NOVEL BIFUNCTIONAL CATALYTIC SYSTEMS FOR THE SCR OF NO$_X$ USING HYDROCARBONS AS REDUCTANTS: STEP ONE, NO OXIDATION

S.C. CHRISTOFOROU *
E.F. ILIOPOULOU
E.A. EFTHIMIADIS
A.A. NIKOLOPOULOS and
I.A. VASALOS

*Chemical Process Engineering Research Institute
and Department of Chemical Engineering
Aristotle University of Thessaloniki
PO Box 361
GR - 57 001, Thermi-Thessaloniki*

*to whom all correspondence should be addressed
tel: +30-31-498120, fax: +30-31-498180
e-mail: christof@alexandros.cperi.certh.gr
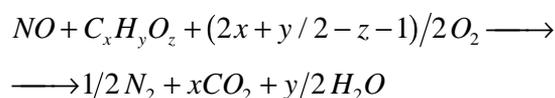
ABSTRACT

The oxidation of NO over Co-, Pt- and Rh-based catalysts was studied by combined catalytic activity and FT-IR studies. The activity of Co-, Pt- and Rh-based catalysts was measured in the presence and absence of H$_2$O and SO$_2$ in the feed. The activity studies showed that the support (Al$_2$O$_3$, TiO$_2$, ZrO$_2$) of Pt catalysts significantly affects the extent of the oxidation reaction, in addition to the metal content and calcination temperature over Co/Al$_2$O$_3$ catalyst. The highest activity was measured over 5 % Co/Al$_2$O$_3$ calcined at 450 ˚C, while Pt/ and Rh/Al$_2$O$_3$ catalysts exhibited significant activity (absence of SO$_2$). The presence of 200 ppm SO$_2$ inhibited irreversibly the NO oxidation mainly over Co/ and Rh/alumina. In the presence of 10 % H$_2$O in the feed the activity of all catalysts weakly decreased, reversibly. FT-IR studies, over fresh Rh/Al$_2$O$_3$, showed the formation of Rh-NO$^+$, Al-NO$_2$ and Al-NO$_3$ species, while over presulfated catalyst only the Rh-NO$^+$ species was detected. Activity and FT-IR studies were used to propose a mechanism for the NO oxidation, in the presence and in the absence of SO$_2$.

INTRODUCTION

The selective catalytic reduction of nitrogen oxides by hydrocarbons (HC-SCR) has been studied as a candidate method for the cleanup of flue gases from the NOx that are emitted both from stationary (power stations, incinerators, FCC units, diesel engines) and mobile sources (lean-burn engines, diesel engines). Problems linked with the presence of NO$_x$ in the atmosphere are health problems to humans (bronchitis, pneumonia) and air pollution (depletion of the ozone layer, acid rain, greenhouse effect).

The development of an efficient SCR method based on the use of hydrocarbons or oxygenates as reducing agents is an alternative solution to the NH$_3$-SCR method that is currently applied for the cleanup of flue gases. This is an attractive method for the purification of exhaust gases emitted from mobile sources where the use of NH$_3$ is not feasible. The SCR of NO is expressed by the general reaction:

$$NO + C_xH_yO_z + (2x + y/2 - z - 1)/2\,O_2 \longrightarrow$$

$$\longrightarrow 1/2\,N_2 + xCO_2 + y/2\,H_2O$$

Previous works (Sasaki *et al*., 1992, Tanaka *et al*., 1994) aiming at the reaction mechanism of the HC-SCR of NO showed that the initial mechanistic step of the reaction involves the oxidation of NO to NO_2, followed by the reduction of NO_2. Based on this, catalysts were designed in such a way that the individual steps, which lead to the dinitrogen formation, take place subsequently in two different systems. Recently, Iwamoto *et al*. (1998) reported that the intermediate addition of a reductant (IAR) into an $NO+O_2$ stream between an oxidation catalyst (NO $\rightarrow NO_2$) and a reduction catalyst ($NO_2 \rightarrow N_2$) is a very effective method for the reduction of NO_x to N_2. The combination of Pt-MFI (oxidation catalyst) and Zn-MFI (reduction catalyst) was proved to be the most effective catalytic system for the IAR method.

