ELSEVIER

Catalysis Today 40 (1998) 15–26

CATALYSIS TODAY

# The effect of $CH_4$, $H_2O$ and $SO_2$ on the NO reduction with $C_3H_6$

Evangelos A. Efthimiadis*, Gesthimani D. Lionta, Sophia C. Christoforou, Iacovos A. Vasalos

*Chemical Process Engineering Research Institute and Dept. of Chemical Engineering, Aristotelian University of Thessaloniki, P.O. Box 1517, 54006 University City, Thessaloniki, Greece*

## Abstract

NO reduction experiments were carried out in a fixed-bed reactor loaded with metal/alumina catalysts. Two hydrocarbons, methane and propene, were used as the reducing agents for the NO reduction. The former hydrocarbon exhibited relatively low $NO_x$ conversions and it was burned at high temperatures. The addition of methane to a propene-containing feed gas stream did not cause any inhibition or enhancement on the NO reduction activity over the Pt/alumina catalyst. The presence of water in the feed gas stream caused a small, reversible, inhibition effect over the Pt/, Cu/ and Ni/alumina catalysts. The maximum NO conversion was measured over Ni/alumina, followed by that over Cu/and Pt/alumina. The peak temperature varied with the catalyst, but it was not affected by the addition of water to the feed gas stream. The presence of $SO_2$ in the feed gas stream did not affect the $NO_x$ conversion over Pt/alumina, it caused a significant irreversible loss of activity over other metal/alumina catalysts and it enhanced the activity of Rh/alumina. © 1998 Elsevier Science B.V.

## 1. Introduction

Nitrogen oxides ($NO_x$) are among the toxic gases that are produced during chemical processes where oxygen and nitrogen coexist at high temperatures. The combustion of fossil fuels and the regeneration of catalysts used in the cracking of heavy hydrocarbons are examples of processes where $NO_x$ are formed. These oxides can be catalytically reduced to nitrogen using a reducing agent. Ammonia has been used as the reductant for the cleanup of flue gas streams from stationary sources. Problems associated with the use of ammonia can be solved with the application of the Selective Catalytic Reduction of NO with hydrocarbons in the presence of excess oxygen.

Iwamoto [1] in a recent article classified the catalytic processes for the NO removal in an oxygen rich atmosphere to the catalytic NO decomposition and the selective catalytic reduction of NO by hydrocarbons. The author summarized the research work on the NO reduction over different catalytic systems. He concluded that the NO decomposition is, in principal, the best method, but the SCR of NO with hydrocarbons is an alternative practical method to the presently used systems.

Amiridis et al. [2] reviewed the catalytic activity of zeolitic systems and of supported noble metals. The experimental results over different catalysts and the proposed reaction mechanisms were summarized. In conclusion, they noticed that the presence of water and $SO_2$ in the feed gas stream can inhibit the NO reduction, while the formation of undesirable gas products such as $N_2O$ and $SO_3$ was also noticed.

---

*Corresponding author. E-mail: efthimia@alexandros.cperi.forth.gr

0920-5861/98/$32.00 © 1998 Elsevier Science B.V. All rights reserved.
*PII* S0920-5861(97)00113-2

Water is among the gas species that exist in $NO_x$-containing gas streams. Hamada [3] and Hirabayashi et al. [4] noticed that the activity of Pt-based catalysts (Pt/alumina in the former study and Pt/ZSM5 in the latter study) was not affected by the presence of water in the feed gas stream. On the contrary, the addition of water to the feed gas stream in the experiments of Miyadera [5] caused a significant decrease in the $NO_x$ conversion over the Cu/alumina catalyst. Experiments over Co/ZSM5 showed a reversible loss of activity [6] upon the addition of water in the reactive gas mixture, especially at temperatures lower than 450°C. The experimental data of the same study showed that the presence of water changes the selectivity of the hydrocarbon toward NO reduction and the empirical orders of reaction with respect to the concentrations of the involved gases.

Sulfur exists in most of the fossil fuels that are used in the power production processes. As a result, sulfur is typically converted to $SO_2$ under the oxidizing conditions of these units. This remark implies that in a commercial application the de$NO_x$ catalyst should maintain its performance with an $SO_2$-containing feed gas stream. Li and Armor [7] examined the effect of the $SO_2$ addition to the feed gas stream over Co-ZSM5 and Co-ferrierite using an $NO/CH_4/O_2$ reactive gas mixture. $SO_2$ enhanced the activity when the former catalyst was tested at high temperatures, but it inhibited the NO reduction over the latter catalyst. TPD studies showed that a significant fraction of the active sites of both catalysts was covered by the adsorbed $SO_2$. Li and Armor attributed the effect of the $SO_2$ on the catalytic activity of the two catalysts to the inhibition of the methane oxidation reaction by the adsorbed $SO_2$. It was also postulated that $SO_2$ is preferentially adsorbed on the outer surface of the porous catalyst. Therefore, the location of the active sites of each catalyst can determine the effect of the $SO_2$ on the activity of the catalyst. On the other hand, the experimental data of Kikuchi et al. [8] showed that the catalytic performance of H-Fe-silicate and Cu-ZSM5 was hardly affected by the presence of $SO_2$ in the feed gas stream ($NO/C_3H_6/O_2$). $SO_2$ caused a small initial decrease in the catalytic activity of $Sn/Al_2O_3$ (reactive gas mixture: $NO/O_2/CH_3OH/H_2O/SO_2$) [9]. Following that, the catalyst was stable after 60 h of continuous operation.

Previous experimental works showed that gases that do not participate directly in the NO reduction can affect the extent of the reaction. Parameters that determine the above behavior are the catalyst (active site and support solid) and the reaction conditions. The scope of this study is to examine the effect of gas species that usually exist in the feed gas stream of a de$NO_x$ unit such as methane, water and sulfur dioxide on the extent of the SCR of NO over alumina-based catalysts using propene as the reductant.

