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Influence of NH_3 and NO oxidation on the SCR reaction mechanism on copper/nickel and vanadium oxide catalysts supported on alumina and titania

Silvia Suárez[a,1], Seong Moon Jung[b,2], Pedro Avila[a,1],
Paul Grange[b,2], Jesús Blanco[a,*]

[a] Instituto de Catálisis y Petroleoquímica, CSIC, Camino de Valdelatas s/n, 28049 Madrid, Spain
[b] Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain,
Croix du Sud 2/17, B1348 Louvain-la-Neuve, Belgium

Abstract

The influence of ammonia and nitric oxide oxidation on the selective catalytic reduction (SCR) of NO by ammonia with copper/nickel and vanadium oxide catalysts, supported on titania or alumina have been investigated, paying special attention to N_2O formation. In the SCR reaction, the VTi catalyst had a higher activity than VAl at low temperatures, while the CuNiAl catalyst had a higher activity than CuNiTi. A linear relationship between the reaction rate of ammonia oxidation and the initial reduction temperature of the catalysts obtained by H_2-TPR showed that the formation rate of NH species in copper/nickel catalysts would be higher than in vanadia catalysts. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) showed that copper/nickel catalysts presented ammonia coordinated on Lewis acid sites, whereas ammonium ion adsorbed on Brønsted acid sites dominated on vanadia catalysts. The NO oxidation experiments revealed that copper/nickel catalysts had an increase of the NO_2 and N_2O concentrations with the temperature. NO could be adsorbed on copper/nickel catalysts and the NO_2 intermediate species could play an important role in the reaction mechanism. It was suggested that the presence of adsorbed NO_2 species could be related to the N_2O formation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: SCR; NH_3 oxidation; NO oxidation; Copper–nickel oxide; Vanadium oxide; Nitrous oxide

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1. Introduction

The selective catalytic reduction (SCR) of NO_x with ammonia has been extensively studied as a catalytic technology for NO_x elimination from stationary sources [1]. Nevertheless, there is still an open discussion concerning the chemical and mechanistic aspects involved in this process, mainly those related with N_2O formation. The superiority of NH_3 as a reductant for the SCR reaction is due to the fact that all other reducing agents are susceptible to oxidation by O_2 instead of reacting with NO_x [2].

A great number of catalysts systems have been investigated for this reaction, for example supported noble metals and supported Fe_2O_3 or Cr_2O_3. But for industrial applications copper [3,4] and vanadium supported catalysts have shown excellent results

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[*] Corresponding author. Tel.: +34-91-585-48-02;
fax: +34-91-585-47-89.
E-mail addresses: grange@cata.ucl.ac.be (P. Grange),
jblanco@icp.csic.es (J. Blanco).
[1] Tel.: +34-91-585-48-80; fax: +34-91-585-48-60.
[2] Tel.: +32-10-47-36-48; fax: +32-10-47-36-49.

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[5–7]. The addition of small quantities of NiO to CuO/Al_2O_3 catalysts enhance the segregation of copper on the surface and the Ni^{2+} leads to a Cu^{2+} redistribution with an increase in the tetrahedral site population by Cu^{2+} [8]. Thus, copper/nickel alumina catalysts have shown superior performances in NO_x elimination from the tail gas in nitric acid plants [3,9,10].

When SO_2 is present in the flue gas from power generation units, sulphur resistance is among the catalysts requirements, and titania (anatase) is used extensively as a support due to its resistance to sulphur oxide poisoning [11]. Another widely used support is γ-alumina due to the high surface area compared with TiO_2.

Two types of reaction mechanisms have been proposed in the literature over these catalytic systems namely Eley–Rideal and Langmuir–Hinshelwood. The Eley–Rideal type process does not involve strongly adsorbed NO species [12], whereas in the Langmuir–Hinshelwood mechanism adsorbed NO is suggested to play an important role in the reaction [13].

In a previous paper [14], the performance of copper/nickel and vanadium catalysts in a monolithic form supported on titania (anatase) and γ-alumina, at low temperature 180–230 °C for different NO/NO_x and NH_3/NO_x ratios was studied. The operation conditions selected for the catalytic activity measurement were close to those found for lower pressure nitric acid plants tail gases. For this application, where SO_2 is not present, vanadium content can be higher, obtaining a more active catalyst for NO_x elimination at lower temperature [6,15].

