as a function of temperature. In gas phase without the presence of catalyst, the formation of CO<sub>2</sub> was found only at low temperature regimes less than 350 °C. Its formation curve was volcano shape with the maximum of CO<sub>2</sub> formation at 250 °C. While the formation of CO<sub>2</sub> over the catalyst was higher than that in gas phase alone over all temperatures between 200-450 °C. In low temperature regime between 200-350 °C, it gave volcano shape of CO<sub>2</sub> formation as well. The formation reached the maximum level at the same temperature of 250 °C. In comparison to gas phase, there was CO<sub>2</sub> formation at high temperature regime between 350-450 °C. It increased with the temperature. The maximum amount was obtained between 400-450 °C. Figure 5.6 illustrated the formation of products involving nitrogen-containing compounds. In the presence of NO in the reactant stream, N<sub>2</sub> and N<sub>2</sub>O were already formed at the temperature as low as 200 °C. Then, their formations were dropped down versus the increasing of the temperature. While NO and NO<sub>2</sub> were produced significantly at the temperature higher than 350 °C and increased continuously along with the temperature until 450 °C.

#### 5.4.2 Discussion

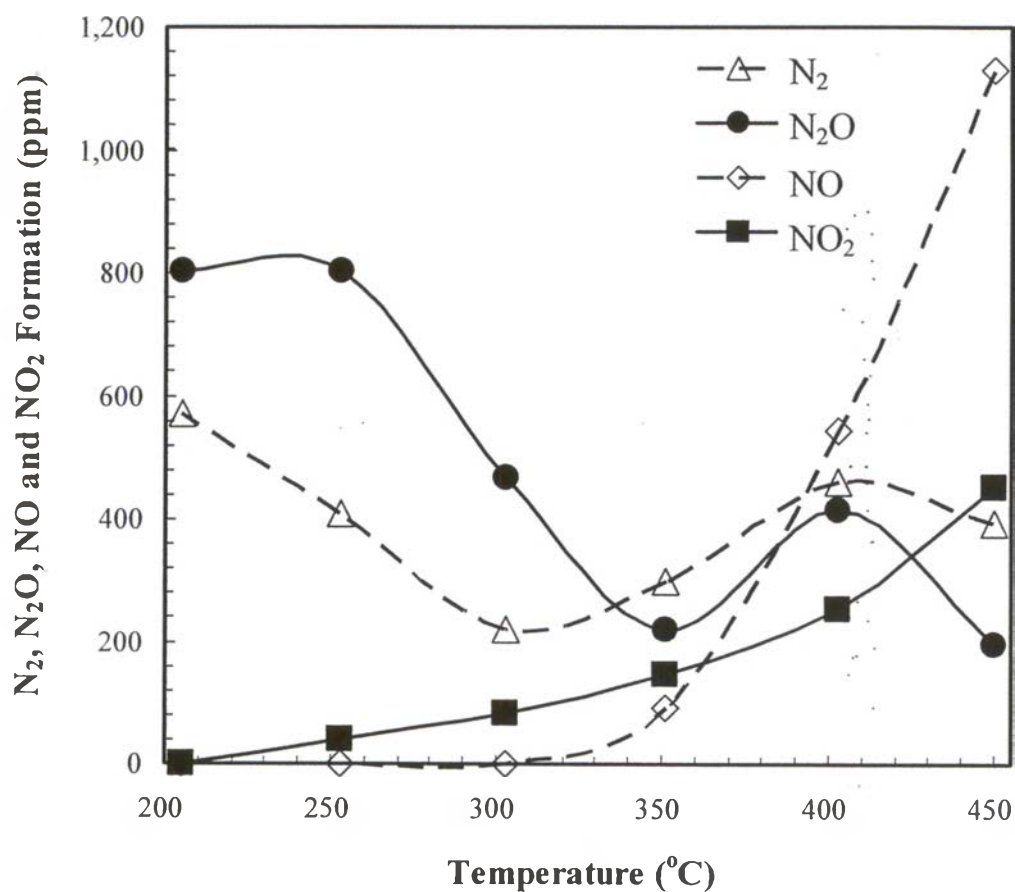
##### 5.4.2.1 *The Activity of NO<sub>x</sub> Reduction as a Function of Water and Urea*

When the different water quantities were used with the comparative urea concentrations as shown in Figure 5.2, the temperature of maximum NO<sub>x</sub> conversion shifted to the lower temperature. The higher water concentration in the feed stream gave the maximum NO<sub>x</sub> conversion at 250 °C instead of 300 °C. It was concluded that higher content of water enhanced the hydrolysis rate which resulted in the higher amounts of NH<sub>3</sub> produced. This process could occur at the temperature as low as 200 °C as shown in Figure 5.3. Therefore, NO<sub>x</sub> reduction was improved and shifted the maximum NO<sub>x</sub> conversion to lower temperatures. However, higher NO<sub>x</sub> conversion than ca. 40% could not be achieved



**Figure 5.5** The activity of NO<sub>x</sub> reduction in gas phase and on 2% Pt-SG. Reaction conditions: 650 ppm NO, 450 ppm urea, 6% O<sub>2</sub>, 15% H<sub>2</sub>O balanced in He, SV = 105,075 cm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>.