## 2. Experimental

The catalytic reaction unit consists of the feed gas system, a three-zone furnace controlled by PID controllers, and the gas analysis system. All experiments took place in a quartz flow reactor of 2 cm. o.d. The catalyst was placed in the middle of two 1 cm long zones of quartz. Mass flow controllers were used to control the flow rate of gases of standard composition. When water was added to the reactive gas mixture, pure He was saturated with water at 50°C and the $H_2O$/He gas mixture was then mixed with the other gases. All lines prior to the reactor were heated at 100°C to avoid any water condensation. The flow rate of the inlet gas was 1000 ml/min and the reactor loading was 0.5–4 g. As a result, the catalyst to flow ratio (W/F) was 0.24 or 0.03 g s $cm^{-3}$, respectively. Details of the reaction unit can be found elsewhere [10].

Samples from the exit gas stream were analyzed to determine the extent of the SCR reaction and to identify the gas products. The nitrogen oxides (NO and $NO_2$) were measured in a $NO_x$ analyzer of Thermo Environmental, model 42H. The concentrations of CO and $CO_2$ were measured in a Dual Channel NDIR analyzer of Rosemount, model NGA 2000. The $SO_2$ concentration was measured in a pulsed fluorescent analyzer of Thermo Electron, Model 40. Gas samples were automatically injected in a Varian 3600 CX Gas Chromatograph, equipped with TCD and FID detectors. A Molecular sieve 13X column was used for the separation of the inorganic species and a Haysep N column for the separation of the organic species. Gas mixtures of standard composition were used to calibrate the gas analysis system.

In the presentation of the experimental results we present the concentration of NO, $NO_2$, and $NO_x$ or the

$NO_x$ conversion, the latter defined as the percentage of the inlet NO that is converted to $N_2$ and $N_2O$. The $C_3H_6$ and the $SO_2$ conversions are defined as the percentage of the initial $C_3H_6$ and $SO_2$ concentrations that is consumed in the reactor, the former determined by the GC analysis and the latter by the $SO_2$ analyzer.

## 3. Materials

Two Pt/alumina catalysts have been used in this study: a catalyst from Ketjen AKZO (with commercial name CK303) and a catalyst prepared in CPERI (Pt/Al). The Pt content in the former catalyst was 0.3% wt, while that of the latter catalyst was 2% wt. Pt/Al was prepared by the impregnation of γ-alumina (supplied by Engelhard) with hexachloroplatinic acid solution. The alumina was supplied in the extrudate form. The extrudates were crushed and sieved to separate the particles of 180–355 μm. Following the impregnation, Pt/Al was dried at 120°C and then calcined at 600°C. In the presentation of our reactivity data we use the names Pt/Al1, Pt/Al2, Pt/Al3 and Pt/Al4 that refer to the Pt/Al catalyst prepared in different batches under identical preparation conditions. The comparison between the experimental data measured over different batches of the Pt/Al catalyst showed an excellent reproducibility. A series of metal/alumina catalysts was prepared using metal nitrate solutions and applying the same preparation procedure with the Pt/Al catalyst. Rh/alumina (Rh/Al) was prepared from a $RhCl_3$ solution using the impregnation technique, as well. Finally, In/alumina (In/Al) was prepared using the ion exchange technique from a $In(NO_3)_3$ 0.01 M solution. The metal content in each of the catalysts was measured by the ICP/AES technique. Table 1 summarizes the catalysts that were prepared and tested in this study.

Table 1
Catalysts used in the SCR experiments

| Catalyst Name | Metal | %, Metal in Catalyst |
|---|---|---|
| Pt/Al1, Pt/Al2,Pt/Al3,Pt/Al4 | Pt | 2% |
| CK303 | Pt | 0.3% |
| Cu/Al | Cu | 2% |
| Co/Al | Co | 2% |
| Sn/Al | Sn | 2% |
| Rh/Al | Rh | 2% |
| Ni/Al | Ni | 2% |
| In/Al | In | 1% |

## 4. Results and discussion

NO reduction experiments were carried out to study the effect of two reducing agents, of the water and of the sulfur dioxide in the feed gas stream on the activity of metal/alumina catalysts.

### 4.1. *Effect of two reducing agents on the NO reduction*

The coexistence of more than one hydrocarbons in the reactive gas mixture can either enhance or inhibit the NO reduction. In previous SCR experiments a ‘selective’ hydrocarbon (e.g. propene) or a ‘nonselective’ hydrocarbon (e.g. methane) was employed as the reducing gas. We used a mixture of methane and propene in our SCR studies to examine any possible synergism between the two hydrocarbons over the Pt/alumina catalyst.

Burch and Millington [11] defined the reduction capacities of organic or inorganic compounds as the quantity of oxygen required to oxidize almost completely the reducing agent while still leaving some reducing power (e.g. CO). According to this definition the ratio of the propene and the methane reduction capacities is 2.67. This value is close to the carbon ratio of propene and methane. We, therefore, decided to use a reactive gas mixture of 500 ppmv NO, 500 ppmv $C_3H_6$, 5% $O_2$, He balance as our reference reactive gas mixture. In the next series of experiments we replaced the 500 ppmv of $C_3H_6$ with 1350 ppmv of $CH_4$. Following that, we used a third reactive gas mixture that contained 500 ppmv $C_3H_6$ and 1350 ppmv $CH_4$. The experimental results are shown in Fig. 1–3, respectively. The reactor loading in these experiments was 4 g and the total flow rate was 1000 ml/min. The $NO_x$ and $C_3H_6$ conversion vs. temperature curves in Fig. 1 are typical for Pt/alumina catalysts. We define the peak temperature ($T_{peak}$) as the temperature that corresponds to the max. $NO_x$ conversion and where complete consumption of the propene is measured. When methane was the reducing agent the $NO_x$ conversion (Fig. 2) was very low and the hydrocarbon was burned at high temperatures

