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Mechanistic differences in the selective reduction of NO by propene over cobalt- and silver-promoted alumina catalysts: kinetic and in situ DRIFTS study

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Abstract

The distribution of gaseous products and the nature of the surface species generated during the selective catalytic reduction of NO with C_3H_6 in the presence of excess O_2 (i.e. C_3H_6-SCR) were studied over both a 0.4% Co/γ-Al_2O_3 catalyst and a sulphated 1.2% Ag/γ-Al_2O_3 catalyst. The results were compared with those previously reported for the C_3H_6-SCR over 1.2% Ag/γ-Al_2O_3 and γ-Al_2O_3. High concentrations of NO_2 were observed in the product stream of the SCR reaction over the 0.4% Co/γ-Al_2O_3 and sulphated 1.2% Ag/γ-Al_2O_3 materials. The results show that (as in the case of the γ-Al_2O_3 and also probably that of the 1.2% Ag/γ-Al_2O_3) the NO_2 was formed via an alternative route to the direct oxidation of NO with O_2. The yields of NO_2 were higher over the Co/γ-Al_2O_3 than over the other materials and in contrast to the other materials, no NH_3 was produced over the Co/γ-Al_2O_3 catalyst. Based on these results and those of in situ DRIFTS experiments, a global reaction scheme incorporating organo-nitrogen species as key intermediates is proposed. In this scheme, NO, propene and oxygen react to form organo-nitro and/or organo-nitrito adsorbed species, the reaction products of which combine to yield N_2. The results reported here suggest that Co preferentially promotes the formation of nitrito-compounds which can readily decompose to NO_2, whereas Ag preferentially promotes the formation of nitro-compounds (from reaction of strongly bound ad-NO_x species) which can decompose to isocyanates and ammonia. The sulphation of the 1.2% Ag/γ-Al_2O_3 reduced the surface concentration of strongly bound ad-NO_x species which were thought to react with the reductant or derived species to yield the organo-nitrogen species. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: NO; NO_2; Propene; Silver; Cobalt; Alumina; Sulphate; DRIFTS

1. Introduction

Alumina is one of the most active single metal oxides for the selective catalytic reduction (SCR) of NO in the presence of excess O_2 using light alkanes (other than methane), alkenes and oxygenated molecules such as alcohols [1–8]. In addition, unpromoted alumina selectively yields N_2 rather than N_2O, the latter compound being often observed in the case of platinum-promoted materials [9]. When using hydrocarbons as reductants, the alumina is only active at the high temperatures (typically above 500°C), but promotion of the alumina by a wide range of metals and metal oxides such as platinum [10,11], silver [12,13], cobalt [14–16] and copper [17,18] can lower

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the temperature of reduction of NO. The exact role of these compounds on the enhancement of the catalytic activity of the alumina is not trivial and depends on the nature of the promoter and reductant employed and also the experimental conditions. For instance, two markedly different reaction mechanisms have been reported for the SCR of NO over Pt/γ-Al_2O_3 when using propene and propane as reducing agents [19]; the alumina being a crucial component for the reaction to occur in the case of using the alkane [20]. Interestingly for the $n C_8H_{18}$-SCR of NO over Pt/γ-Al_2O_3, the occurrence of the two mechanisms could be observed, but only when different experimental conditions applied (i.e. at varying reductant partial pressure) [21].

Silver–alumina materials have recently been the focus of much interest as catalysts for the SCR of NO with alkenes [13,22–26] and oxygenated molecules [12,25,27–29] and the effect of SO_2 on their activity was the object of further contributions [22,25,29,31,32]. In the case of the C_3H_6-SCR of NO over Ag/γ-Al_2O_3 catalysts, the different oxidation states of the silver phase (depending on the silver loading over the alumina [13]) were associated with different activity and selectivity patterns [26]. In particular, the oxidic silver phase of a low loading material, i.e. 1.2 wt.% Ag/γ-Al_2O_3, was shown to promote the oxidation of NO to adsorbed NO_x (ad-NO_x) species. It was suggested that the ad-NO_x species subsequently reacted with propene to form organo-nitro and organo-nitrito compounds, as in the case of silver supported on a TiO_2–ZrO_2 mixed oxide [33]. IR bands were assigned to organo-nitrogen species on the surface of silver–alumina catalysts in some in situ IR studies [24,28], including work in our laboratory [26]. The assignment of these IR bands were essentially made by comparison with the IR bands associated with organo-nitrogen species observed over other materials [18,33–35]. The decomposition and reaction of these species through various intermediates (such as NO_2, isocyanates, amines) was proposed to lead to the formation of N_2 [24,36–40].

In the case of the C_3H_6-SCR of NO over Co/Al_2O_3, it was suggested that the role of the promoter was to oxidise NO with O_2 to form NO_2 which subsequently reacted with the alkene on the alumina to yield N_2 [14,15]. This assumption relied mostly on the fact that: (1) over the alumina, the C_3H_6-SCR of NO_2 to N_2 proceeded much faster than that of NO, and (2) the C_3H_6-SCR of NO_2 over alumina proceeded much faster than the C_3H_6-SCR of both NO and NO_2 over the cobalt-promoted sample. However, other results published on the oxidation of NO to NO_2 over Co/Al_2O_3 materials apparently contradicted this view [16]. The measured activity for NO oxidation to NO_2 was found to be too low to be able to account for the related SCR activity. It was suggested that the deactivation of the catalyst by strongly bound surface nitrates was possible when no reductant was available [41].

This paper uses the results of kinetic and in situ DRIFTS analyses to compare the roles of cobalt and silver during the C_3H_6-SCR of NO over γ-Al_2O_3-based samples. The data are discussed with reference to recent results from our laboratory showing that the NO_2 observed over unpromoted alumina during the C_3H_6-SCR of NO was not formed via the direct oxidation of NO with O_2 [42]. In addition, a deeper insight into the nature of the surface species present over a 1.2 wt.% Ag/γ-Al_2O_3 during the C_3H_6-SCR of NO is presented. The in situ DRIFTS spectra obtained during the SCR reaction are compared to reference spectra obtained with the reactants admitted separately over the catalyst; the effect of pre-sulphation with SO_2 was also examined.

2. Experimental

2.1. Catalysts preparation and characterisation

The γ-Al_2O_3 utilised was supplied by Alcan (AA400) and had a total surface area of 148 $m^2 g^{-1}$. The silica was supplied by Rhône Poulenc (DBM 250) with a total surface area of 250 $m^2 g^{-1}$. For the preparation of the silver- and cobalt-promoted materials, appropriate amounts of silver and cobalt nitrate (both from BDH, analytical grade) were dissolved in a volume of de-ionised water equal to that of the porous volume of the supports. The solutions were then deposited by dry impregnation at room temperature. Unless otherwise stated, the samples were dried for 14 h at 120°C and then calcined at 630°C for 6 h in synthetic air. N_2-adsorption at 77 K using a Micromeretics system was used to measure the surface area of the samples. Prior to these measurements, the samples were each out-gassed for 2 h at 200°C under a dynamic vacuum (i.e. with a residual pressure lower than 20 Pa). Atomic absorption spectroscopy measurements were performed in order to determine the promoter content of the catalysts. The loadings of promoters on the alumina or silica are reported in wt.%. The sulphated silver–alumina sample was prepared by exposing the corresponding fresh sample to a stream composed of 100 ppm SO_2+5% O_2 in Ar for 10 h at 630°C.

2.2. Catalytic tests

A quartz flow microreactor (3 mm internal diameter) was used for the catalytic tests, the catalytic bed being held in place by quartz wool plugs. The temperature of reaction was measured inside the reactor, just before the catalyst bed, by a thermocouple enclosed in a quartz tube. Unless otherwise stated, the temperature of the reactor furnace was reduced from 600 to 300°C in 50 or 25°C intervals, dwelling at each temperature for 1 h. The data points reported were taken 5 and 20 min before the end of the dwelling stage at each temperature. The reactant gases used were high purity 1% NO/He (BOC), 1% C_3H_6/He (Air Products), O_2 (BOC, 99.9%) and Ar (BOC 99.99%). The actual feed compositions used in each of the experiments reported in this paper are shown in the legends of the appropriate figures. Analysis of the reaction products was carried out using a Nicolet 550 FT-IR spectrophotometer fitted with a gas-cell of volume 0.22 dm^3. The gas-cell and the lines of the system were heated at 90°C. The concentration of a given species was measured by integrating the peaks in selected regions of its absorbance spectrum and comparing these to a calibration curve. The integration intervals were selected to avoid wherever possible overlap between the different species (Table 1). However, NO_2 had to be integrated in a region of the spectrum where C_3H_6 also absorbs and these products were therefore quantified together using matrix-based calculations (QuantIR® software); the same applied to the combination of N_2O and CO. A relative precision better than ±2% was estimated for the measured concentrations of the different species. As N_2 is not IR active and hence could not be detected, its concentration was calculated assuming that there was mass balance of 100% for all the nitrogen-containing molecules. The relative precision obtained on the value of N_2 was therefore estimated to be better than 4% (statistical value derived from the addition of the four independent measurements of the concentrations of NO, NO_2, N_2O and NH_3). Hydrogen cyanide which was only observed at higher temperatures over the alumina catalyst was not quantified but this was thought to affect the N-balance only to a minor extent [17]. The yields were calculated on a nitrogen-atom basis, i.e. N_2 yield=20% meaning that 20% of the NO molecules was converted to N_2. A blank experiment using an empty reactor showed no significant conversion of NO up to 600°C. On the other hand, the conversion of propene was ca. 6% at this temperature.