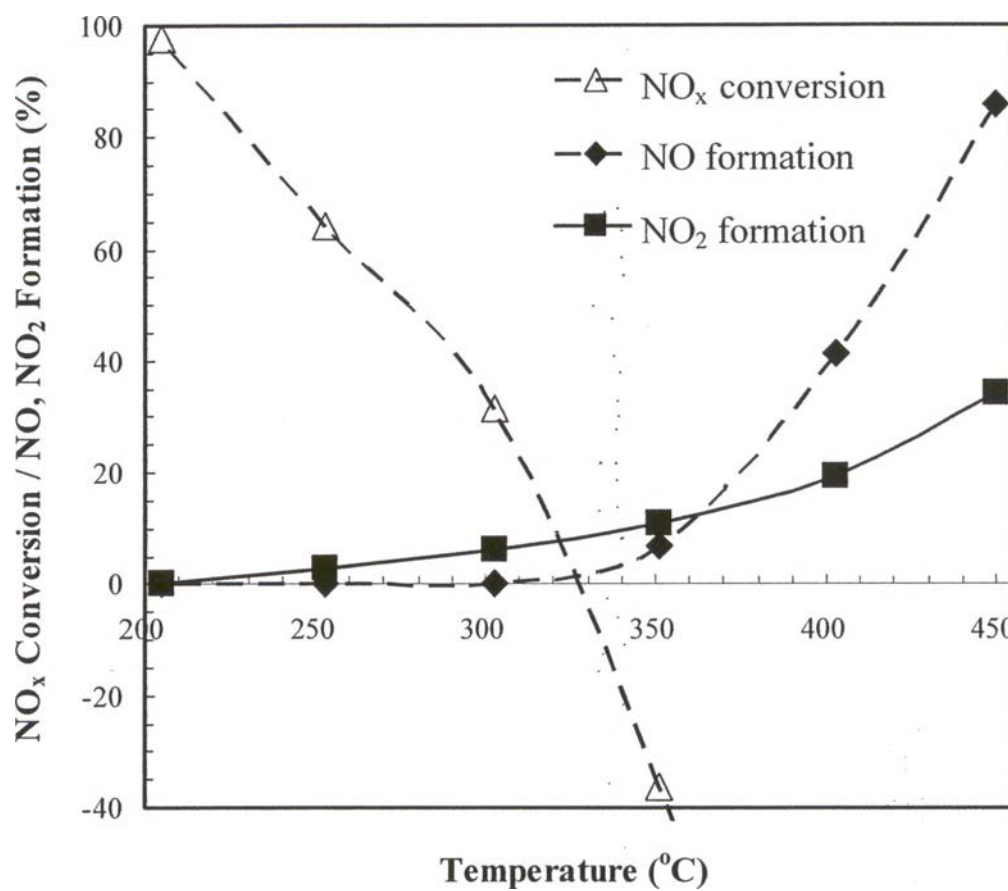
**Figure 5.6** The formation of products in NO<sub>x</sub> reduction over 2% Pt-SG. Reaction conditions: 650 ppm NO, 450 ppm urea, 6% O<sub>2</sub>, 15% H<sub>2</sub>O balanced in He, SV = 105,075 cm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>.

due to insufficient quantity of urea to produce its derivatives used to converted all  $\text{NO}_x$ .

In comparison, Figure 5.1 showed that it gave the maximum  $\text{NO}_x$  conversion ca. 94% at 200 °C when higher amount of urea as 286 ppm was used. According to the stoichiometry, the maximum nitrogen-containing compounds which could be produced from urea were equivalent to ca. 580 ppm. Within  $\pm 3\%$  of experimental error, it almost matched up with 610 ppm  $\text{NO}_x$  converted at the maximum conversion. It suggested that urea could produce its derivatives through decomposition and/or hydrolysis processes to reduce and/or couple with  $\text{NO}_x$  as deposits on the surface at temperature as low as 200 °C. The side reactions for deposition will be described latter in the next section.