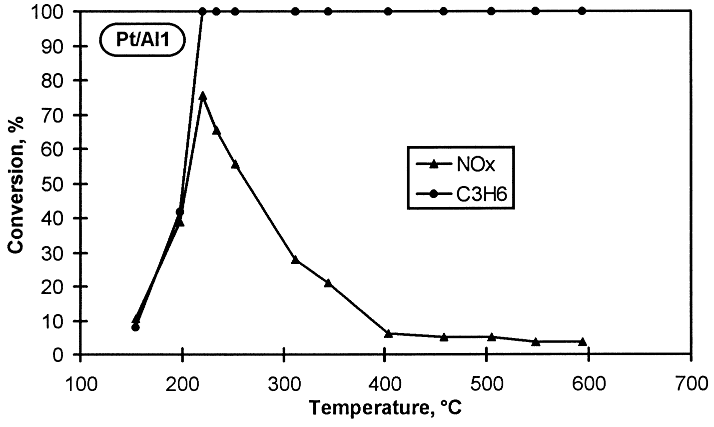

Fig. 1. Temperature effect on the $NO_x$ and the $C_3H_6$ conversion over Pt/alumina.

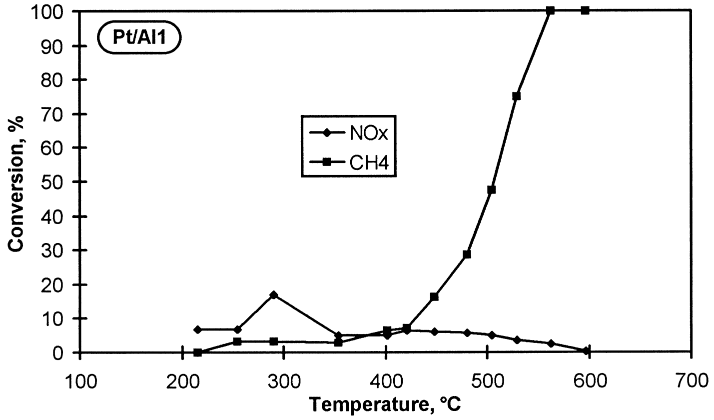

Fig. 2. Temperature effect on the $NO_x$ and the $CH_4$ conversion over Pt/alumina.

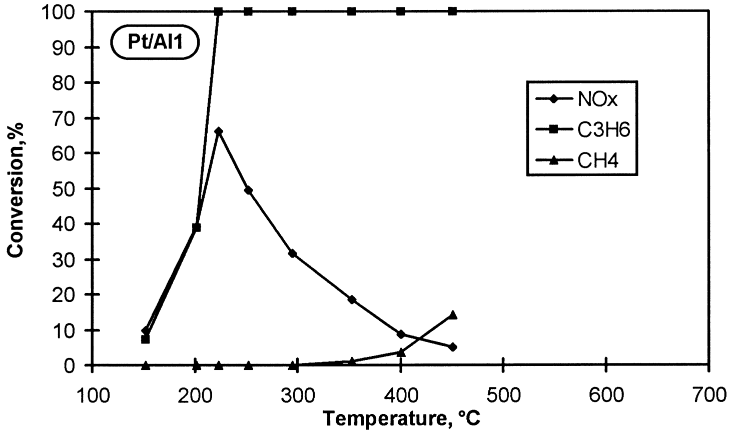

Fig. 3. Temperature effect on the $NO_x$, the $CH_4$ and the $C_3H_6$ conversion over Pt/alumina.

(>500°C). The coexistence of 1350 ppmv $CH_4$ and 500 ppmv $C_3H_6$ in the feed gas stream (Fig. 3) gave similar $NO_x$ conversions to those measured in Fig. 1 where there was no $CH_4$ in the inlet gas. Experiments were also carried out using 1000 ppmv NO, 1000 ppmv $C_3H_6$ and/or 2700 ppmv $CH_4$, 5% $O_2$, in He. The results of these experiments were in agreement with those shown in Figs. 1–3.

NO reduction experiments were carried out by Cho [12] over a Cu/ZSM5 monolith catalyst using a feed gas stream where two selective hydrocarbons ($C_2H_4$ and $C_3H_6$) coexisted. The experimental data of the above study showed that the contribution of $C_3H_6$ to the NO reduction is negligible in the presence of $C_2H_4$. This antagonistic kinetic interaction was attributed to competitive adsorption/diffusion processes in the micropores of the zeolite. The diffusion coefficient of propene is smaller than that of methane implying that intraparticle diffusion cannot explain the difference in the activities of the experiments shown in Figs. 1 and 2. Moreover, the experimental data shown in Fig. 3 indicate that there is no synergistic interaction between the two hydrocarbons. The low activity of Pt/Al1 when methane is the reducing agent can be attributed to the generation of reduced active sites at high temperatures, where the NO adsorption is limited and the reoxidation of the reduced sites by oxygen is favored [13].