2.3. Thermogravimetric analysis

Weight changes associated with passing NO and O_2 over different materials were measured as a function of time using an intelligent gravimetric analyser (IGA) supplied by Hiden Analytical and capable of detecting changes in mass of ±0.1 μg. Samples of 100 mg were first annealed in a He stream of 100 $cm^3\,min^{-1}$ at 450°C for 3 h. The temperature was then reduced to 400°C and the system was flushed with a 400 $cm^3\,min^{-1}$ stream of 2.5% O_2/He for 1 h. At this stage, 500 ppm of NO was introduced into the stream and the weight changes were recorded.

2.4. Diffuse reflectance FT-IR analysis

The diffuse reflectance FT-IR measurements were carried out in situ in a high temperature cell (Spectra-Tech®) fitted with ZnSe windows. The

Table 1
Integration regions used for the quantification of gaseous species with IR

Molecule	NO	N_2O and CO	NO_2 and C_3H_6	NH_3
Quantity measured	Peak area	Peak area	Peak area	Peak height
Integration interval (cm^{-1})	1878.7–1872	2220–2100	2960–2900	931[a]

[a] Peak extends over the range 940–924 cm^{-1}.

sample for study (ca. 30 mg) was finely ground and placed in a ceramic crucible the temperature of which could be varied from 20 to 800°C. All the samples were calcined in situ at 630°C prior to analysis. Unless otherwise stated, the temperature of the sample was increased from room temperature in 100°C steps, dwelling ca. 1 h at each step of temperatures. The spectra reported here were taken after dwelling at a given temperature for 40 min. The absorbance measured in the presence of the reaction stream over the catalyst relative to that of the same material at the same temperature under a stream of argon are reported. At a resolution of $2\,\mathrm{cm}^{-1}$, 64 or 128 scans were usually recorded.

The *W*/*F* during the catalytic and DRIFTS experiments were different, typically $60\times10^{-3}\,\mathrm{g\,s\,cm}^{-3}$ in the former case and $18\times10^{-3}\,\mathrm{g\,s\,cm}^{-3}$ in the latter. While no spectrokinetic analyses were attempted in the present work, the DRIFTS experiments provided instead a qualitative description of the nature and reactivity of the species observed at the catalyst surface at different temperatures. As all the samples analysed by DRIFT were similar (i.e. same alumina support promoted with low weight percents of Ag or Co and/or sulphated) and the catalysts were packed into the crucible in the same fashion, it can be approximated that the same mass/volume of sample was analysed in each case. Therefore, the concentrations of a given surface species from two different samples could be directly compared through the corresponding absorbance measured in each case.

3. Results

3.1. Activity of Co/γ-Al_2O_3 and sulphated Ag/γ-Al_2O_3 catalysts for the C_3H_6-SCR of NO

Fig. 1 shows the propene and NO conversions and the yields of N_2, NO_2, N_2O and NH_3 for the title reaction over 0.4% Co/γ-Al_2O_3 ($135\,\mathrm{m}^2\,\mathrm{g}^{-1}$), 1.2% Ag/$\gamma$-$Al_2O_3$ ($141\,\mathrm{m}^2\,\mathrm{g}^{-1}$) and γ-Al_2O_3 ($148\,\mathrm{m}^2\,\mathrm{g}^{-1}$). The plots of the alumina- and silver-promoted sample were described in an earlier study [26] and therefore are not described in detail here; these plots are reproduced for the sake of comparison with the cobalt-promoted sample.

The results show that (as in the case of the silver-promoted sample) the addition of cobalt to the alumina shifted the plots for propene and NO conversions to lower temperatures when compared to the case of the unpromoted alumina. High yields of N_2 were obtained in the 400–600°C temperature range. The main difference between the Co and Ag samples was the absence of ammonia in the product stream from the Co sample. All the three materials yielded minor concentrations of N_2O. The dotted line in the plot giving the conversion of NO_2 represents the thermodynamic equilibrium limit associated with the following reaction:

$$NO+\tfrac{1}{2}O_2 \Leftrightarrow NO_2 \qquad (1)$$

It can be clearly seen that (as in the case of alumina [26,42]) the NO_2 yield obtained over the cobalt–alumina catalyst exceeded the equilibrium limit of reaction (1) at temperatures >475°C. In the case of the silver–alumina, the NO_2 yield also appeared to be above the thermodynamic limit although the exceedance was smaller than over the Co/γ-Al_2O_3 and similar to the precision of the measurement (i.e. ca. 2%).

Fig. 2 shows the plots associated with the activity of a sulphated 1.2% Ag/γ-Al_2O_3 for the title reaction. The effect of the pre-sulphation of our 1.2% Ag/γ-Al_2O_3 on the propene conversion and N_2 yield was described in detail elsewhere [32]. Compared with the unsulphated material (see Fig. 1), the plots for NO and propene conversions were shifted towards higher temperatures and the maximum yield of N_2 was lower. Interestingly, the NO_2 yield appeared to be significantly above the thermodynamic limit of reaction (1), upon completion of propene conversion. The curve of NO_2 yield exhibited a minimum at ca. 475°C; such a behaviour was also observed on the unsulphated sample at ca. 425°C (see Fig. 1), although the minimum was less marked in this case. In addition, the reaction over the sulphated material yielded significantly more ammonia than the unsulphated sample. It is worth noting that the temperature of maximum NH_3 yield corresponded to the minimum of NO_2 yield in the case of both the sulphated and unsulphated silver–alumina materials.

Fig. 3 shows the molar ratios of NO_2/NO (calculated from data collected during the C_3H_6-SCR of NO) as a function of temperature over the four

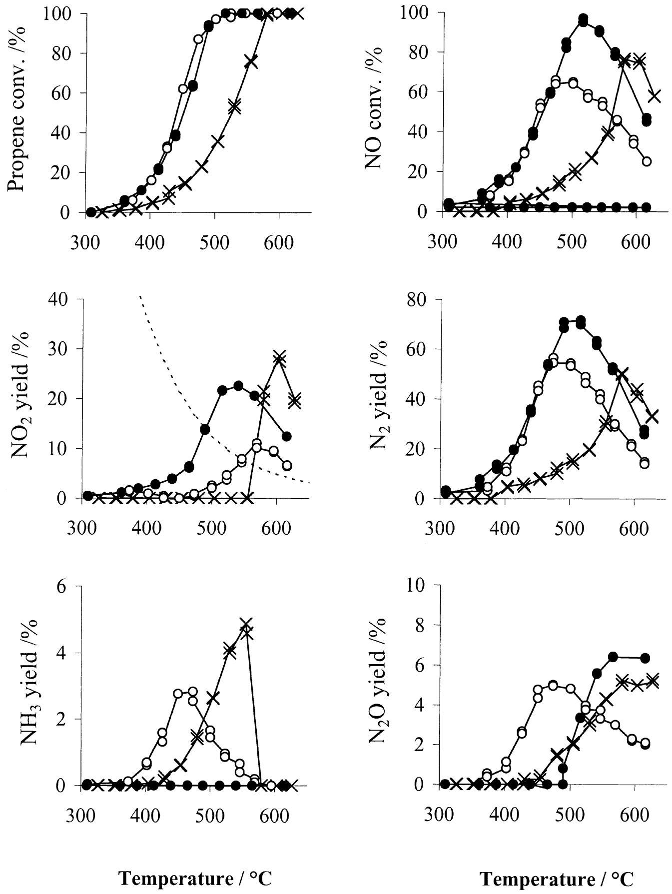

Fig. 1. C_3H_6-SCR of NO over γ-Al_2O_3 (×), 1.2% Ag/γ-Al_2O_3 (○) and 0.4% Co/γ-Al_2O_3 (●) as a function of temperature. Feed: 0.05% NO+0.05% C_3H_6+2.5% O_2/He, W/F=0.06 g s cm^{-3} (GHSV ~50 000 h^{-1}). The dotted line in the plot giving the NO_2 yield represents the thermodynamic limit of NO_2 yield associated with the reaction $NO+\frac{1}{2}O_2 \Leftrightarrow NO_2$.

catalysts reported in the present study and compares these curves to the ratio associated with reaction (1). The difference between the experimental ratios and those predicted by thermodynamics is apparent for all the samples. At 480°C, the experimental NO_2/NO ratio measured during the reaction over the cobalt–alumina sample was ca. 40-fold higher than the thermodynamic ratio.

3.2. Activity of Co/γ-Al_2O_3 and Ag/γ-Al_2O_3 catalysts for the oxidation of NO to NO_2

Fig. 4 shows the activity of silver- and cobalt-promoted alumina catalysts for the oxidation of NO to NO_2. No other products of reaction other than NO_2 were observed. On one hand, the four samples reported in the Section 3.1 (i.e. γ-Al_2O_3, unsulphated and sulphated 1.2% Ag/γ-Al_2O_3 and 0.4% Co/γ-Al_2O_3) exhibited a low activity for the title reaction; the NO_2 yield reaching the equilibrium curve only at temperatures above 600°C. On the other hand, the catalysts with high loadings of cobalt (i.e. 8% Co/γ-Al_2O_3 and 6% Co/SiO_2) had significantly higher activities. In the case of the 8% Co/γ-Al_2O_3, the calcination temperature had a marked effect on the oxidation activity: the sample calcined at 630°C was an order of magnitude less active than that calcined at 450°C. In contrast, the calcination temperature had little effect on the NO oxidation activity of the 6% Co/SiO_2 sample.