In addition, the activity became negative between 300 and 350 °C during the reduction of  $\text{NO}_x$ . As mentioned previously, nitrogen-containing compounds such as  $\text{HNCO}$  or  $\text{NH}_3$  derived from urea through decomposition/hydrolysis processes were oxidized with oxygen giving nitrogen species as described in Figure 5.4. It indicated that at high temperatures,  $\text{NO}$  and  $\text{NO}_2$  were produced in higher amounts through the oxidation so that their quantities were greater than that converted in the reduction as illustrated in Figure 5.7. The negativity of  $\text{NO}_x$  conversion concurrent with the formation of  $\text{NO}$  and  $\text{NO}_2$  started at the same temperature around 330 °C. Consequently, the net  $\text{NO}_x$  conversion became negative at high temperatures.

Furthermore, the preliminary results of the analysis of condensate collected at the exit of the reactor showed that the quantities of  $\text{NH}_3$  were less than 2 ppm at all temperatures. Hence, all  $\text{NH}_3$  was used as a reductant in the  $\text{NO}_x$  reduction and/or stored on the catalyst surface at low temperatures and it was converted to  $\text{NO}$  and  $\text{NO}_2$  at high temperatures. Similarly,  $\text{HNCO}$  produced from urea decomposition was easily oxidized to  $\text{NO}$  and  $\text{NO}_2$  at high temperatures as well [23]. Ramis et al. [24] showed that oxy-dehydrogenation of  $\text{NH}_3$ , which led to  $\text{NH}_2$  and  $\text{H}$ , was the initial step in  $\text{NO}$  reduction. It can speculate that the oxygen reacted with either  $\text{NH}_3$  or  $\text{HNCO}$  to form  $\text{NH}_2$  or  $\text{NH}$  initially. These species further reduced  $\text{NO}$  to  $\text{N}_2$  and  $\text{N}_2\text{O}$  at temperature below 350 °C. While, they were oxidized in parallel with the  $\text{NO}_x$  reduction at high temperatures.



**Figure 5.7** The correlation of NO<sub>x</sub> conversion and NO and NO<sub>2</sub> formation over 2% Pt-SG. Reaction conditions: 650 ppm NO, 450 ppm urea, 6% O<sub>2</sub>, 15% H<sub>2</sub>O balanced in He, SV = 105,075 cm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>.

#### 5.4.2.2 *The Decomposition and Hydrolysis of Urea and Side Reactions*

The formation of CO<sub>2</sub> came from hydrolysis reaction of urea and/or oxidation of HNCO [23]. From the experiments as shown in Figure 5.3, it was found that CO<sub>2</sub> formation occurred between 200-350 °C in the absence of oxygen. It implied that the urea decomposition and hydrolysis took place simultaneously in these temperature ranges. Schabere et al. [13] mentioned that urea polymers like cyanuric acid and ammeline were formed predominantly above 250 °C and they decomposed significantly after 300 °C. Therefore, the CO<sub>2</sub> formation in the presence of oxygen after 250 °C was likely produced from the oxidation of products decomposed from these polymers. Because the amount of CO<sub>2</sub> formation was higher than that of urea containing in the feed stream, it indicated that the polymers derived from urea were accumulated on the catalyst surface. Furthermore, the decomposition and hydrolysis of urea could occur homogeneously as shown in Figure 5.6 between 200-350 °C. However, these processes were enhanced heterogeneously via catalysis over all temperatures.

In addition, various nitrogen compounds were observed during the decomposition/hydrolysis of urea in the presence of oxygen. It showed that nitrogen-containing products such as NH<sub>3</sub> and HNCO from urea decomposition/hydrolysis were oxidized into N<sub>2</sub>, N<sub>2</sub>O, NO and NO<sub>2</sub>. The oxidation of N<sub>2</sub> and N<sub>2</sub>O occurred at low temperatures whereas the oxidation of NO and NO<sub>2</sub> occurred significantly at high temperatures above 300 °C. In addition to the oxidation, the higher amounts of N<sub>2</sub> and N<sub>2</sub>O in the presence of NO in the feed stream were produced from the reduction of NO<sub>x</sub>. This could be concluded that both reduction of NO<sub>x</sub> and oxidation of nitrogen-containing compounds take place simultaneously over all temperatures from 200 to 450 °C. The NO<sub>x</sub> reduction occurs predominantly at low temperature regimes from 200 to 300 °C. While the oxidation of nitrogen-containing took place significantly at high temperature above 300 °C.

From the experiments with 15-17% water containing in the reactant stream, solid deposits was found on the thermocouple below 200 °C. It was likely ammonium nitrate. It was reported that the ammonium nitrate can be formed at low temperatures below 200 °C [6-7,25-26] according to reaction (5).



However, it is known that ammonium nitrate is a very unstable compound. Its formation is a reversible process. It can decompose rapidly at the temperatures above 200 °C [7,26-27]. Madia et al. [26] suggested that N<sub>2</sub>O formation in NO<sub>x</sub> reduction at low temperatures probably involved ammonium nitrate or nitroamine as an intermediate species.