### 4.2. *Effect of water on the NO reduction*

Experiments were carried out using a feed gas with the following composition: 2000 ppmv NO, 2000 ppmv $C_3H_6$, 5% $O_2$ and 5% $H_2O$ in He. The

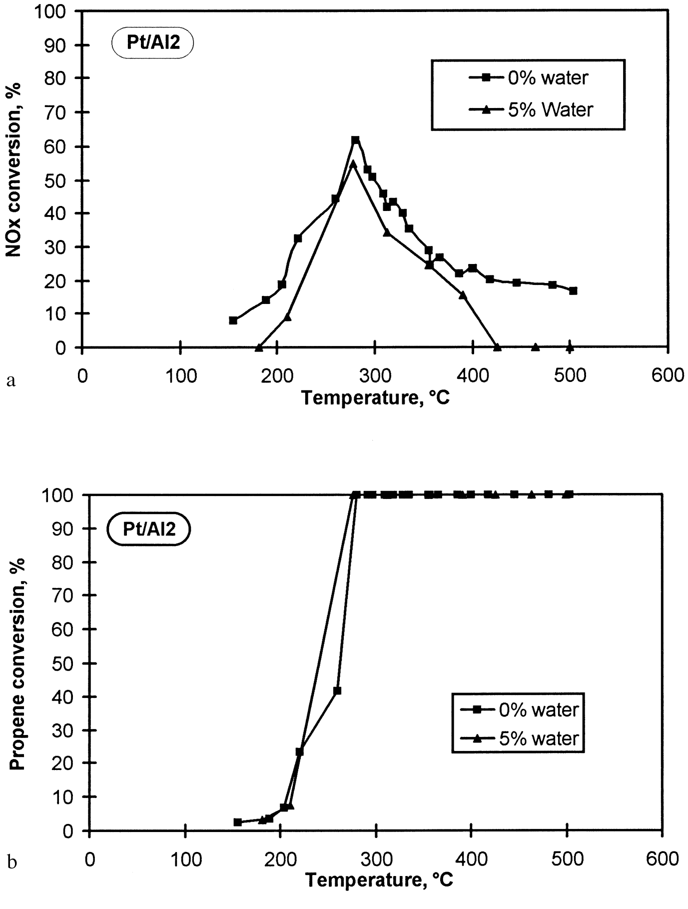

Fig. 4. (a) Effect of 5% water on the $NO_x$ conversion over Pt/alumina. (b) Effect of 5% water on the $C_3H_6$ conversion over Pt/alumina.

reactor loading was 4 g of the Pt/Al2 catalyst and the total flow rate was 1000 ml/min. Experimental results are presented in Fig. 4(a) for a feed gas stream that contained 0% and 5% $H_2O$. The variation of the $NO_x$ conversion with the temperature exhibits the same 'volcano' type curve in the presence or in the absence of water in the feed gas. The addition of water did not cause a significant loss of activity. The propene conversion (Fig. 4(b)) was not affected by the presence of water in the feed gas stream, as well. We examined the stability of the Pt/Al2 catalyst at 285°C in the experiment shown in Fig. 5. During the first 750 min the feed gas stream contained 5% $H_2O$, while in the second stage of this experiment that lasted 450 min the $H_2O$ was replaced by He. The experimental data of Figs. 4 and 5 imply that the presence of water in the feed gas stream does not affect the $NO_x$ conversion significantly. The catalytic activity of Pt/alumina remained unchanged after 22 h of reaction.

Experiments were also carried out using different initial NO concentrations (500–3500 ppmv) at two reaction temperatures (at 228°C, a temperature lower than $T_{peak}$, and at 285°C, a temperature higher than $T_{peak}$) under the reaction conditions used in Fig. 4. In agreement with the experimental results that we have recently presented (0% water) [10] an increase in the initial NO concentration leads to lower $NO_x$ conversions when the inlet gas stream contains 5% water vapor. In general, no significant change in the catalytic activity of Pt/alumina was noticed when the reactive gas was shifted from a 0% to a 5% water-containing gas mixture.

The mass balance for nitrogen in the experiments that contained water in the feed gas stream showed that a small percentage of the inlet nitrogen (N from the inlet NO) was not recovered at the exit of the reactor. This remark led to us to analyze the water that was condensed and collected at the exit of the reactor. The chemical analysis of this sample showed that it contained significant amounts of nitrates and negligible amounts of nitrites. It was, therefore, postulated that water reacted with $NO_x$ producing nitrates. In the presence of Pt $NO_2$ reacts with $H_2O$ to form $HNO_3$ during the commercial production of nitric acid from $NH_3$ and $O_2$ [14]. We, therefore, reported the $NO_x$ conversions calculated from the GC analysis rather than the $NO_x$ analyzer readings in those experiments where the feed gas stream contained water and the reactor was loaded with Pt/alumina. When the other catalysts of this study were loaded in the reactor, the $NO_x$ conversions calculated from the $NO_x$ analyzer were, within 5%, equal to those calculated from the GC analysis.

In Fig. 6 we present experimental data over the Cu/Al catalyst for a feed gas stream that contained 5% water along with those for a dry feed gas stream. The reaction conditions were the same as those in Fig. 4. The inhibition effect of water on the experimental data was limited and the peak temperature did not change. The presence of water did not cause a significant change in the propene conversion vs. temperature curve, as well.

Experiments were carried out over the Ni/Al catalyst to test its NO reduction capacity in the presence of

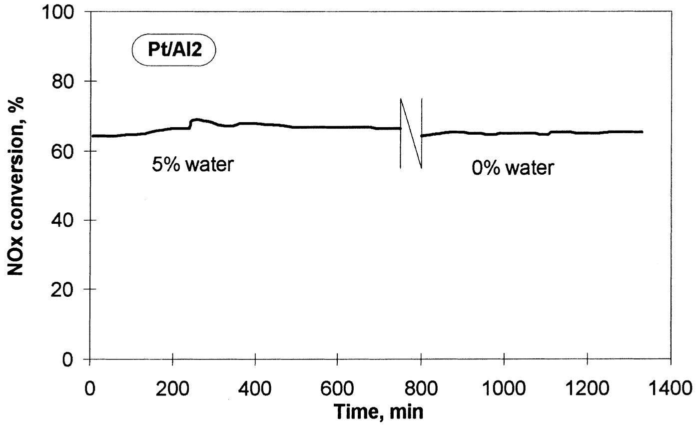

Fig. 5. Evolution of $NO_x$ conversion with the reaction time over Pt/alumina.