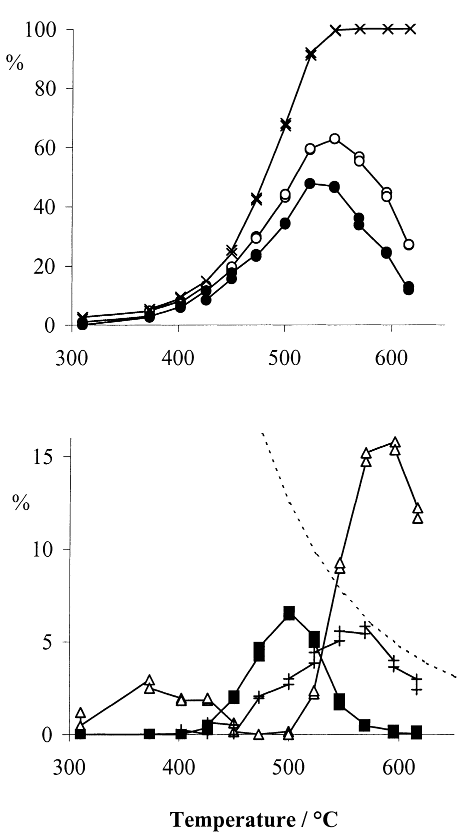

Fig. 2. C_3H_6-SCR of NO over sulphated 1.2 wt.% Ag/γ-Al_2O_3: propene conversion (×), NO conversion (○), N_2 yield (●), NO_2 yield (Δ), N_2O yield (+) and NH_3 yield (■) as a function of temperature. Feed: 0.05% NO+0.05% C_3H_6+2.5% O_2/He, W/F=0.06 g s cm^{-3} (GHSV ~50 000 h^{-1}).

3.3. Thermogravimetric studies of the reaction: $NO+\frac{1}{2}O_2\Rightarrow ad\text{-}NO_x$

The formation of ad-NO_x species over the Al_2O_3 and the unsulphated and sulphated Ag/γ-Al_2O_3 and the 0.4% Co/γ-Al_2O_3 was studied by thermogravimetric analyses at 400°C under a flow of NO and O_2 (Fig. 5). It has been already reported that one of the roles of silver was to promote the formation of ad-NO_x species [26] as evidenced by the faster weight uptake observed over the 1.2% Ag/γ-Al_2O_3 as compared to the case of the γ-Al_2O_3. In contrast, the sulphated silver sample and the cobalt material showed significantly less rapid weight uptakes as compared with the case of the alumina.

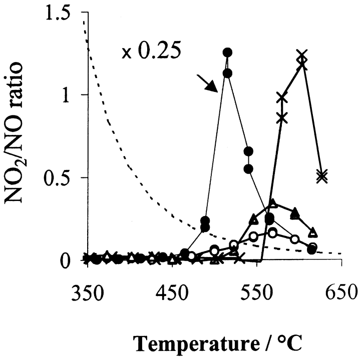

Fig. 3. NO_2/NO ratio measured during the C_3H_6-SCR of NO over γ-Al_2O_3 (×), 1.2% Ag/γ-Al_2O_3 (○), sulphated 1.2% Ag/γ-Al_2O_3 (Δ), and 0.4% Co/γ-Al_2O_3 (●) as a function of temperature. Feed: 0.05% NO+0.05% C_3H_6+2.5% O_2/He, W/F=0.06 g s cm^{-3} (GHSV ~50 000 h^{-1}). The dotted line represents the NO_2/NO ratio at the thermodynamic equilibrium of the reaction $NO+\frac{1}{2}O_2 \Leftrightarrow NO_2$.

3.4. In situ DRIFTS of the oxidation of NO over Ag/γ-Al_2O_3

The aim of the results presented in Sections 3.4 and 3.5 is to provide reference DRIFTS spectra of surface species generated by the oxidation of NO and the oxidation of propene over the alumina supported materials. The assignments derived from these analyses are used in the description of the SCR reaction data presented in Section 3.6. Fig. 6 shows the DRIFTS spectra of the surface species formed during the oxidation of NO with O_2 over the 1.2% Ag/γ-Al_2O_3 at different temperatures. The band observed at 1230 cm^{-1} at a temperature of 100°C was assigned to a nitrite species (chelate or bridging NO_2^-), whereas that at 1567 cm^{-1} was typical of bidentate nitrate NO_3^- compounds [43–46]. The large width and asymmetry of the bands in both cases probably indicated the presence of several species. The minor bands at 1465 and 1320 cm^{-1} could be indicative of linear and monodentate nitrites, respectively [46]. The intensity of the bands associated with nitrites decreased with increasing temperature, in agreement with the results reported by Kijlstra et al. [46]. At the higher temperatures (300–500°C), only the nitrate bands were observed. At least two sets of nitrate bands were present, the association that we propose from other experiments (not shown) being 1550+1250 cm^{-1}

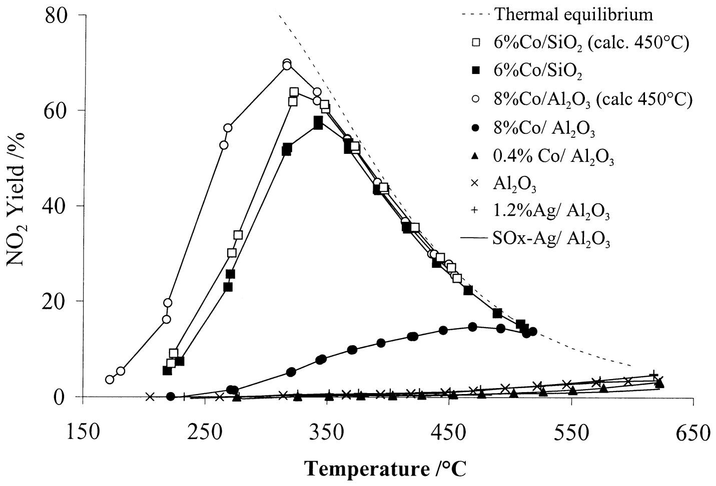

Fig. 4. The activity of various catalysts for the oxidation of NO to NO_2 as a function of temperature. Unless otherwise stated, all the samples were calcined at 630°C prior use. Feed: 0.05% NO+2.5% O_2/He. The dotted lines represents the NO_2 yield at the equilibrium of the reactions $NO+\frac{1}{2}O_2 \Leftrightarrow NO_2$.

(i.e. nitrate “A”) and 1580+1305 cm^{-1} (nitrate “B”). The overlapping of the two signals giving rise to the broad band between 1600 and 1500 cm^{-1}. (The assignments of the main IR bands are summarised in Table 2.) At 600°C, no traces of ad-NO_x species could be detected on the surface of the material.

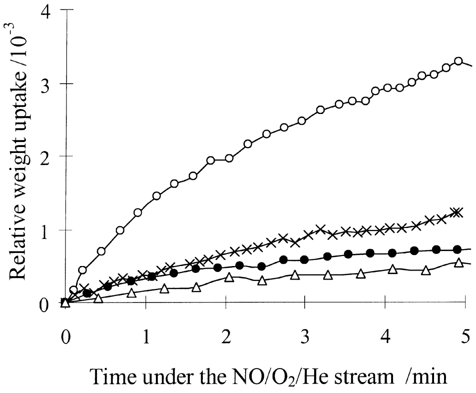

Fig. 5. Thermogravimetric analysis of the formation of ad-NO_x species at 400°C over γ-Al_2O_3 (×), 1.2% Ag/γ-Al_2O_3 (○), sulphated 1.2% Ag/γ-Al_2O_3 (Δ), and 0.4% Co/γ-Al_2O_3 (●) as a function of time. Feed: 0.05% NO+2.5% O_2.

3.5. In situ DRIFTS of the oxidation of C_3H_6 over Ag/γ-Al_2O_3 and γ-Al_2O_3 catalysts

Fig. 7 shows the DRIFTS spectra of the surface species formed during the oxidation of C_3H_6 with O_2 over the 1.2% Ag/γ-Al_2O_3. At 100°C, bands in the C–H vibration region and two bands at ca. 1456 and 1580 cm^{-1} were observed. These bands can be related to carboxylate groups such as those in acrylate species (i.e. 1450 and 1567 cm^{-1} over alumina [47]). The 1450 cm^{-1} band can also be attributed to an alkoxide species (note that no band at ca. 1650 cm^{-1} associated with C=C was observed) [48].