## 5.5 Conclusions

- When there are an adequate amount of urea for reducing NO<sub>x</sub> and sufficient water content present in the feed stream, high NO<sub>x</sub> reduction activity almost 100% conversion can be obtained at the temperature as low as 200 °C.
- Water enhanced the hydrolysis process resulting in the higher amount of reducing agent for NO<sub>x</sub> reduction. So the maximum NO<sub>x</sub> conversion was shifted to lower temperature.
- Nitrogen-containing compounds derived from the decomposition/hydrolysis of urea such as NH<sub>3</sub> and HNCO can be oxidized with oxygen in the feed stream to form N<sub>2</sub>, N<sub>2</sub>O, NO and NO<sub>2</sub>. Therefore the net NO<sub>x</sub> conversion becomes negative at temperature above ca. 300 °C.
- The reduction of NO<sub>x</sub> occurs predominantly at low temperature regime between 200-300 °C. While the competitive oxidation of nitrogen-containing compounds take places significantly above 300 °C.

## 5.6 Acknowledgements

Financial support of this research by the Thailand Research Fund (TRF-RGJ Program) and the Petroleum and Petrochemical College is gratefully acknowledged. We also appreciated additional support provided by the National Center of Excellence for Petroleum and Petrochemicals, and Advance Materials, Thailand.

## 5.7 References

- [1] P. Forzatti, *Catal. Today* 62 (2000) 51-65.
- [2] P. Forzatti, *Appl. Catal. A: Gen.* 222 (2001) 221-236.
- [3] W. Held, A. Koenig, T. Richter, SAE Technical Paper 900496 (1990) 209-216.
- [4] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B: Environ.* 18 (1998) 1-36.
- [5] M. Kleemann, M. Elsener, M. Koebel, A. Wokaun, *Ind. Eng. Chem. Res.* 39 (2000) 4120-4126.
- [6] H.L. Fang, H.F.M. DaCosta, *Appl. Catal. B: Environ.* 46 (2003) 17-34.
- [7] O. Kröcher, *Stud. Surf. Sci.* 171 (2007) 261-289.
- [8] G. Piazzesi, M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, *Catal. Commun.* 7 (2006) 600-603.
- [9] G. Piazzesi, O. Kröcher, M. Devadas, A. Wokuan, *Appl. Catal. B: Environ.* 65 (2006) 55-61.
- [10] P. Hauck, A. Jentys, J.A. Lercher, *Catal. Today* 127 (2007) 165-175.
- [11] J. Geith, T.M. Klapötke, *J. Mol. Struct.* 538 (2001) 29-39.
- [12] M. Kobel, E.O. Strutz, *Ind. Eng. Chem. Res.* 42 (2003) 2093-2100.
- [13] P.M. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach, J. Brauer, *Thermochim. Acta* 424 (2004) 131-142.
- [14] M. Koebel, M. Elsener, *J. Chromatogr., A* 689 (1995) 164-169.
- [15] M. Koebel, M. Elsener, T. Marti, *Combust. Sci. Technol.* 121 (1996) 85-102.
- [16] L. Xu, R.W. McCabe, R.H. Hammerle, *Appl. Catal. B: Environ.* 39 (2002) 51-63.
- [17] J.A. Sullivan, O. Keane, *Appl. Catal. B: Environ.* 61 (2005) 244-252.
- [18] C.A. Jones, D. Stec, S.C. Larsen, *J. Mol. Catal. A: Chem.* 212 (2004) 329-336.
- [19] C. Ciardelli, I. Nova, E. Tronconi, B. Konrad, D. Chatterjee, K. Ecke, M. Weibel, *Chem. Eng. Sci.* 59 (2004) 5301-5309.
- [20] A. Sullivan, J.A. Doherty, *Appl. Catal. B: Environ.* 55 (2005) 185-194.
- [21] K. Shimizu, A. Satsuma, *Appl. Catal. B: Environ.* 77 (2007) 202-205.
- [22] E. Seker, E. Gulari, *J. Catal.* 194 (2000) 4-13.
- [23] F. Acke, B. Westerberg, M. Skoglundh, *J. Catal.* 179 (1998) 528-536.



- [24] G. Ramis, L. Yi, G. Busca, M. Turco, E. Kotur, R.J. Willey, *J. Catal.* 157 (1995) 523-535.
- [25] M. Koebel, M. Elsener, G. Madia, *Ind. Eng. Chem. Res.* 40 (2001) 52-59.
- [26] G. Madia, M. Koebel, M. Elsener, A. Wokaun, *Ind. Eng. Chem. Eng.* 41 (2002) 4008-4015.
- [27] M. Koebel, G. Madia, M. Elsener, *Catal. Today* 73 (2002) 239-247.