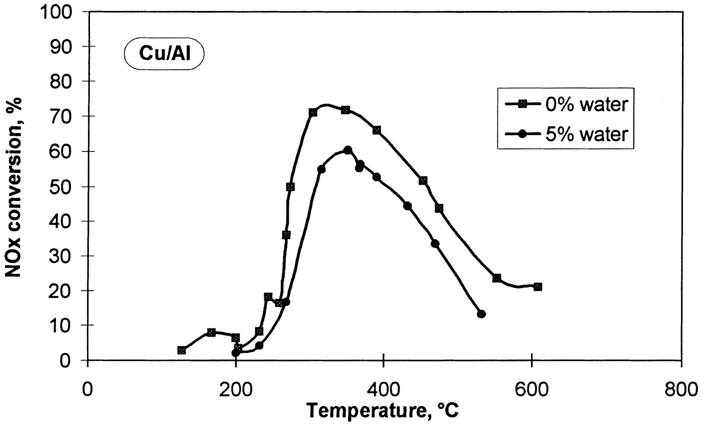

Fig. 6. Effect of 5% water on the $NO_x$ conversion over Cu/alumina.

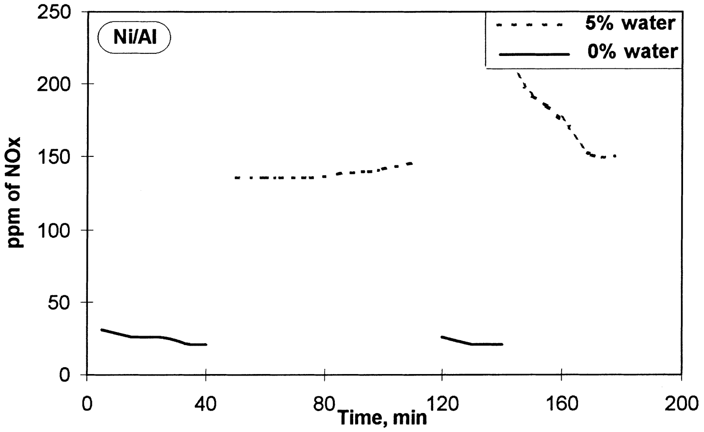

Fig. 7. Effect of 5% water on the $NO_x$ conversion over Ni/alumina.

5% water in the feed gas stream as shown in Fig. 7. The composition of the reactive gas, the catalyst weight and the flow rate were identical to those used in Fig. 4 and the reaction temperature was 518°C. The addition of 5% water at about 40 min after the initialization of the experiment caused a small increase in the $NO_x$ concentration at the exit of the reactor that returned to its initial value when the water was replaced by He. It was, therefore, shown that water has a reversible, inhibition effect over Ni/Al. Similar results were observed over the Pt/alumina and the Cu/alumina catalysts. The variation of the $NO_x$ conversion with the reaction temperature for a feed gas stream that contained 0% or 5% water followed the same trend as that over Pt/Al1 and Cu/Al (Figs. 4 and 6, respectively), i.e., the presence of water caused a small decrease in the $NO_x$ conversion at a given reaction temperature.

The reversible, inhibition effect of water on the NO reduction over different catalysts was attributed by different researchers to the competitive adsorption between water and NO [15] or the competitive adsorption between water and a hydrocarbon [16] for active sites. The reactive gas mixture in the former study was $NO/C_3H_6/O_2/H_2O$ and in the latter one $NO/CH_4/O_2/H_2O$. Our experimental results are in agreement with the above explanation for the effect of water on the activity of alumina-based catalysts. Nevertheless, this inhibition effect is weak with respect to that reported by other works where ZSM5-based catalysts were tested (e.g., Kikuchi and Yogo ($NO/CH_4/O_2/H_2O$), [17]: In/ZSM5, Ga/ZSM5 and Co/ZSM5; Burch and Scire ($NO/C_3H_6/O_2/H_2O$), [15]: Co/ZSM5).

### 4.3. *Effect of $SO_2$ on the NO reduction*

SCR experiments were carried out at different temperatures in the range of 200–500°C to study the effect of the $SO_2$ presence in the feed gas stream to the extent of the NO reduction and the propene consumption. The $NO_x$ and propene conversion vs. temperature curves over CK303 for a 0 and a 200 ppmv $SO_2$-containing feed gas stream are presented in Fig. 8. The $NO_x$ conversion vs. temperature curve for a feed gas stream that contained 0 ppmv $SO_2$ almost coincided with that of an inlet gas stream that contained 200 ppmv $SO_2$. The same applied for the propene conversion vs. temperature curve. $T_{peak}$ did not change with the addition of $SO_2$ to the feed gas stream. The propene consumption at temperatures lower than $T_{peak}$ increased slightly with the presence of $SO_2$ in the feed gas stream. The same $SO_2$ effect on the $NO_x$ and $C_3H_6$ conversion was also noticed over the Pt/alumina catalyst (Pt/Al1) that was prepared in our laboratory.

The $NO_x$ and $SO_2$ concentration at the exit of the reactor were measured in the experiment presented in Fig. 9, where feed gas streams containing 0 or

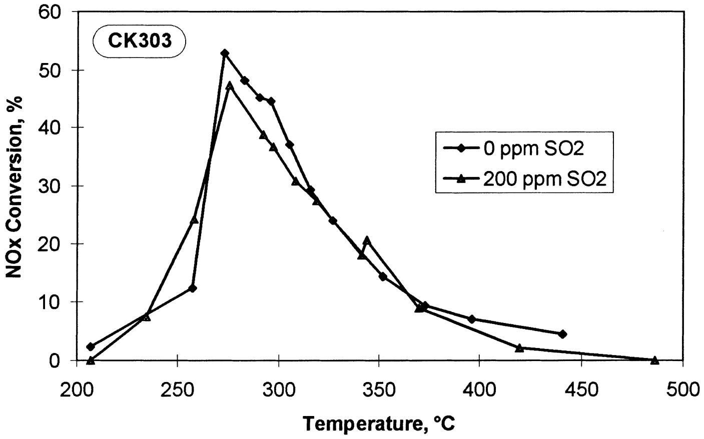

Fig. 8. Effect of 200 ppmv $SO_2$ on the $NO_x$ conversion over Pt/alumina.