Water and SO_2 are among the gas species that exist in NO_x-containing gas streams. The effect of the above gases on the extent of SCR of NO_x has been studied in previous works (Efthimiadis *et al*., 1998a; Burch and Walting, 1998 and Li *et al*., 1993). Their presence inhibited the activity of most catalysts. Xue *et al*. (1996) reported that Pt-based catalysts are very active for the oxidation of both NO and SO_2, but the presence of SO_2 suppressed dramatically the NO oxidation while the presence of NO enhanced the SO_2 oxidation.

The design and synthesis of a novel, bifunctional catalytic system for the selective catalytic reduction (SCR) of NO_X with hydrocarbons or oxygenates in the presence of excess oxygen, where NO_2 is formed in the interior of the catalyst pore structure and subsequently is reduced to N_2 at the catalysts surface, is the overall scope of an active research project.

The scope of this work was to study the initial step of the reaction mechanism that leads to the NO reduction, that is the NO oxidation. Metal-based catalysts were prepared and were tested under reaction conditions similar to those of exhaust streams (presence of SO_2 and H_2O in the feed). FTIR experiments were carried out over a Rh/alumina catalyst in order to study the mechanism of the NO oxidation over this catalyst.

EXPERIMENTAL
Experimental set-up
Reactivity experiments were carried out in a catalytic reaction unit, which consists of the feed gas system, a three-zone furnace controlled by PID controllers and the gas analysis system. Details of the reaction unit can be found elsewhere (Lionta *et al*., 1996). All experiments took place in a quartz flow reactor of 2 cm o.d. The catalyst was placed in the middle of two zones of inert material (quartz). The loading was 2 g and the flow rate 1000 ml min^{-1} (W/F=0.12 g s cc^{-1}). The composition of the reactive gas was 1000 ppmv NO, 5 % O_2, 0 or 200 ppmv SO_2, 0 or 10 % H_2O in He. 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. Samples from the exit gas stream were analysed to identify the gas products. The nitrogen oxides (NO and NO_2) were measured in a chemiluminesce NO_x analyser of Thermo Environmental, model 42H. The SO_2 concentration was measured in a pulsed fluorescent analyser 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 Hayesep N column for the separation of the organic species.

FTIR studies were performed on a NICOLET 740 spectrometer, equipped with an MCT detector, KBr beam splitter and a High Temperature/High Pressure (HTHP) environmental chamber (Spectra, 0030-102). The cell was equipped with a furnace, a cooling water jacket, a ZnSe window and gas inlet and outlet streams. About 50 mg of the catalyst in powder form were placed in the chamber. The sample was pretreated at 500˚ C for 30 min under 20 % O_2 in He flow and then cooled to the desired temperature. For sulphated samples the pretreatment temperature was 420˚C to avoid the decomposition of the sulphates. Absorbance spectra from 64 scans were averaged every 1 or 5 min, at a 4 cm^{-1} resolution. Background spectra were recorded prior to each experiment under pure He flow. The reported spectra were calculated from the difference between the actual and the corresponding background spectra.

Materials
Alumina, zirconia and titania were used as the supports of our catalysts. Extrudates of γ-alumina were supplied by Engelhard while extrudates of

zirconia and titania were supplied by Norton. The extrudates were crushed and sieved to separate particles of 180-355 μm. All catalysts of this study were prepared using the dry impregnation technique. Pt-based catalysts were prepared by the impregnation of the above supports with hexachloroplatinic acid solution. Co-based catalysts were prepared using nitrate solution, while Rh-based catalysts using chloride solution of the corresponding metals. The nominal metal loading of the noble-based catalysts was 2 %, while that of the Co-based catalysts varied between 0.3-5 % Co. Following the impregnation, the catalysts were dried at 120 ˚C and then calcined at 600 ˚C (Pt and Rh). The calcination temperature of Co/alumina varied in the range of 450-800 ˚C.