The aim of this work was to clarify the influence of ammonia and nitric oxide, oxidation on the SCR of NO by ammonia on these catalytic systems, using powder samples and operating in a wider temperature range (180–450 °C). To obtain more information about the behaviour of these systems, H_2-TPR, NH_3-TPD and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) NH_3 oxidation experiments were carried out.

2. Experimental

2.1. Catalysts preparation

Copper/nickel (CuNiAl, CuNiTi), and vanadium oxide (VTi, VAl) monolithic catalysts were prepared as described elsewhere [14]. Monolithic supports based on titania and alumina with natural silicates as binders, were manufactured in our laboratories by extrusion. After heat treatment of the support, the catalysts were prepared by impregnation of the monoliths with aqueous solutions of copper nitrate, nickel nitrate or vanadyl sulphate. The monolithic catalysts were crushed in order to carry out the catalyst characterisation and activity measurements. The particle size used for catalytic activity measurement was between 75 and 100 μm.

2.2. Catalysts characterisation

The copper, nickel and vanadium contents were determined by inductively coupled plasma (ICP) optical emission spectroscopy (Perkin-Elmer Optima 3300DV) of dissolutions of the ground catalysts in acid solutions. The compositions of the catalysts are shown in Table 1, which have been selected taking into account the results obtained in preliminary studies.

Surface areas were measured by nitrogen adsorption/desorption. These were determined using a Micromeritic 1320 ASAP, outgassing the samples overnight at 250 °C to a vacuum of $<10^{-4}$ Torr to ensure a dry clean surface.

Table 1
Catalysts composition, surface area and NH_3 adsorbed

Name	Active phase	Support	Content (wt.%)	BET area ($m^2\,g^{-1}$)	NH_3 ($\mu mol\,m^{-2}$)
CuNiAl	CuO/NiO	Al_2O_3	6.4/0.6	157	2.3
VAl	V_2O_5	Al_2O_3	5.5	135	3.3
CuNiTi	CuO/NiO	TiO_2	1.7/0.2	108	2.0
VTi	V_2O_5	TiO_2	5.1	55	5.1

The catalyst reducibility was studied by H_2-TPR using 0.15 g of sample and a total flow of 45 ml min^{-1}. After cleaning the surface with He flow from r.t. to 500 °C and cooling down, a dilute hydrogen in inert gas mixture (5 vol.% H_2:N_2) was incorporated in the feed, monitoring hydrogen consumption with a TCD detector increasing the temperature from r.t. to 500 °C at a rate of 10 °C min^{-1}.

The quantity of adsorbed ammonia on the catalysts was measured by NH_3-TPD using 0.15 g of sample and a total flow of 50 ml min^{-1}. After ammonia adsorption on the catalysts at 25 °C during 30 min, ammonia was removed from the system using He during 120 min until no ammonia was detected. Then, the temperature was increased in He gas to 500 °C at a rate of 10 °C min^{-1}. A boric acid solution of 0.05 M was introduced in the reactor outlet to trap the desorbed ammonia. Afterwards, the solution was titrated with a sulphuric acid solution of 0.005 M, using an ammonia indicator. The quantities of ammonia adsorbed per square metre for the catalysts are collated in Table 1.

In situ DRIFTS spectra were collected in a Brucker IFS88 infrared spectrometer with KBr optics and a DTGS detector. Pure samples were placed inside a commercial controlled environment chamber (Spectra-Tech 0030.103) attached to a diffuse reflectance accessory (Spectra-Tech collector). Samples were heated from r.t. to 500 °C under 30 ml min^{-1} He flow to eliminate any adsorbed water. After cooling to r.t., NH_3 (1000 ppm), O_2 (2.5%) and He (balance) were introduced to the cell and the temperature was increased at a rate of 10 °C min^{-1}, obtaining spectra (200 scans for every 4 cm^{-1}) at 180 and 300 °C after stabilisation for 30 min.