At 200°C, the C–H vibrations were no longer observable on the catalyst surface, only weak bands being present between 1700 and 1400 cm^{-1}. At 300°C, the spectrum featured a broad peak at 1590 cm^{-1} and two other large bands at 1650 and 1454 cm^{-1}, while no definable band was observed in the C–H stretching region. These bands could be attributed to aromatic species (1590+1454 cm^{-1} [49]) or polyene compounds (e.g. 1590 cm^{-1} to the C=C stretching of –C=C–C=C– [50]). In spite of the oxidative nature of the feed in SCR reactions, the formation of carbonaceous residues has been reported over several catalysts [51–53] and is hence possible in the

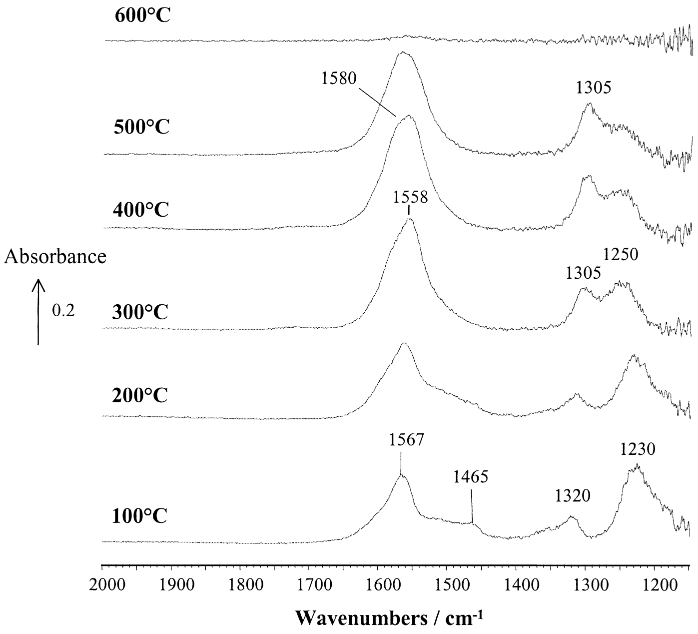

Fig. 6. In situ DRIFTS of 1.2% Ag/γ-Al_2O_3 during the reaction of NO and O_2. Feed: 0.05% NO+2.5% O_2/Ar.

Table 2
Bands observed on alumina-based materials during DRIFTS experiments and the corresponding surface species and vibrations to which they were assigned (s=symmetric, a=asymmetric, ν=stretching, δ=bending)

Wave number (cm^{-1})	Surface species	Vibration
1230	Bidentate or chelating nitrite NO_2^-	ν^a_{ONO}
1320	Monodentate nitrite NO_2^-	
1465	Linear nitrite NO_2^-	
1550	Nitrate “A” NO_3^-	$\nu_{N=O}$
1250		ν^a_{ONO}
1580	Nitrate “B” NO_3^-	$\nu_{N=O}$
1305		ν^a_{ONO}
1575	Free carboxylate COO^-/acetate	ν^a_{OCO}
1460		ν^s_{OCO}
2905	Formate $HCOO^-$	ν_{CH}
1595		ν^a_{OCO}
1395		δ_{CH}
1380		ν^s_{OCO}
2230, 2250	Isocyanate –NCO	
2135	Cyanide –CN	
1645	Organo-nitrite or oxime?	$\nu_{N=O}$ or $\nu_{N=C}$
ca. 1650	Carboxylic acid or oxygenate?	
ca. 1590, 1454	Aromatics, polyene, acrylate?	
1456+2924	Alkoxide?	

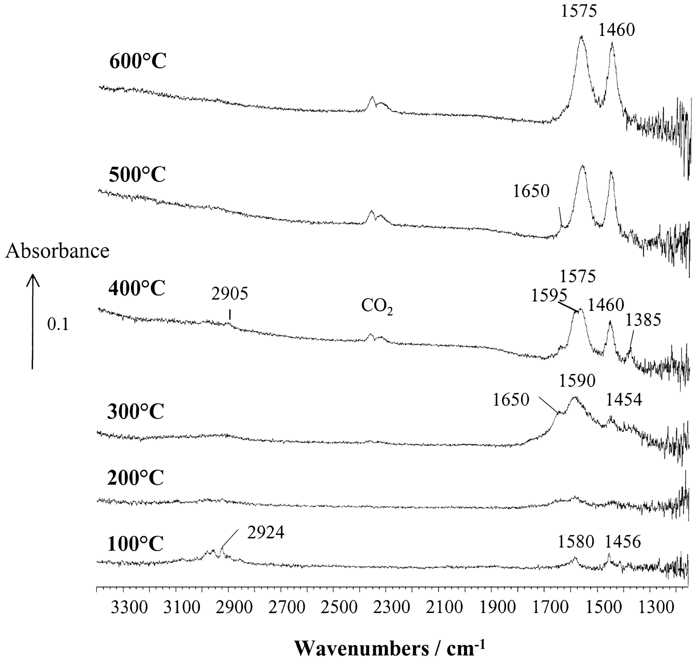

Fig. 7. In situ DRIFTS of 1.2% Ag/γ-Al_2O_3 during the reaction of propene and O_2. Feed: 0.05% C_3H_6+2.5% O_2/Ar.

present case. The presence of carboxylic acids or other oxygenated molecules was also possible (band at 1650 cm^{-1}, extending up to 1800 cm^{-1} probably indicating the presence of carbonyl groups) [47,54]. No combustion activity was noticed up to 300°C as evidenced by the absence of a gaseous CO_2 band at 2360 cm^{-1}. The gaseous CO_2 band was clearly visible from 400°C upwards. At 400°C, the two strong bands at 1575 and 1460 cm^{-1} indicated the presence of a carboxylate species which could be part of an acetate group. The IR spectra of bridged or bidentate acetates present mainly two bands at ca. 1575+1465 cm^{-1} (i.e. asymmetric and symmetric stretching vibration of the carboxylate group of the acetate), while the –CH bands are essentially not observable [54]. Therefore, it is difficult to distinguish an acetate from a free carboxylate species (adsorbed CO_2) which shows the OCO vibrations at ca. the same wave numbers. The weaker peaks at 2905+1595+1385 cm^{-1} are attributable to formate species [55]. The intensity of the band at 1650 cm^{-1} decreased significantly at 400°C compared to the intensity at 300°C. At 500 and 600°C, the formate species were no longer present and only the carboxylate group remained in addition to a weak signal at 1650 cm^{-1}. The wave numbers of the main IR bands and their proposed assignments are summarised in Table 2.

Similar spectra were observed during the in situ DRIFTS analysis of the propene oxidation over the unpromoted alumina (Fig. 8). However, no adsorbed species could be detected at 100°C. As in the case of the silver–alumina, the light off of the combustion of propene occurred between 300 and 400°C. The formate and the carboxylate bands were clearly observed at temperatures of up to 500°C.

3.6. In situ DRIFTS of the C_3H_6-SCR of NO over 1.2% Ag/γ-Al_2O_3

Fig. 9 shows the in situ DRIFTS spectra of the surface species formed during the title reaction over the silver-promoted alumina. Some of the spectra reported in Fig. 9 are described elsewhere [26], and therefore only the comparison of the spectra obtained in the case of reacting NO and propene, respectively, is done. At 100°C, the C–H bands and that of the various nitrites and nitrates observed in the case of reacting NO and C_3H_6 separately were also present during

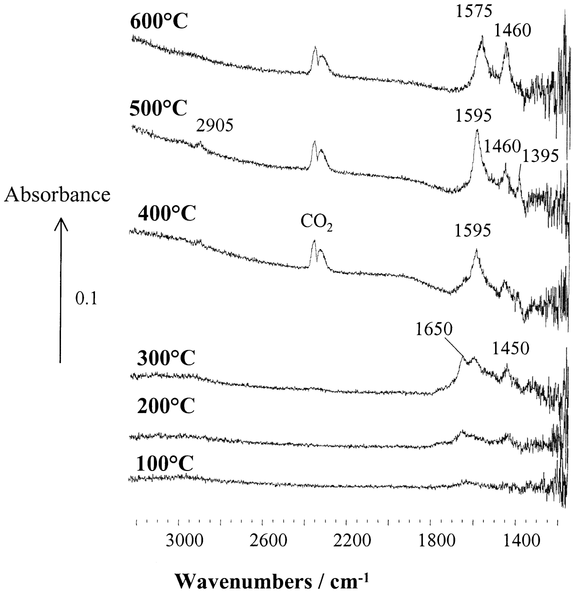

Fig. 8. In situ DRIFTS of γ-Al_2O_3 during the reaction of propene and O_2. Feed: 0.05% C_3H_6+2.5% O_2/Ar.

the SCR reaction. The light off of the reaction occurred between 300 and 400°C, as evidenced by the appearance of the CO_2 bands. A major characteristic of the spectra related to the SCR reaction was the presence of isocyanate species (2230 and 2250 cm^{-1}) at 300°C and cyanide species (2130 cm^{-1}) at 300 and 400°C [37,44,56–58]. A band at 1645 cm^{-1} was also observed at 400°C (shoulder) and 500°C. At 500 and 600°C, the intensities of the bands of nitrates "A" and "B" were modified as compared to the case of the NO+O_2 reaction. The intensities of nitrate "B" bands (e.g. 1305 cm^{-1}) being more diminished than those of nitrate "A" (e.g. 1250 cm^{-1}) (see Fig. 6). In addition, the nitrate "A" species could still be observed at 600°C along with carboxylate groups, contrary to the case of the reaction without propene.