EXPERIMENTAL RESULTS
NO oxidation data

A series of Co/Al$_2$O$_3$ catalysts with metal loading varying from 0.3 up to 5 % Co calcined at different temperatures were prepared to examine the effect of the calcination temperature and the amount of impregnated metal on their activity. The first experimental point was reached at higher reaction time than the others were. This was attributed to the gradual removal of Cl species derived from the metal precursors. The dashed line in Figure 1 corresponds to the equilibrium NO$_2$/NO$_x$ percentage for a feed of 1000 ppm NO, 5% O$_2$ in He, at different temperatures. According to the experimental results of this figure, the higher the Co amount and the lower the calcination temperature the higher the NO oxidation yield is. The highest activity (about 80 % conversion) was observed over 5 % Co/alumina calcined at 450˚C. Kung *et al.* (1997) noticed a similar behaviour that was attributed to differences in the Co oxidation state and dispersion. They postulated that low calcination temperatures and high loadings lead to the formation of Co$_3$O$_4$ clusters. On the contrary, high temperatures or low loadings lead to the formation of CoO of high dispersion on the support. Co$_3$O$_4$ acts as an oxidation catalyst while CoO as a reduction one. Therefore, 5% Co/alumina calcined at 450˚C resulted in the formation of CoO. When the same sample was calcined at 600˚C the migration of Co anions was enhanced and, in the same time, Co anions of higher oxidation state were formed. Therefore, 5 % Co/alumina calcined at 450˚C resulted in the formation of CoO. When the same sample was calcined at 600˚C the migration of Co anions was enhanced and, in the same time, Co anions of higher oxidation state were formed.

2 % Pt was impregnated on different supports, (alumina, zirconia and titania). The activities of the three samples are compared in Figure 2 under identical reaction conditions (feed: 1000 ppmv NO, 5 % O$_2$ in He). Pt/titania exhibited the highest activity among the examined catalysts. It is generally observed that Pt impregnated on Al$_2$O$_3$ is more dispersed than that impregnated on TiO$_2$. More NO$_2$ is
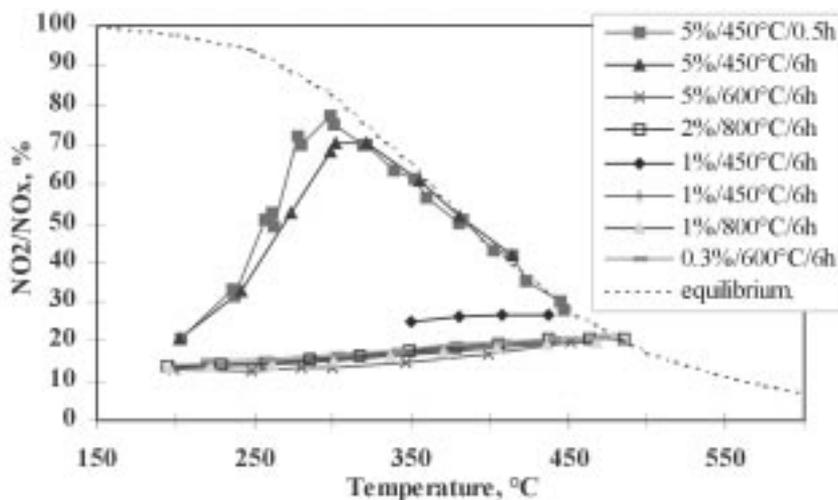

Figure 1. Effect of preparation conditions on the activity of Co/alumina catalysts.