2.3. Catalytic activity measurements

Ammonia and nitric oxide oxidation as well as SCR reactions, were carried out in a continuous flow fixed bed reactor, operating at atmospheric pressure, in a vertical quartz reactor. The inlet and outlet gas compositions were measured using a quadrupole mass spectrometer QMC 311 Balzers coupled to the reactor.

In all cases, temperature treatment in He from r.t. to 500 °C was carried out to clean the catalyst surface from impurities or absorbed water. After cooling down to 180 °C, the gases were introduced to the reactor and the temperature was increased at a rate of 10 °C min^{-1}, remaining 30 min at each temperature to ensure a steady state.

The operating conditions for the experiments were: total flow $F = 100$ ml min^{-1}, GHSV (NTP) $=$ 15,000 h^{-1}, $P = 1$ atm, $T = 180$–450 °C. The gas inlet composition for ammonia oxidation was: $[NH_3] =$ 1000 ppm, $[O_2] = 3$ vol.%, [He]: balance. For nitric oxide oxidation the gas composition was the same but using [NO] $=$ 1000 ppm instead of NH_3. In the case of SCR reaction $[NH_3] = 1000$ ppm, [NO] $= 1000$ ppm, $[O_2] = 3$ vol.% and [He]: balance were used.

3. Results and discussion

3.1. SCR results

The variations of the NO conversion and the N_2O outlet as a function of the temperature are shown in Fig. 1 for all samples. VTi catalyst had higher activity than VAl at temperatures lower than 300 °C, while CuNiAl catalyst had higher activity than CuNiTi over the whole temperature range. VAl catalysts maintains activity near to 95% even at 400 °C. N_2O formation during SCR reaction was detected at temperatures above 300 °C for all the catalysts except for CuNiTi, where

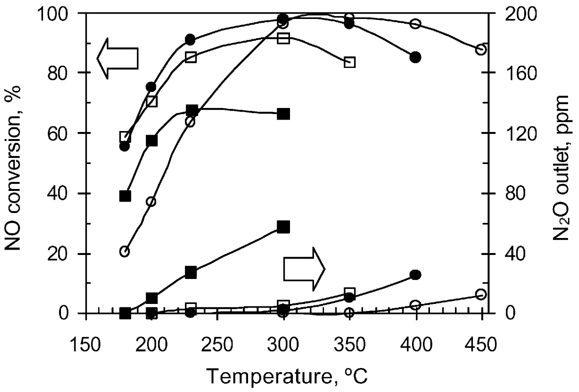

Fig. 1. NO conversion and N_2O formation as a function of the operating temperature for: (○) VAl; (●) VTi; (□) CuNiAl; (■) CuNiTi catalysts. Feed compositions: $[NH_3] = 1000$ ppm, [NO] $= 1000$ ppm, $[O_2] = 3$ vol.%, [He]: balance. Operating conditions: total flow $F = 100$ ml min^{-1}, GHSV (NTP) $= 15{,}000$ h^{-1}, $P = 1$ atm.

N_2O started to be formed at 200 °C reaching a N_2O formation around 60 ppm at 300 °C.

All catalysts displayed a decrease of NO conversion due to the ammonia oxidation reaction: on CuNiTi the activity decrease started at 240 °C, on CuNiAl at 300 °C, on VTi at 330 °C and on VAl at 380 °C. These observations were in agreement with the ammonia oxidation results (Fig. 2a) and corresponded to the point at which 50% of ammonia conversion was reached.

3.2. NH_3 oxidation results

The variation of the NH_3 conversion, and the N_2O, NO formed during reaction as a function of the temperature are represented in Fig. 2a, b, and c, respectively, for all the catalysts. With the same active phase, supports based on titania favour ammonia oxidation at lower temperature and with the same support, CuNi oxides increase the ammonia reaction rate at lower temperatures. In fact, at 280 °C CuNi catalyst had an NH_3 conversion near to 90%. These results were in agreement with the literature where copper-containing catalysts are well known to be active in oxidation reactions [16].