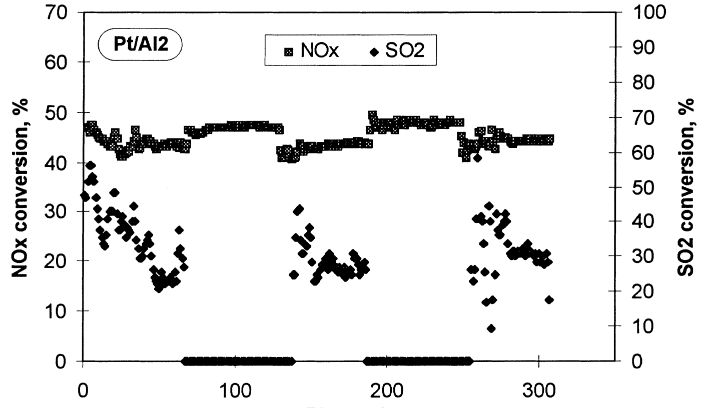

Fig. 9. Variation of the $NO_x$ and $SO_2$ conversion with the reaction time over Pt/alumina.

200 ppmv $SO_2$ were interchanged. The reaction temperature during this experiment was constant and equal to 267°C. The $SO_2$ analyzer data showed that at this temperature one third of the inlet $SO_2$ did not leave the reactor in the form of $SO_2$ implying the formation $SO_3$ and/or the adsorption of $SO_x$ by the catalyst.

The effect of different $SO_2$ concentrations on the extent of the NO reduction over Pt/alumina is shown in Fig. 10. The NO, $NO_2$ and $NO_x$ concentration at the exit of the reactor are shown in this figure along with the inlet $SO_2$ concentration (dashed line). Pt/Al1 was initially exposed to a no-$SO_2$ feed gas stream. When the NO and $NO_2$ concentrations at the exit of the reactor remained stable, 200, 500, 1000 and 0 ppmv $SO_2$ were introduced to the reactor at the same temperature (290°C), successively. The $NO_x$ concentration did not change significantly with the variation of the $SO_2$ concentration. However, it was noticed that the presence of $SO_2$ in the feed gas stream increased the NO and in the same time, decreased the $NO_2$ content at the exit of the reactor. We attributed the above effect of the $SO_2$ presence on the NO and $NO_2$ concentration to the following reaction:

$$SO_2 + NO_2 \rightarrow NO + SO_3 \qquad (1)$$

Pt is a known catalyst for the $SO_2$ oxidation to $SO_3$. Therefore, we believe that Pt can also act as a catalyst in reaction (1). When the $SO_2$ concentration changed from 1000 to 0 ppmv we noticed an increase in the $NO_2$ concentration that was attributed to the reverse reaction (1). Specifically, $SO_3$ adsorbed on the catalyst reacted with NO producing $NO_2$.

The reaction of $Al_2O_3$ with the $SO_2$ and the $O_2$ of the reactive gas mixture can form alumina sulfate ($Al_2(SO_4)_3$) and sulfite ($Al_2(SO_3)_3$). The molar volume of alumina sulfate or sulfite is significantly higher than that of alumina (e.g., molar volume of alumina sulfate/molar volume of alumina=5). Therefore, the formation of the sulfate or the sulfite could lead to a large decrease in the surface area and the void pore space of the catalyst causing loss of the initial activity. We examined the stability of the Pt/Al4 catalyst in the $SO_2$-containing reactive gas mixture using an inlet gas stream of 1000 ppmv NO, 1000 ppmv $C_3H_6$, 500 ppmv $SO_2$, 5% $O_2$, in He at 290°C. The catalyst maintained its initial activity after 15 h of reaction. A catalyst sample was collected at the end of this experiment to study its weight change with the temperature in a thermogravimetric reactor. This sample exhibited a 28% wt loss in the temperature range of 400–865°C. The comparison of the physical properties (surface area and pore size distribution) of the fresh and the reacted Pt/Al4 catalyst did not show any significant changes in pore structure of the catalyst after the reaction. Therefore, we attributed the weight change that was measured in the TGA experiment to the desorption of adsorbed $SO_x$ species. However, our experimental data show that these adsorbed species do not inhibit the NO reduction over Pt/alumina.

Zhang et al. (1992) [18] studied the effect of the $SO_2$ presence in the activity of platinum catalysts. They

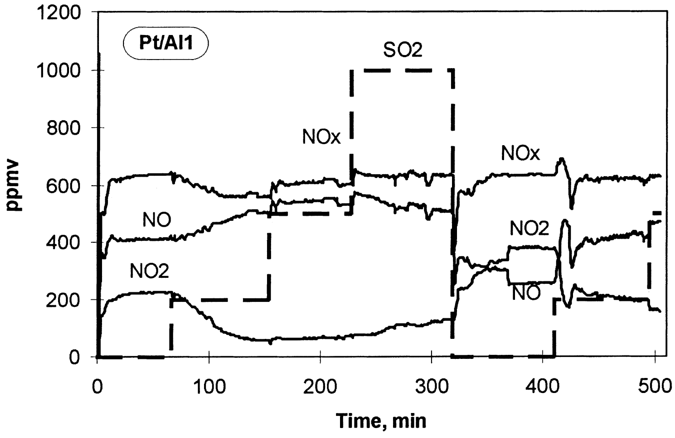

Fig. 10. Effect of different $SO_2$ concentrations on the NO, $NO_2$ and $NO_x$ concentrations over Pt/alumina.

observed that $SO_2$ inhibited the propene combustion, thus favoring the $NO_x$ reduction. We did not notice any significant change in the activity of our Pt/alumina catalysts when we added $SO_2$ to the feed gas stream and we attribute the difference in the activity of the two catalytic systems to the support solids that were used in the two studies.