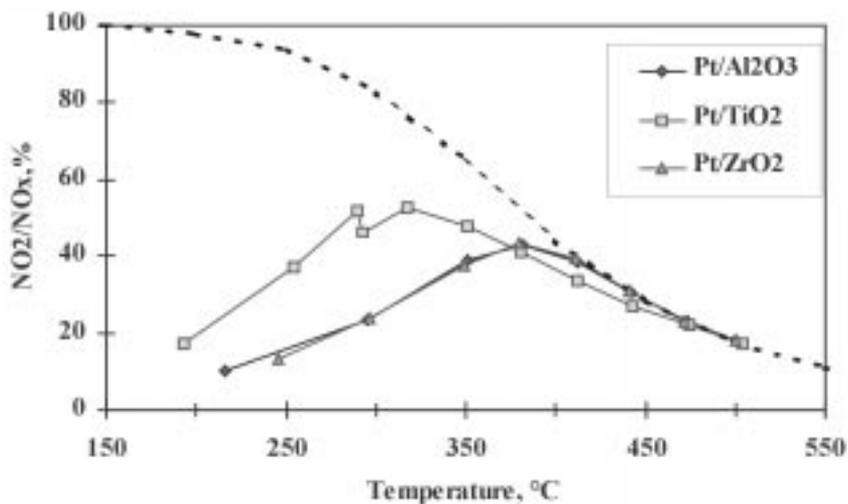*Figure 2*. Activity of Pt-based catalysts on different supports.

produced over Pt/TiO_2 than over Pt/Al_2O_3 (Fig. 2) implying that the oxidation of NO is enhanced by the formation of Pt aggregates. No significant differences were noticed between the activities of Pt/alumina and Pt/zirconia. At high temperatures (T>400°C) all curves coincide with the equilibrium curve (dashed curve) implying that the extent of the NO oxidation is controlled by thermodynamic limitations. When Co was impregnated on alumina and titania we did not notice any significant difference on the NO oxidation yield, while Rh/alumina was more active than Rh/titania. Therefore, the interaction of the impregnated metal with the support may affect the NO oxidation rate.

Xue *et al*. (1996) studied the role of the support, the Pt loading and the dispersion on the NO and SO_2 oxidation. They classified the Pt-based catalysts according to their oxidation activity as follows: $Pt/SiO_2>Pt/Al_2O_3>Pt/ZrO_2$, while increase in the Pt loading from 0.1 to 5 % enhanced the catalytic activity, as well.

In Figure 3 we compare the activity of alumina-based catalysts in the presence and the absence of SO_2 in the feed. The max. NO_2/NO_x percentage was measured at different temperatures for each catalyst in the following order: Co>Rh>Pt (absence of SO_2). The presence of SO_2 deactivated all catalysts especially at low
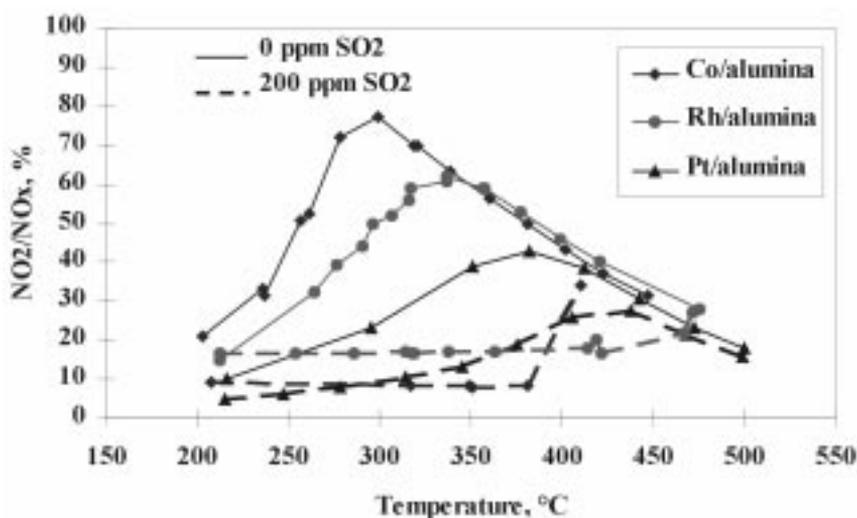

Figure 3. Effect of SO_2 on the NO oxidation over alumina-based catalysts.

temperatures. We attributed this deactivation to the formation of cobalt sulphate on the Co/alumina sample upon its exposure to the SO$_2$-containing feed. For the same feed, lower inhibition was noticed over Pt/alumina that was attributed to the formation of aluminum sulphate. The deactivation was significantly limited over Pt/titania where no sulphates are formed. We also performed transient experiments where SO$_2$ was added and then removed from the feed at a constant temperature. After the SO$_2$ removal from the feed, the initial activity of the catalysts was not recovered, implying an irreversible loss of activity. This is in accordance to our explanation that the deactivation is due to the sulphate formation, since sulphates decompose at high temperatures and under a reducing atmosphere.