3.7. *In situ DRIFTS of the C_3H_6-SCR of NO over 0.4% Co/γ-Al_2O_3*

The in situ DRIFTS spectra observed during the title reaction over the cobalt-promoted alumina (Fig. 10) were different from that obtained over the silver-promoted sample (Fig. 9). At 100°C, no signal in the C–H region could be detected in the case of the Co-sample. Ill-defined bands from 1700 to 1500 cm^{-1} were observed, which may be due to ad-NO$_x$ species (e.g. organo-nitrate or nitrito compounds [59]) and/or compounds formed from the reaction of propene (see Fig. 7). On one hand, the intensity of the band at

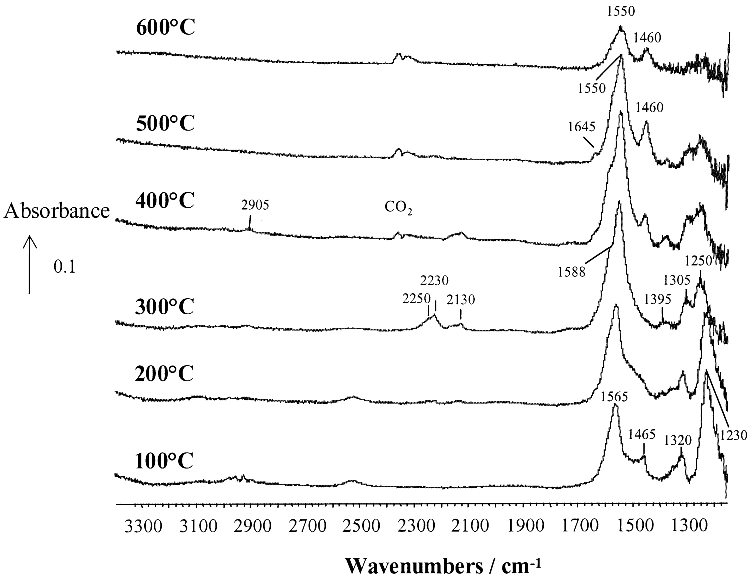

Fig. 9. In situ DRIFTS of 1.2% Ag/γ-Al_2O_3 during the C_3H_6-SCR of NO. Feed: 0.05% NO+0.05% C_3H_6+2.5% O_2/Ar.

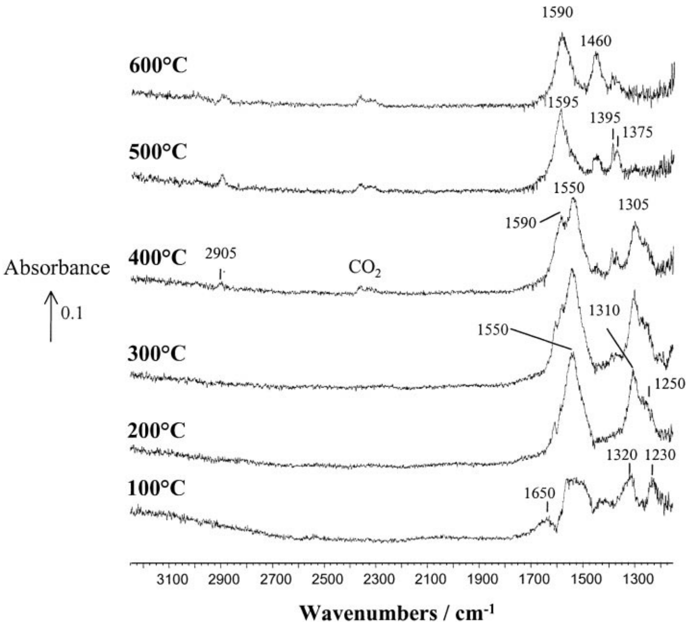

Fig. 10. In situ DRIFTS of 0.4 wt.% Co/γ-Al_2O_3 during the C_3H_6-SCR of NO. Feed: 0.05% NO+0.05% C_3H_6+2.5% O_2/Ar.

1230 cm^{-1} attributable to nitrite species was significantly weaker (ca. fourfold) than that observed on the silver sample. On the other hand, the band of the nitrite at 1320 cm^{-1} exhibited a similar intensity in both cases. At 200°C, the nitrite at 1230 cm^{-1} disappeared, while the bands of nitrates “A” and “B” were strong. In contrast to the case of the silver sample, the intensity of the absorption due to nitrate “B” (ca. 1305 cm^{-1}) was greater than that of species “A” (1250 cm^{-1}). Neither isocyanate nor cyanide species could be detected at any temperature over the Co sample. The presence of gas phase CO_2 at 400°C showed that light off of the propene commenced between 300 and 400°C. At 400°C, significant concentrations of formate and nitrate species were observed. At 500 and 600°C, the nitrate species were no longer present on the surface of the catalyst which was instead covered with formate and carboxylate groups.

3.8. In situ DRIFTS of the C_3H_6-SCR of NO over unpromoted γ-Al_2O_3

The in situ DRIFTS spectra observed during the title reaction over the unpromoted γ-Al_2O_3 catalyst were studied in detail at 300°C as a function of time-on-stream (Fig. 11). The alumina was oxidised in situ in air at 630°C before introducing the reactant stream at 300°C. Interestingly, strong bands associated with nitrite species (1320 and especially 1235 cm^{-1}) were initially observed while gas-phase methane was evolved (band at 3016 cm^{-1} and the corresponding rotational side bands). A broad peak from 1650 to 1500 cm^{-1} could be observed (possibly due to carbonaceous deposits) in addition to a band at 1460 cm^{-1}, probably associated with carboxylate or acetate species. The nitrite species gradually disappeared from the surface while formates gradually increased with increasing time-on-stream. A very weak band at 1550 cm^{-1} was observed, possibly indicating the presence of nitrate “A”.

3.9. In situ DRIFTS of the C_3H_6-SCR of NO over sulphated 1.2% Ag/γ-Al_2O_3

The in situ DRIFTS spectra observed during the title reaction over a sulphated 1.2% Ag/γ-Al_2O_3 were compared with that obtained over the corresponding unsulphated sample (Fig. 12). Earlier work on the sulphated material showed that both the alumina and the silver were covered with surface sulphate species characterised by broad IR bands between 1400 and 1300 cm^{-1} in the dry state [32]. The negative band at

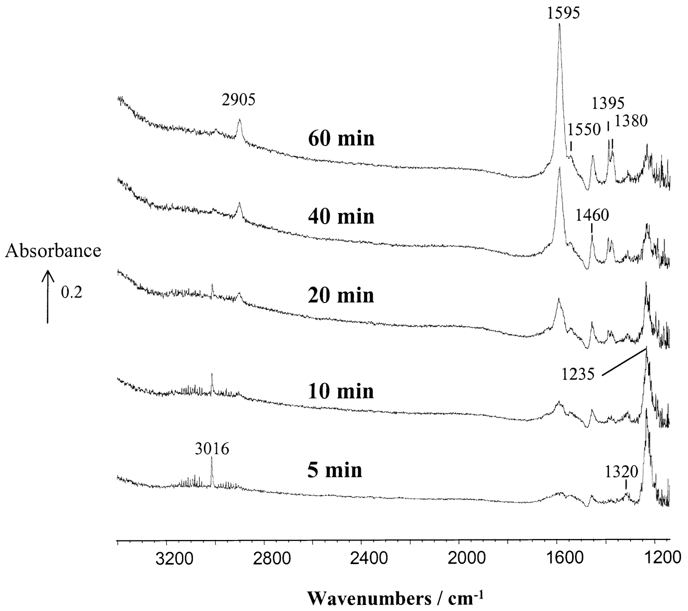

Fig. 11. In situ DRIFTS of γ-Al_2O_3 during the C_3H_6-SCR of NO at 300°C. The alumina was oxidised in situ in air at 630°C before introducing the reactive stream at 300°C. Feed: 0.05% NO+0.05% C_3H_6+2.5% O_2/Ar.

ca. 1380 cm^{-1} observed in the case of the sulphated sample could be attributed to the conversion of the corresponding sulphate bands present in the background spectrum (measured in dry argon) to a hydrogen sulphate species which is known to form in moist atmospheres such as that formed from reaction of the feed [60]. The latter species gave rise to a large and intense absorption band below 1300 cm^{-1} and made analysis of the spectra in this region impossible. Some CO_2 was observed at 300°C over the sulphated material compared with that at 400°C over the unsulphated material. This observation was in agreement with the somewhat higher activity for propene conversion at 300°C of the sulphated sample compared to that of the corresponding unsulphated material.

Neither isocyanate nor cyanide species could be observed on the sulphated sample at any temperature. At 300 and 400°C, the sulphated material exhibited, a band around 1600 cm^{-1} which could be associated with formate species but the very weak signal in the C–H stretch region and the masking of the 1395–1380 cm^{-1} region made this analysis inconclusive. The structure of the bands in the 1650–1500 cm^{-1} region at the three temperatures reported for both samples was complex. In addition to the signal due to the formates and carboxylate species (i.e. 1570+1460 cm^{-1}), several bands which could be assigned to nitrate species were observed. At 400 and 500°C, the intensity of these nitrate bands was much lower than that observed in the case of the unsulphated silver–alumina sample. At 500°C, the carboxylate bands were the predominant peaks present on the sulphated material and as in the case of the unsulphated sample, a band at 1650 cm^{-1} could also be observed.