Experimental data at 501°C are presented in Fig. 11 for feeds containing 0 and 200 ppmv $SO_2$. The $NO_x$ conversion over the Co/Al catalyst that was not exposed to $SO_2$ was 52%. Upon the addition of $SO_2$ to the feed gas stream the $NO_x$ conversion dropped to 11%. Following that, the $SO_2$ addition to the reactive gas mixture caused a significant increase in the NO concentration, while the corresponding change in the $NO_2$ concentration was small. On the other hand, no change in the NO and $NO_2$ concentrations were measured over the previously exposed to $SO_2$ catalyst when the $SO_2$ was replaced by He.

Rh/alumina was used in the experiment shown in Fig. 12. The reaction temperature was maintained constant and equal to 305°C during the experiment. Initially the $SO_2$-free reactive gas mixture was fed to the reactor. About two hours later 200 ppmv $SO_2$ were added to the previous mixture. As a result, the $NO_x$ conversion increased from 32% to 49% and in the same time the $NO_2$ concentration decreased significantly. Therefore, the presence of $SO_2$ enhanced the NO reduction and inhibited the NO oxidation. The latter was also noticed over Pt/alumina (Fig. 10), though the $NO_x$ conversion was not affected by the presence of $SO_2$. Four hours after the initialization of

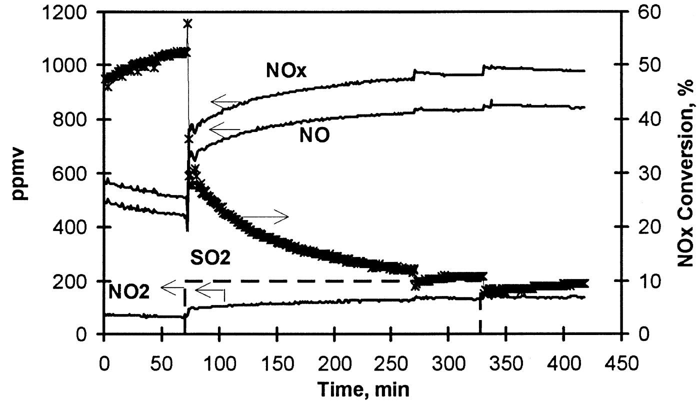

Fig. 11. Effect of different $SO_2$ concentrations on the $NO_x$ concentration and conversion over Co/alumina.

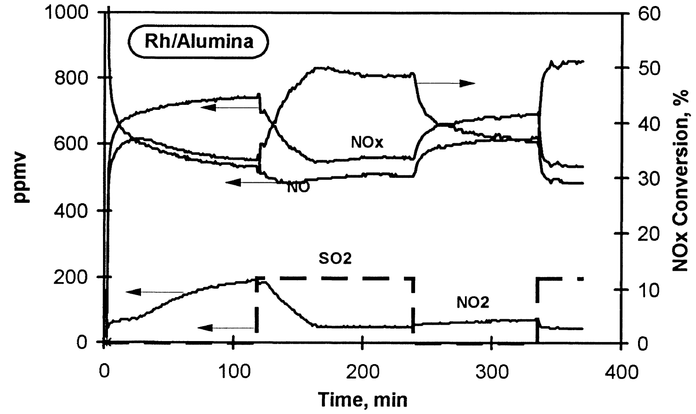

Fig. 12. Effect of different $SO_2$ concentrations on the $NO_x$ concentration and conversion over Rh/alumina.

the experiment the $SO_2$ was replaced by He. This change in the composition of the reactive gas mixture caused a decrease in the $NO_x$ conversion (37%). Contrarily to the results of Fig. 10, the $NO_2$ concentration remained almost constant at this stage of the experiment. Finally, we noticed an increase in the $NO_x$ conversion (51%) when 200 ppmv $SO_2$ were added to the reactor for the second time.

A significant loss of activity with the reaction time was measured over Rh/ZSM5 in previous studies [19,15], while no deactivation was noticed over the Rh/alumina of this work (Fig. 12). Li and Armor [19] attributed the loss of activity over Rh/ZSM5 to the formation of rhodium oxide, while Burch and Scire [15] to the migration of rhodium atoms or ions in the zeolitic channels and the concomitant formation of larger less active aggregates.

Experiments similar to those presented in Figs. 9–12 were carried out over Cu/, Sn/ and In/alumina. In Table 2 we listed the $NO_x$ conversion measured at different $SO_2$ concentrations over the metal/alumina catalysts of this study. We used the experimental data of this table to classify the catalysts to three categories according to their tolerance to $SO_2$.

a) Catalysts tolerant to $SO_2$. The activity of Pt/alumina (Pt/Al and Ck303) remained unaffected by the presence of $SO_2$ in the feed gas stream. The same remark applied for the propene consumption.

b) Catalysts deactivated by $SO_2$. Catalysts of this study (Cu/,Co/, Sn/ and In/alumina) lost a significant fraction of their initial activity when they were exposed to $SO_2$. A possible explanation for this behavior is the coverage of the active sites by $SO_x$ and probably the formation of metal sulfates. The latter can explain the irreversible loss of activity of catalysts initially exposed to $SO_2$.

c) Catalysts activated by $SO_2$. The enhancement in the activity of the Rh/alumina catalyst is probably coupled with the concurrent dissociative adsorption of propene. Specifically, we noticed a 12°C decrease in the peak temperature when we added 200 ppmv $SO_2$ to the reactive gas mixture. Barbier and Duprez [20] summarized the effect of $SO_2$ on the oxidation of different reductants over several metal/alumina catalysts. They noticed that inhibition or enhancement of the oxidation reaction is possible depending on the catalyst and the reductant. The enhanced performance of Rh/alumina in the presence of $SO_2$ is probably linked with the formation of sulfates on the catalyst, though further research is needed for the clarification of the involved reaction mechanism.