In Fig. 2b, N_2O formation increased with temperature during ammonia oxidation reaction. This indicated that the ammonia was mainly oxidised to N_2 (Eq. (1)), but also a small quantity of ammonia was oxidised to N_2O according to Eq. 2

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (1)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (2)$$

In Fig. 2c, the NO formation is represented as a function of the temperature. The NO was formed at relatively high temperature compared with N_2O. The NO formed could be explained by ammonia oxidation reaction (Eq. (3)) or nitrous oxide oxidation to a higher oxidation state (Eq. (4)):

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (3)$$

$$N_2O + \tfrac{1}{2}O_2 \rightarrow 2NO \qquad (4)$$

When the ammonia oxidation reaction rate was plotted as a function of the initial reduction temperature of the catalysts, obtained by H_2-TPR, a relationship between the catalyst reducibility and the reaction rate was observed. Moreover, it can be noticed that the onset temperature of reduction by hydrogen influenced the activation of ammonia. The different reducibility between CuNi catalysts and V-based catalysts was directly related to ammonia oxidation (Fig. 3).

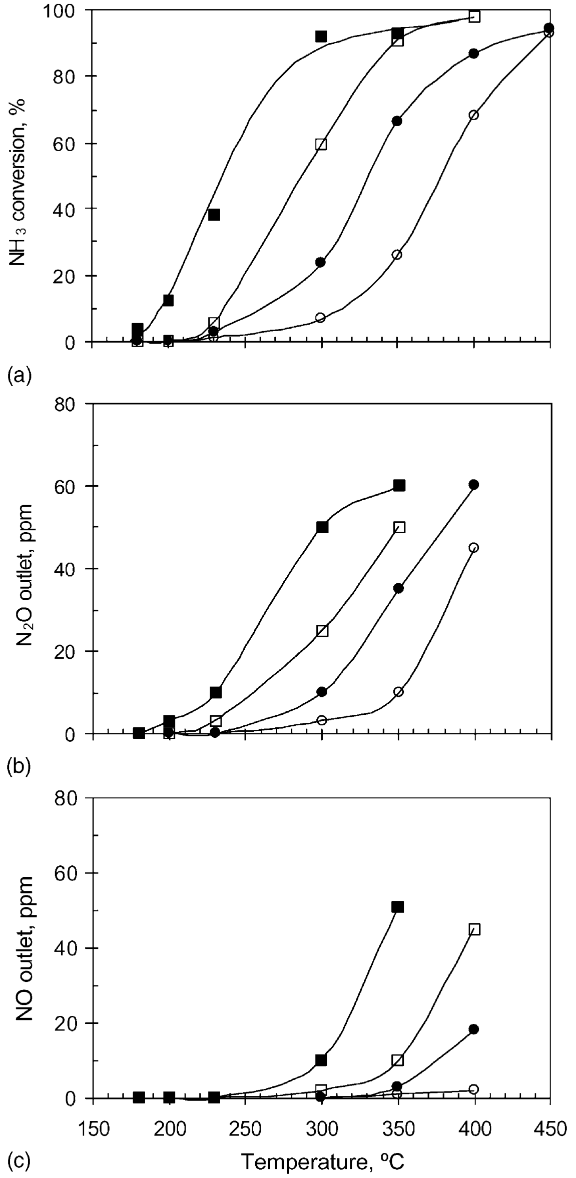

Fig. 2. (a) NH_3 conversion; (b) N_2O formation; (c) NO formation as a function of the operating temperature: (■) CuNiTi; (□) CuNiAl; (●) VTi; (○) VAl. Feed compositions: $[NH_3] = 1000$ ppm, $[O_2] = 3$ vol.%, [He]: balance. Operating conditions: total flow $F = 100\,\mathrm{ml\,min^{-1}}$, GHSV (NTP) $= 15{,}000\,\mathrm{h^{-1}}$, $P = 1$ atm.