4. Discussion

4.1. Formation of NO_2 during the C_3H_6-SCR of NO over promoted γ-Al_2O_3

Similar to the alumina and the unsulphated and sulphated 1.2% Ag/γ-Al_2O_3, the 0.4% Co/γ-Al_2O_3 exhibited a low activity for the oxidation of NO to NO_2 (Fig. 4). This behaviour contrasted with that of the 8% Co/γ-Al_2O_3 and 6% Co/SiO_2 samples which showed a high activity and reached equilibrium conversion at ca. 300°C (500°C in the case of the 8% Co/γ-Al_2O_3 calcined at 630°C). However, the former catalysts exhibited a high activity for the C_3H_6-SCR of NO (at

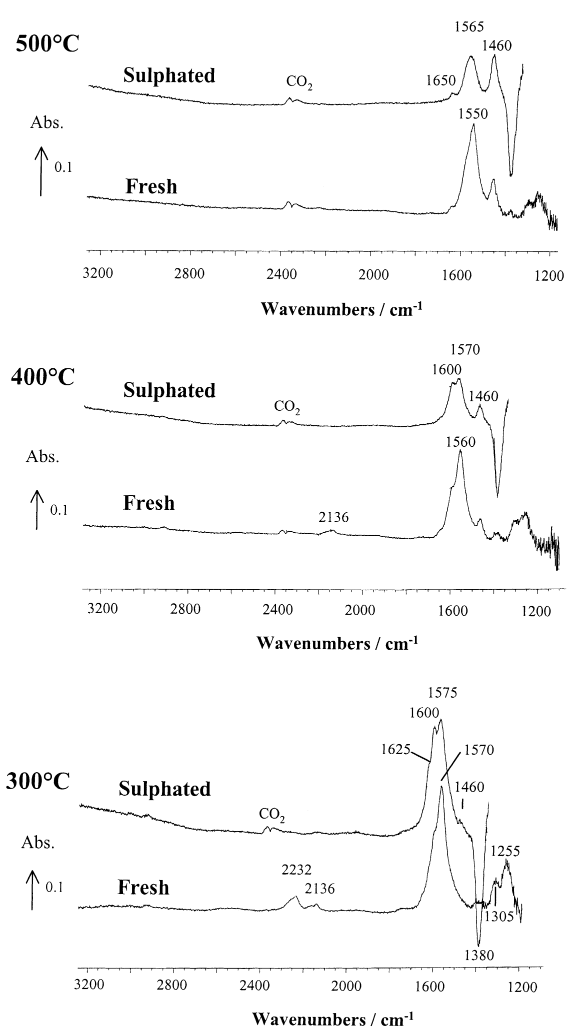

Fig. 12. In situ DRIFTS of 1.2% Ag/γ-Al_2O_3 and the corresponding sulphated material during the C_3H_6-SCR of NO. Feed: 0.05% NO+0.05% C_3H_6+2.5% O_2/Ar.

temperatures above 400°C, see Fig. 1), whereas the latter materials did not give any significant reduction of NO but were very active for the combustion of the reductant (not shown). The SCR data are in agreement with the findings of Hamada et al. [14] and Okazaki et al. [61] who showed that a lower cobalt loading and a higher catalyst calcination temperature favour the SCR reaction at the expense of the combustion of the reductant to give CO_2 and water. The active phase for the combustion of propene was attributed to Co_3O_4 and the active phase for the SCR was proposed to be dispersed Co^{2+} species (e.g. $CoAl_2O_4$ or isolated Co species) [15,16]. In our case, the high loading of cobalt on the alumina and silica probably favoured the formation of supported Co_3O_4 particles which were also active for the oxidation of NO to NO_2. The calcination of the alumina sample at the higher temperature probably converted part of the Co_3O_4 to the less active $CoAl_2O_4$. In contrast, the formation of a mixed oxide with silica seemed to have been less significant at the calcination temperatures used as only little difference in the catalytic activity occurred with changing calcination temperature. The nature of the cobalt phase of the 0.4% Co/γ-Al_2O_3 calcined at 630°C has not yet been elucidated and as a result it is not possible to confirm that the Co is in a dispersed state as opposed to Co_3O_4. Nevertheless, it is apparent that the active Co/γ-Al_2O_3 catalyst for the SCR reaction was a poor catalyst for the oxidation of NO_2.

The kinetic and thermodynamic data reported in this work showed that (as in the case of alumina, reported elsewhere [26,42]) the NO_2 observed during the C_3H_6-SCR of NO over the sulphated 1.2% Ag/γ-Al_2O_3 and the 0.4% Co/γ-Al_2O_3 were not formed through reaction (1). An oxidation mechanism based on reaction (1) could not allow the experimental NO_2/NO ratio to exceed the corresponding thermodynamic limit (see Fig. 3). A similar conclusion could probably be drawn for the case of the unsulphated 1.2% Ag/γ-Al_2O_3 although the offset of the experimental data with respect to the related thermodynamic value is closer to the experimental error. As suggested in the case of the alumina [42], a reaction mechanism allowing such high NO_2/NO ratios could be based on the formation and combustion of organo-nitrogen species by reaction of NO, C_3H_6 and O_2. Recent work in our laboratory [37] showed that the oxidation of *tert*-butyl nitrite (*tert*-butyl-O–N=O) over alumina yielded high selectivity to NO_2, contrary to the case of several organo-nitro compounds (R–NO_2) which preferably formed NH_3. It is interesting to notice that NO_2/NO ratios higher than that predicted by thermodynamics were also observed in the case of homogeneous reactions involving typical de-NO_x feed [62]. Other authors suggested that the formation of organo-nitrito intermediates played a key role in the homogeneous partial oxidation of hydrocarbons in the presence of NO [63,64]. In view of these reports, we propose that the formation of NO_2 during the C_3H_6-SCR of NO over the alumina-based catalysts reported here probably involved the formation and combustion of organo-nitrito species, possibly via some gas-phase reactions.

Previous in situ IR work over silver–alumina catalysts [24,26] suggested that a band observed at ca. $1650\,cm^{-1}$ during the C_3H_6-SCR of NO could be attributed to an organo-nitrito compounds. However, the present in situ IR study showed that a band at a similar wave number could also be obtained under an $O_2+C_3H_6$ flow, showing that in this case the band could not be attributable solely to organo-nitrogen species. Therefore, additional work is needed (e.g. IR study using ^{15}N [33,34]) to assess whether or not the species absorbing at ca. $1650\,cm^{-1}$ formed in course of the SCR reaction was an organo-nitrite.

4.2. Reaction mechanism model of the C_3H_6-SCR of NO over promoted γ-Al_2O_3

In the case of transition metal oxides supported on alumina, the role of strongly bound nitrate species (i.e. ad-NO_x) as possible intermediates of the SCR reaction has been suggested [65]. Spectrokinetic analyses over alumina showed that the rate of consumption of nitrates was similar to that of the formation of N_2 [54]; in this study, the authors also reported that the nitrates were reacting with partially oxidised hydrocarbons such as acetates. The presence of reduced species of nitrogen in the gas-phase (e.g. NH_3) or at the catalyst surface (e.g. –NCO over the unsulphated silver–alumina) was evident in the results presented here. It is interesting to notice that NH_3 could only be observed when the concentration of NO_2 was low and vice versa (see Figs. 1 and 2 or Ref. [26]).

Fig. 13 gives a schematic representation of a proposed reaction mechanism for the SCR of NO by propene over cobalt- and silver-promoted alumina catalysts. This model is based on the results of experiments described in this paper and on observations made concerning the intermediary [66] and reactivity of organo-nitrogen compounds. One of the crucial roles of O_2 is to react with NO and the reductant to form various surface ad-NO_x (x>1) species and par-

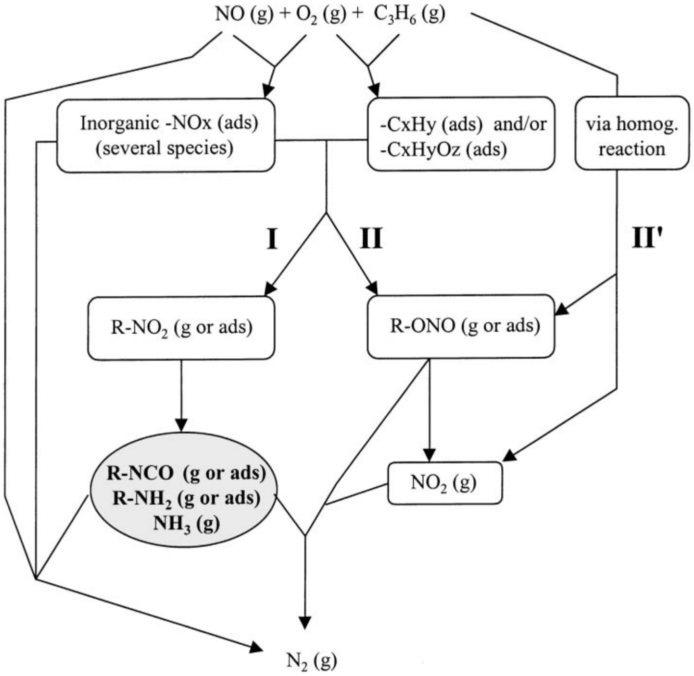

Fig. 13. Simplified reaction scheme of the C_3H_6-SCR of NO over γ-Al_2O_3 and the low loading Ag and Co/γ-Al_2O_3 giving the nature of the different species likely to be involved. It is proposed that the reduction to N_2 occurs through the reaction of oxidised and reduced (species in shaded circle) nitrogen compounds.