Table 2
$NO_x$ conversion measured at different $SO_2$ concentrations

| Catalyst | Temperature,°C | $NO_x$ Conversion, % (ppmv $SO_2$) | | | | |
|---|---|---|---|---|---|---|
| | | 0 | 200 | 500 | 1000 | 0 [a] |
| Pt/Al | 290 | 40 | 45 | 42 | 40 | 40 |
| CK303 | 347 | 18 | 17 | 17 | NT | 17 |
| Cu/Al | 387 | 50 | 25 | NT | NT | 30 |
| Co/Al | 501 | 52 | 11 | NT | NT | 9 |
| Sn/Al | 430 | 60 | 18 | NT | NT | 26 |
| Rh/Al | 305 | 32 | 49 | NT | NT | 37 |
| In/Al | 480 | 42 | 13 | NT | NT | NT |

[a] Previously exposed to an $SO_2$-containing mixture.
NT=Not Tested.

## 5. Conclusions

The addition of methane, a nonselective reducing gas, to the propene-containing feed gas stream did not change the extent of the $NO_x$ reduction over Pt/alumina. When methane was used as the sole reducing agent, the $NO_x$ conversion was very low and methane was burned at high temperatures. The oxidation temperature of methane was higher than the one that corresponds to the maximum $NO_x$ conversion over Pt/alumina and this can be the reason for the low activity of the Pt/alumina catalyst when methane was the sole reducing agent.

NO reduction experiments showed that the presence of water in the feed gas stream caused a small, reversible, inhibition effect in the NO reduction over Pt/, Cu/ and Ni/alumina catalysts. The formation of small amounts of nitrates that was noticed over the Pt/alumina catalyst was attributed to the reaction of $NO_2$ with the $H_2O$.

We classified the catalysts of this study according to their tolerance to the $SO_2$ presence as follows:

(a) Catalysts tolerant to $SO_2$. The catalytic activity of the Pt/alumina catalysts (CK303 and Pt/Al) was not affected by the addition of $SO_2$ to the feed gas stream. In the presence of $SO_2$ the NO concentration increased and the $NO_2$ concentration decreased implying the reaction of the $SO_2$ with the $NO_2$ over Pt/alumina.

(b) Catalysts deactivated by $SO_2$. The catalytic activity of the Co/, Cu/, Sn/ and In/alumina catalysts was severely decreased after their exposure to an $SO_2$-containing feed gas stream. Transient experiments showed that the loss of catalytic activity due to the $SO_2$ was irreversible. The deactivation of these catalysts was attributed to the formation of metal sulfates and to the coverage of the active sites by sulfur oxides.

(c) Catalysts activated by $SO_2$. The presence of $SO_2$ in the feed gas stream enhanced the NO reduction and the propene oxidation over Rh/alumina. A possible explanation for this behavior is that sulfates facilitate the dissociative adsorption of propene over Rh/alumina, though we continue our research studies to support this explanation.

## Acknowledgements

This work was funded by the Commission of the European Community, under Contract EV5V-CT094-0535.

## References

[1] M. Iwamoto, Catal. Today 29 (1996) 29.
[2] M.D. Amiridis, T. Zhang, R.J. Farrauto, Appl. Catal. B 10 (1996) 203.
[3] H. Hamada, Catal. Today 22 (1994) 21.
[4] H. Hirabayashi, H. Yahiro, N. Mizuno, M. Iwamoto, Chem. Lett. (1992) 2235.
[5] T. Miyadera, Appl. Catal. B 2 (1993) 199.
[6] Y. Li, P.J. Battavio, J.N. Armor, J. Catal. 142 (1993) 561.
[7] Y. Li, J.N. Armor, Appl. Catal. B 5 (1995) L257.
[8] E. Kikuchi, K. Yogo, S. Tanaka, M. Abe, Chem. Lett. (1991) 1063.
[9] M. Tabata, H. Hamada, F. Suganuma, T. Yoshinari, H. Tsuchida, Y. Kintaichi, M. Sasaki, T. Ito, Catal. Lett. 25 (1994) 55.
[10] G.D. Lionta, S.C. Christoforou, E.A. Efthimiadis, I.A. Vasalos, Ind. Eng. Chem. Res. 35 (1996) 2508.
[11] R. Burch, P.J. Millington, Appl. Catal. B 2 (1993) 101.
[12] B.K. Cho, J. Catal. 142 (1993) 418.
[13] R. Burch, P.J. Millington, A.P. Walker, Appl. Catal. B 4 (1994) 65.
[14] G.T. Austin, Shreve's Chemical Process Industries, Mc Graw-Hill, NY, 1984.
[15] R. Burch, S. Scire, Appl. Catal. B 3 (1994) 295.
[16] T. Tabata, M. Kokitsu, O. Okada, Appl. Catal. B 6 (1995) 225.
[17] E. Kikuchi, K. Yogo, Catal. Today 22 (1994) 73.
[18] G. Zhang, T. Yamaguchi, H. Kawakami, T. Suzuki, Appl. Catal. B 1 (1992) L15.
[19] Y. Li, J.N. Armor, Appl. Catal. B 2 (1993) 239.
[20] J. Barbier Jr., D. Duprez, Appl. Catal. B 4 (1994) 105.