We examined the effect of the addition of water in the standard feed on the catalytic activity. Our experimental results showed that upon the addition of 10 % water, Co/ and Rh/alumina catalysts lost part of their initial activity, while the Pt/alumina catalyst maintained most of its initial activity. We performed step changes in the water concentration by adding and removing the water from the feed. The results of this series of experiments are shown in Figure 4. The presence of water in the feed caused a reversible deactivation of all the noble metal-based catalysts. We attributed this inhibition to the competitive adsorption of NO and water on the same active sites. Experimental results aiming at the effect of water on the catalytic reduction of NO$_x$ over different catalysts (Burch and Watling 1998, Li et al., 1993) showed that water inhibited the N$_2$ production reversibly, as well.

FTIR studies

In situ-Fourier Transform Infrared (FT-IR) studies were performed over fresh and presulfated Rh/alumina samples to identify species adsorbed on the catalytic surface during the NO adsorption and oxidation. When the fresh catalyst was exposed to a NO/He feed, at 350 ˚C, the following bands were detected: Rh-NO$^+$ at 1906 cm^{-1} (Hyde et al., 1984, Solymosi and Sarkany 1979, Bamwenda et al., 1995, Chafik et al., 1997) and NO$_2$-Al$_2$O$_3$ at 1592 cm^{-1} (Hyde et al., 1984, Bamwenda et al., 1995, Davydov, 1990). Solymosi and Sarkani (1979) reported that NO is adsorbed either associatively on fully oxidized Rh sites: Rh*+NO → Rh-NO$^+$, or dissociatively on reduced Rh sites: Rh* + NO → Rh-NO$^-$ → Rh-N+Rh-O. Upon the addition of O$_2$ to the feed (Figure 5) the IR spectra showed an increase in the intensity of the NO$_2$- species on alumina, the appearance of nitrate species on alumina at 1294 cm^{-1} (Chafik et al., 1997, Davydov, 1990) and a shoulder at 1624 cm^{-1} that was attributed to $^{Al-O}_{Al-O}$>NO (Davydov, 1990).

The arrangement of our FT-IR apparatus did not allow the performance of experiments with SO$_2$-containing feed. Therefore, we presulfated a sample for 33 h using a feed of 1000 NO, 1000 ppm C$_3$H$_6$, 1000 ppm SO$_2$, 5 % O$_2$ in He at 330˚C.
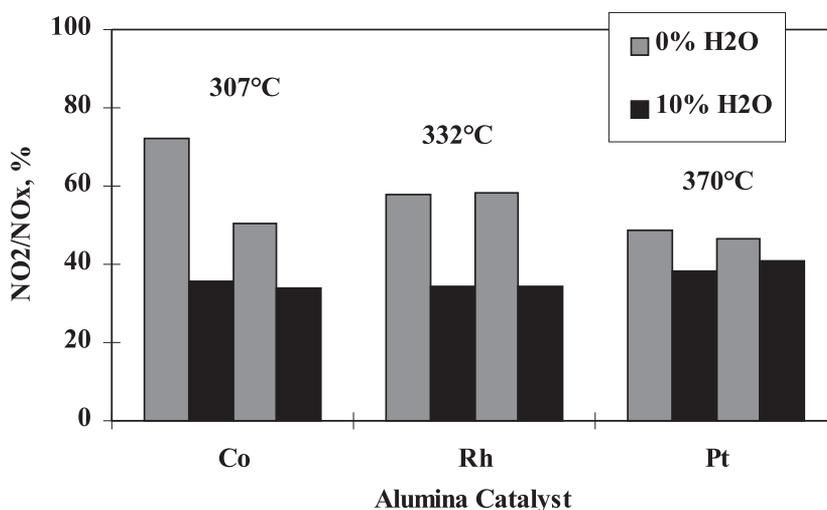