tially oxidised hydrocarbons [54]. One of the promoting roles of silver [26] and cobalt would be to favour these oxidation steps (but not primarily NO to NO_2 as proposed in Ref. [14,15]). These species could then react according to two distinct routes. Firstly (route I), organo-nitro species (R–NO_2) would be formed and would subsequently react/decompose over the catalyst to give rise to isocyanates, amino-groups and finally ammonia [35–40,67]. Secondly (route II), organo-nitrito compounds would be formed and would subsequently be oxidised to NO_2 [37]. In addition to route II, the formation of NO_2 via homogeneous reaction, possibly triggered by the catalyst surface, could not be excluded (route II′) [62]. Eventually, the reduced forms of nitrogen formed from route I (–NCO, R–NH_2 and NH_3) would react with the oxidised forms of nitrogen (e.g. organo-nitrito or NO_2) to yield N_2 [24,68,69]. In addition, the reduced forms of nitrogen could also react directly with NO or the inorganic ad-NO_x to yield N_2 [24].

4.3. Effect of the sulphation on the SCR activity of the 1.2% Ag/γ-Al_2O_3

The selectivities to N_2, NO_2, N_2O and NH_3 of the kinetic data obtained for the C_3H_6-SCR of NO over the sulphated and unsulphated 1.2% Ag/γ-Al_2O_3 were similar (see Figs. 1 and 2). The main difference was a shift of ca. 50°C towards higher temperatures of the plots associated with the sulphated sample compared to that of the unsulphated material. The in situ IR data showed that the concentration of ad-NO_x species was significantly lower on the sulphated catalyst when compared to the unsulphated sample at the temperatures at which the SCR reaction was operating (i.e. $T \geq 400°C$) (Fig. 12). Two main reasons could explain these findings; firstly, Burch et al. [8] reported that the sulphation of alumina reduced the numbers of strong chemisorption sites for NO_x species. Secondly, earlier work showed that one of the role of silver was to promote the oxidation of NO to ad-NO_x species [26,32] and this work (Fig. 5) showed that the sulphated silver was less active for this reaction. Therefore, the lower SCR activity observed on our sulphated Ag/γ-Al_2O_3 could be attributed to the loss of some of the adsorption sites for NO_x and/or the lower activity of sulphated silver for the oxidation of NO to ad-NO_x species.

While high concentrations of NH_3 (probably derived from isocyanates) could be observed during the SCR over the sulphated sample, no isocyanate species could be evidenced by in situ IR at any temperature on this sample, this being in contrast to the unsulphated material at 300°C. The isocyanate groups observed over the unsulphated sample could have arisen from one of the ad-NO_x species that was not present over the sulphated form of the sample at this temperature. It has to be stressed that the –NCO species were observed over the unsulphated material only at a temperature at which the catalyst showed no significant activity (i.e. 300°C). This fact stresses that such species were highly reactive at higher temperatures and the corresponding surface coverage was probably too low to allow detection. It is possible that isocyanate species were not detected over the sulphated sample simply because the species were only present in detectable quantities over a narrow temperature range (less than the 100°C intervals at which DRIFTS spectra were recorded).

The determination of the nature of the adsorption sites of the isocyanate species (i.e. two main bands at 2250 and 2230 cm^{-1}) over our silver–alumina catalyst is difficult. Over a 5% Ag/γ-Al_2O_3, Sumiya et al. [24] reported two bands at 2260 and 2230 cm^{-1} which were suggested to be that of –NCO species located on the γ-Al_2O_3 and the silver phase, respectively. This assignment is in agreement with the data of Solymosi and Bansagi [57] reporting the asymmetric vibration of –NCO over γ-Al_2O_3 at higher wave numbers, i.e. ca. 2260 cm^{-1}. However, Anderson et al. [18] proposed that bands at 2261 and 2241 cm^{-1} could be associated with –NCO species on the alumina. Other results showed that the adsorption of cyclohexyl isocyanate over alumina lead to a broad band at 2228 cm^{-1} [37]. These reports stress the need for further investigations on the location/wave numbers of –NCO groups over these materials.

4.4. Differences in the promotion of γ-Al_2O_3 by Ag or Co

The 1.2% Ag/γ-Al_2O_3 and 0.4% Co/γ-Al_2O_3 catalysts reported in this work gave similar propene conversions and yields of N_2 as a function of temperature (Fig. 1). However, the cobalt-promoted material yielded significantly more NO_2 than the Ag-sample but no NH_3 was detected. At temperatures ≥400°C (i.e. temperatures at which a significant SCR activity was observed), the nature of the surface species observed by in situ DRIFT of the Co-sample (Fig. 10) were markedly different from those observed on the Ag-material (Fig. 9). Significantly lower concentrations of nitrate species were detected on the Co sample, similar to the case of the unpromoted alumina [26].

Although this data appears contradictory at first sight, the facts described above can be rationalised by taking into account the model proposed here (Fig. 13) and other IR data. In the case of the C_3H_6-SCR of NO_2 over alumina [26], both nitrates and formates could be observed by DRIFTS at 300°C, before the light off of the SCR reaction occurred between 300 and 400°C. However, only the formate species could be observed at $T \geq 400°C$, in spite of the presence of NO_2 (and O_2) in the feed. Therefore at the temperatures at which the SCR proceeded, the consumption rate of the inorganic ad-NO_x species was significantly higher than the rate of their formation. A similar conclusion could be made for the 0.4% Co/γ-Al_2O_3 during the C_3H_6-SCR of NO. This assumption is supported by the fact that the cobalt sample appeared to be significantly less active for the formation of ad-NO_x species than both the alumina and the silver-promoted alumina (Fig. 5).

The reaction between NO_2 and NH_3 (yielding N_2 [68]) was probably fast over the catalysts reported here, this was evident from the fact that when NO_2 was detected NH_3 was not and vice-versa (Figs. 1 and 2). During the C_3H_6-SCR of NO over 0.4% Co/γ-Al_2O_3, the reaction rates of routes II and II′ (leading to NO_2) were probably higher than that of route I (leading to NH_3) (Fig. 13). This hypothesis would explain the fact that no NH_3 could be observed in this case (Fig. 1), as the proportion of oxidised nitrogen species produced was always greater than that of reduced species. Therefore, a large concentration of NO_2 remained unreacted, this eventually decomposing back to NO and O_2 [26]. Overall, the promoting effect of cobalt could possibly be explained by an increased rate of the conversion of the reductant to an intermediate species such as an oxygenated compound which would subsequently form an organo-nitrito by reaction with ad-NO_x species. In the case of the alumina and the unsulphated and sulphated 1.2% Ag/γ-Al_2O_3, the rate of route I was probably greater than that of routes II–II′ at the temperatures corresponding to the maximum of N_2 and NH_3 yields (these temperatures being approximately equal), as no NO_2 could be observed at this point. However, it has to be acknowledged that the reduced nitrogen species such as NH_3 or –NCO could also directly react with the NO or ad-NO_x species to form N_2 and this further complicates quantitative analyses of such a reaction scheme.

The transient DRIFT data obtained over the alumina (Fig. 11) suggested that the ad-NO_x species and the formates were adsorbed on the same type of sites. The fact that the 1.2% Ag/γ-Al_2O_3 exhibited significantly higher concentrations of ad-NO_x species and lower concentrations of formates as compared to the cases of the Co-sample could be related to a higher formation rate and/or a higher stability of all or some of the ad-NO_x over the Ag-material. Bulk silver nitrate ($AgNO_3$) is a very stable compound and only decomposes at ca. 440°C [30]. The threefold higher loading of the silver material compared to cobalt would also favour the spill-over of the nitrates from the silver onto the alumina. It should also be emphasised that various inorganic nitrites and at least two different types of nitrates were present over these alumina-based materials and that the reactivity of these ad-NO_x species was probably different.

The simplified reaction model presented in Fig. 13 could probably be applied to numerous other transition metal oxides supported on alumina and other non-reducible oxides. However, it has to be stressed that each of the reaction steps (symbolised by an arrow) could have different rates over different materials and therefore the nature of the side-products and surface species coverages would vary from one promoter to another. The rate determining step could also be different in each case, and could also vary with temperature and/or other experimental conditions for a given catalyst.

5. Conclusions

It was shown that the initial step of the C_3H_6-SCR of NO over a 0.4% Co/γ-Al_2O_3 was not the oxidation of NO to NO_2. The high concentration of NO_2 observed during the course of the reaction was produced via another route, possibly via the combustion of organo-nitrito compounds. A similar conclusion could be drawn for a sulphated 1.2% Ag/γ-Al_2O_3 material. Over these samples and the parent materials, nitric oxide was probably first reacted to form strongly bound inorganic ad-NO_x species such as nitrites and nitrates. It is suggested that the ad-NO_x species reacted with the reductant and derived species to form both organo-nitro and organo-nitrito compounds, the reaction products of which combined to yield N_2. However, the assignment of the IR bands observed in situ (e.g. that at ca. $1650\,cm^{-1}$) to organo-nitrogen compounds could not be unequivocally made in the present study. The sulphation of the 1.2% Ag/γ-Al_2O_3 reduced the surface concentration of strongly bound ad-NO_x species, probably by decreasing both the number of adsorption sites available to NO_x and the oxidation activity of the silver promoter. A global C_3H_6-SCR of NO reaction scheme was proposed which accounts for the various side-products and surface species observed on the different samples.