Figure 4. Effect of H$_2$O on the NO oxidation over alumina-based catalysts.
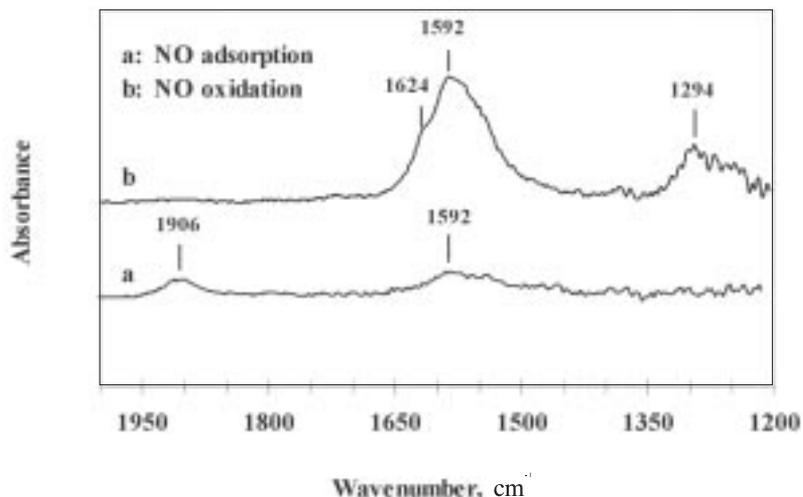
Figure 5. FTIR spectra over fresh Rh/alumina catalysts

When the previous series of experiments were repeated over a presulfated catalyst at the same temperature we noticed only the Rh-NO$^+$ band. In the presence of 5 % O$_2$ in the feed, neither NO$_2$ nor nitrate species were detected on the surface of the presulfated Rh catalyst, as shown in Figure 6. Our FTIR studies confirm our reactivity studies (Fig. 3) that the presence of SO$_2$ inhibits irreversibly the NO oxidation over Rh/alumina.

PROPOSED MECHANISM

We combined our reactivity and FT-IR studies to develop a reaction mechanism for the NO oxidation in the presence and in the absence of SO$_2$ over metal-based catalysts. For a SO$_2$-free feed, NO and O$_2$ can be adsorbed both on the impregnated metal and the support. During our FTIR experiments (Fig. 5a) we noticed that NO is initially adsorbed associatively on Rh active sites (Rh-NO$^+$) and then the band at 1592 cm^{-1} (Al-NO$_2$) was developed. This is in accordance with the results of Ukisu *et al*. (1992). The metal active sites adsorb NO that can be transferred to the support via a spillover mechanism. The presence of O$_2$ in the feed enhanced the band assigned at 1592 cm^{-1} (Al-NO$_2$) and at 1294 cm^{-1} (Al-NO$_3$) (Fig. 5b), supporting the fact that NO$_2$ is held strongly on γ-Al$_2$O$_3$. In conclusion, NO$_2$ is formed either on the metal sites and/or on the metal-sup-
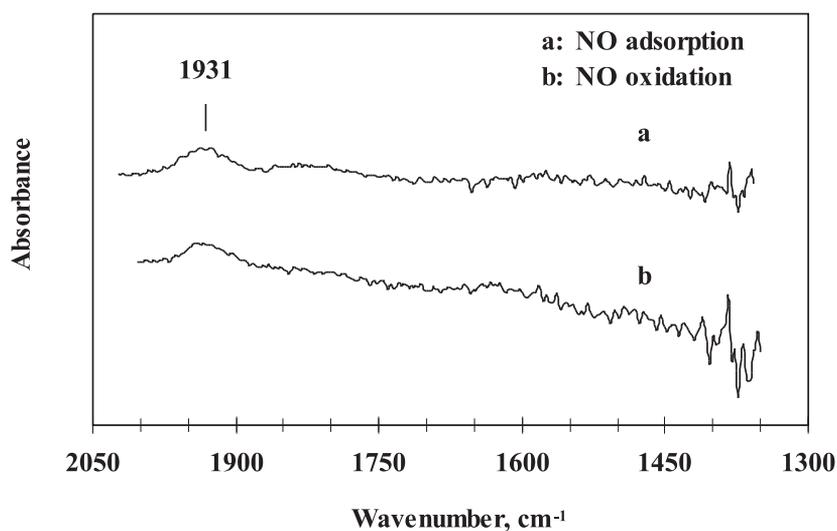