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References

[1] Y. Kintaichi, H. Hamada, M. Tabata, T. Yoshinari, M. Sasaki, T. Ito, Catal. Lett. 6 (1990) 239.
[2] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, Appl. Catal. 75 (1991) L1.
[3] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, T. Yoshinari, Appl. Catal. A 88 (1992) L1.
[4] H. Hamada, Y. Kintaichi, M. Sasaki, M. Tabata, T. Ito, T. Yoshinari, Catal. Today 17 (1993) 111.
[5] H. Hamada, Catal. Today 22 (1994) 21.
[6] M. Tabata, H. Tsuchida, K. Miyamoto, T. Yoshinari, H. Yamazaki, H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, Appl. Catal. B 6 (1995) 169.
[7] K. Masuda, K. Tsujimura, K. Shioda, T. Kato, Appl. Catal. B 8 (1996) 33.
[8] R. Burch, E. Halpin, J.A. Sullivan, Appl. Catal. B 17 (1998) 115.
[9] R. Burch, T.C. Watling, Appl. Catal. B 11 (1997) 207.
[10] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno, H. Obuchi, Appl. Catal. B 2 (1993) 71.
[11] R. Burch, P.J. Millington, A.P. Walker, Appl. Catal. B 4 (1994) 65.
[12] T. Miyadera, Appl. Catal. B 2 (1993) 199.
[13] K.A. Bethke, H.H. Kung, J. Catal. 172 (1997) 93.
[14] H. Hamada, Y. Kintaichi, M. Inaba, M. Tabata, T. Yoshinari, H. Tsuchida, Catal. Today 29 (1996) 53.
[15] N. Okazaki, S. Tsuda, Y. Shiina, A. Tada, Chem. Lett. (1998) 51.
[16] J. Yan, M.C. Kung, W.M.H. Sachtler, H.H. Kung, J. Catal. 172 (1997) 178.
[17] F. Radtke, R.A. Koeppel, E.G. Minardi, A. Baiker, J. Catal. 167 (1997) 127.
[18] J.A. Anderson, C. Marquez-Alvarez, M.J. Lopez-Munoz, I. Rodriguez-Ramos, A. Guerrero-Ruiz, Appl. Catal. B 14 (1997) 189.
[19] R. Burch, J.A. Sullivan, T.C. Watling, Catal. Today 42 (1998) 13.
[20] F. Acke, M. Skoglundh, Appl. Catal. B 22 (1999) L1.
[21] R. Burch, P. Fornasiero, T.C. Watling, J. Catal. 176 (1998) 204.
[22] H.W. Jen, Catal. Today 42 (1998) 37.
[23] E. Seker, J. Cavataio, E. Gulari, P. Lorpongpaiboon, S. Osuwan, Appl. Catal. B 183 (1999) 121.
[24] S. Sumiya, H. He, A. Abe, N. Takezawa, K. Yoshida, J. Chem. Soc., Faraday. Trans. 94 (1998) 2217.
[25] K. Takagi, T. Kobayashi, H. Ohkita, T. Mizushima, N. Kakuta, A. Abe, K. Yoshida, Catal. Today 45 (1998) 123.
[26] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, J. Catal. 187 (1999) 493.
[27] A. Abe, N. Aoyama, S. Sumiya, N. Kakuta, K. Yoshida, Catal. Lett. 55 (1998) 211.
[28] S. Kameoka, T. Chafik, Y. Ukisu, T. Miyadera, Catal. Lett. 51 (1998) 11.
[29] S. Sumiya, M. Saito, H. Fe, Q.C. Feng, N. Takezawa, K. Yoshida, Catal. Lett. 50 (1998) 87.
[30] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 77th Edition, CRC Press, Boca Raton, 1996.
[31] A. Abe, N. Aoyama, S. Sumiya, N. Kakuta, K. Yoshida, Catal. Lett. 51 (1998) 5.
[32] F.C. Meunier, J.R.H. Ross, Appl. Catal. B 24 (1999) 23.
[33] M. Haneda, Y. Kintaichi, M. Iniba, H. Hamada, Catal. Today 42 (1998) 127.
[34] T. Tanaka, T. Okhuhara, M. Misono, Appl. Catal. B 4 (1994) L1.
[35] G. Centi, A. Galli, S. Perathoner, J. Chem. Soc., Faraday Trans. 94 (1996) 5129.
[36] M. Yamaguchi, J. Chem. Soc., Faraday Trans. 93 (1997) 3581.
[37] V. Zuzaniuk, F.C. Meunier, J.R.H. Ross, J. Chem. Soc., Chem. Commun. (1999) 815.
[38] N.W. Cant, A.D. Cowan, A. Doughty, B.S. Haynes, P.S. Nelson, Catal. Lett. 46 (1997) 212.
[39] E.A. Lombardo, G.A. Sill, J.L. d‘Itri, W.K. Hall, J. Catal. 173 (1998) 440.
[40] A. Obuchi, C. Wogerbauer, R. Koppel, A. Baiker, Appl. Catal. B 19 (1998) 9.

[41] J.Y. Yan, H.H. Kung, W.M.H. Sachtler, M.C. Kung, J. Catal. 175 (1998) 294.

[42] F.C. Meunier, J.P. Breen, J.R.H. Ross, J. Chem. Soc., Chem. Commun. (1999) 259.

[43] N.D. Parkyns, Proceedings of the Fifth International Conference on Catalysis, Vol. 12, 1972, p. 255.

[44] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Edition, Wiley/Interscience, New York, 1986.

[45] M. Schraml-Marth, A. Wokaun, A. Baiker, J. Catal. 138 (1992) 3069.

[46] W.S. Kijlstra, D.S. Brands, E.K. Poels, A. Bliek, J. Catal. 171 (1997) 208.

[47] J.A. Anderson, C.H. Rochester, J. Chem. Soc., Faraday Trans. 1 85 (1989) 1117.

[48] G. Busca, G. Ramis, V. Lorenzelli, A. Janin, J.C. Lavalley, Spectrochim. Acta 43A (1987) 489.

[49] S. Bodoardo, R. Chiappetta, F. Fajula, E. Garrone, Micropor. Mater. 3 (1995) 613.

[50] V.A. Mathyshak, O.V. Krylov, Catal. Today 25 (1995) 1.

[51] A. Obuchi, A. Ogata, K. Mizuno, A. Ohi, M. Nakamura, H. Ohuchi, J. Chem. Soc., Chem. Commun. (1992) 247.

[52] A. Obuchi, A. Ogata, K. Mizuno, A. Ohi, H. Ohuchi, Stud. Surf. Sci. Catal. 77 (1993) 333–336.

[53] C. Rottlander, R. Andorf, C. Plog, B. Krutzsch, M. Baerns, Appl. Catal. B 11 (1996) 49.

[54] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, J. Phys. Chem. B 103 (1999) 5240.

[55] G. Busca, J. Lamotte, J.C. Lavalley, V. Lorenzelli, J. Am. Chem. Soc. 109 (1987) 5197.

[56] M.L. Unland, J. Catal. 31 (1973) 459.

[57] F. Solymosi, T. Bansagi, J. Catal. 156 (1995) 75.

[58] B.A. Morrow, M.I. Baraton, Y. Lijour, J.L. Roustan, Spectrochim. Acta 43A (1987) 1583.

[59] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, Boston, 1990, p. 448.

[60] M. Waqif, O. Saur, J.C. Lavalley, S. Perathoner, G. Centi, J. Phys. Chem. 95 (1991) 4051.

[61] N. Okazaki, Y. Katoh, Y. Shiina, A. Tada, M. Iwamoto, Chem. Lett. (1998) 889.

[62] J. Smith, J. Phillips, A. Graham, R. Steele, A. Redondo, J. Coons, J. Phys. Chem. A 101 (1997) 9157.

[63] K. Otsuka, R. Takahashi, K. Amakawa, I. Yamanaka, J. Catal. 185 (1999) 182.

[64] K. Otsuka, R. Takahashi, I. Yamanaka, Catal. Today 45 (1998) 23.

[65] V.A. Sadykov, S.L. Baron, V.A. Matyshak, G.M. Alikina, R.V. Bunina, A.Ya. Rozovski, V.V. Lunin, E.V. Lunina, A.N. Kharlanov, A.S. Ivanova, S.A. Veniaminov, Catal. Lett. 37 (1996) 157.

[66] C. Yokoyama, M. Misono, J. Catal. 150 (1994) 9.

[67] F. Poignant, J. Saussey, J.C. Lavalley, G. Mabilon, Catal. Today 29 (1996) 93.

[68] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.

[69] S. Kameoka, T. Chafik, Y. Ukisu, T. Miyadera, Catal. Lett. 55 (1998) 211.