Figure 6. FTIR spectra over presulfated Rh/alumina catalysts.

port interface, depending on the nature of the catalysts and the reaction conditions, and subsequently, it is stabilised on the alunima. In conclusion, NO$_2$ is formed either on the metal sites and/or on the support sites, depending on the nature of the catalyst and the reaction conditions.

When NO and SO$_2$ coexist in the feed, SO$_2$ is preferentially adsorbed on the catalyst with respect to NO (Efthimiadis *et al*., 1998b). Moreover, in the presence of excess oxygen SO$_2$ is easily oxidised to SO$_3$ (noble metals act as catalysts for this reaction (Xue *et al*., 1996, Summers, 1979)) and sulphates are formed on the catalyst. SO$_3$ can be transferred on the support surface via a spillover mechanism. When the impregnated metal reacts with SO$_2$ to form metal sulphates (e.g., transition metal) the active sites are completely covered by sulphates and as a result the catalyst is irreversibly deactivated by the presence of SO$_2$ in accordance to our reactivity studies (Fig. 3) for Co/alumina catalyst.

Noble metals (e.g. Pt, Rh) do not form sulphates but NO and SO$_2$ oxidation can take place on these sites, resulting to the alumina sulphation (Xue *et al*., 1996). The presence of sulphate species may alter the catalytic properties of the materials, causing an inhibition for the NO oxidation reaction (Fig. 3).

In the case of the Rh/alumina catalyst, according to our FT-IR results (Fig. 5), NO oxidation takes place mainly on the support and/or metal-support interface. Upon the exposure of Rh/alumina to a SO$_2$-containing feed, sulphates that are formed on the alumina surface inhibit the adsorption of NO on the support. Given that the adsorption of NO on Rh sites is not inhibited by the SO$_2$ (Fig. 6) and no NO$_2$ formation was measured in the SO$_2$-containg experiments (Fig. 3) the NO oxidation does not take place over the above sites.

CONCLUSIONS

We studied the NO oxidation over metal-based catalysts that were prepared in CPERI using the dry impregnation technique. The highest NO oxidation yield was measured over 5 % Co/alumina and /titania catalysts, while noble metal catalysts exhibited significant activity, as well.

The support of Pt catalysts affects significantly the extent of the oxidation reaction. The presence of water in the feed caused a moderate, reversible deactivation of the catalysts. When we added SO$_2$ in the feed then transition metal-based catalysts were completely and irreversibly deactivated due to the formation of sulphate species. Noble metal-based catalysts were also affected by the presence of SO$_2$ in the feed. Depending on the nature of the oxidation sites (metal, support or metal/support interface) the addition of SO$_2$ to the feed may change the measured activities.

FT-IR studies over fresh Rh/alumina showed the formation of Rh-NO$^+$, alumina-NO$_2$ and -NO$_3$ species. Addition of O$_2$ caused an increase of the NO$_2$ and nitrate species on alumina. When the presulfated Rh/alumina was exposed to NO/He and NO/O$_2$/ He feeds only the Rh-NO$^+$ band was observed.

We used the experimental results of this study to propose a mechanism for the NO oxidation. In the absence of SO$_2$ in the feed, NO$_2$ can be formed either on the metal and/or on the support sites. In the presence of SO$_2$, NO$_2$ can be formed only on metal sites, provided that they do not react with SO$_2$ to form sulphate species.

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