Studies carried out by Zawasdki [17] and more recently by Germain and Perez [18] proposed the key

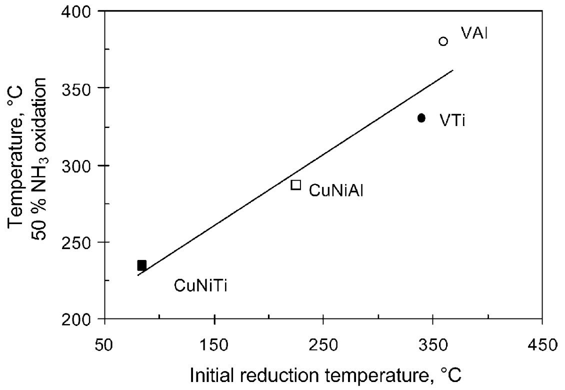

Fig. 3. Temperature at which 50% NH_3 is oxidised as a function of the initial reduction temperature: (■) CuNiTi; (□) CuNiAl; (●) VTi; (○) VAl.

role of NH and NHO species in ammonia oxidation over transition metal oxides. These authors suggested that these species could react with each other giving rise to N_2, N_2O as well as react with molecular oxygen to give NO.

Due to the strong reducibility of copper/nickel catalysts as compared with vanadia catalysts, the formation rate of NH, NHO species over the former would be higher than in the latter, explaining the N_2O and NO formation during the ammonia oxidation reaction. Indeed, at relatively low temperatures ($T = 250\,^{\circ}C$), CuNi catalysts present an appreciable conversion of ammonia to N_2O.

The data of the quantity of ammonia adsorbed on the catalysts calculated by NH_3-TPD are collated in Table 1. A relation between the quantity of ammonia absorbed and the NH_3 reaction rate during NH_3 oxidation was not found. However, VTi catalyst presented higher amounts of NH_3 absorbed per square metre and displayed better NO conversion during SCR reaction in the temperature range 180–300 °C.

The spectra obtained at 180 and 300 °C by in situ DRIFTS during NH_3 oxidation experiments for CuNiTi, CuNiAl, VTi and VAl catalysts are shown in Fig. 4a and b, respectively.

The four bands detected at 3740, 3670, 3585 and 3520 cm^{-1} were assigned to the magnesium silicates of the binder. According to literature, the bands at 3740 and 3670 cm^{-1} correspond to Si–OH and $(Mg)_3OH$ groups, respectively [19], whereas the bands at 3585 and 3520 cm^{-1} represent the asymmetric and symmetric vibration of water due to the easy rehydration of the supports [20,21].

In general, the relative intensity of the peaks due to NH_3 absorbed at 300 °C were lower than at 180 °C. Ammonia coordinated on Lewis acid sites were assigned at 1620, 3384 and 3282 cm^{-1} [22] over CuNi catalysts. Brønsted acidity was not expected on the basis of the lack of Brønsted acidity of TiO_2 [23] support and on the pure copper oxides [24].

On the contrary at 180 °C, ammonium ion adsorbed on Brønsted acid sites dominated on vanadia catalysts with characteristic bands at 1420, 3248, 3056 and 2842 cm^{-1} [25], especially in the case of VAl, although a slight Lewis contribution could be detected as well.

At 300 °C, the main bands assigned to NH_3 absorbed on Brønsted acid sites disappeared on VTi catalyst, whereas in VAl were still presented. This indicates the stronger nature of Brønsted acid sites on VAl catalyst compared with VTi.

3.3. *NO oxidation reaction*

In order to find the role of nitric oxide on the SCR process, the NO oxidation reaction was studied as a function of the temperature at the same operating conditions as SCR and NH_3 oxidation reactions. The results, collected in Fig. 5, show that vanadium-based catalysts had no ability to oxidise the NO, while CuNi catalysts displayed an increase of NO reaction rate (below 5%) when the temperature rose. NO_2 as well as N_2O were detected as reaction products and their concentrations increased with temperature.

Studies carried out by Centi et al. [26] with copper-based catalysts, point out the role of Cu^{2+}–NO_2, Cu^{2+}–N_2O_3 species as intermediate in the SCR reaction. FT-IR studies carried out in our group [9], after adsorption of NO, NH_3 and NO + NH_3 at different temperatures, with similar copper/nickel catalysts, pointed out the ability of these systems to adsorb NO. As a conclusion of this study, it was proposed that ammonia and NO compete for copper sites, although the latter is more weakly adsorbed than the former. Moreover, studies carried out by Knözinger [27] at

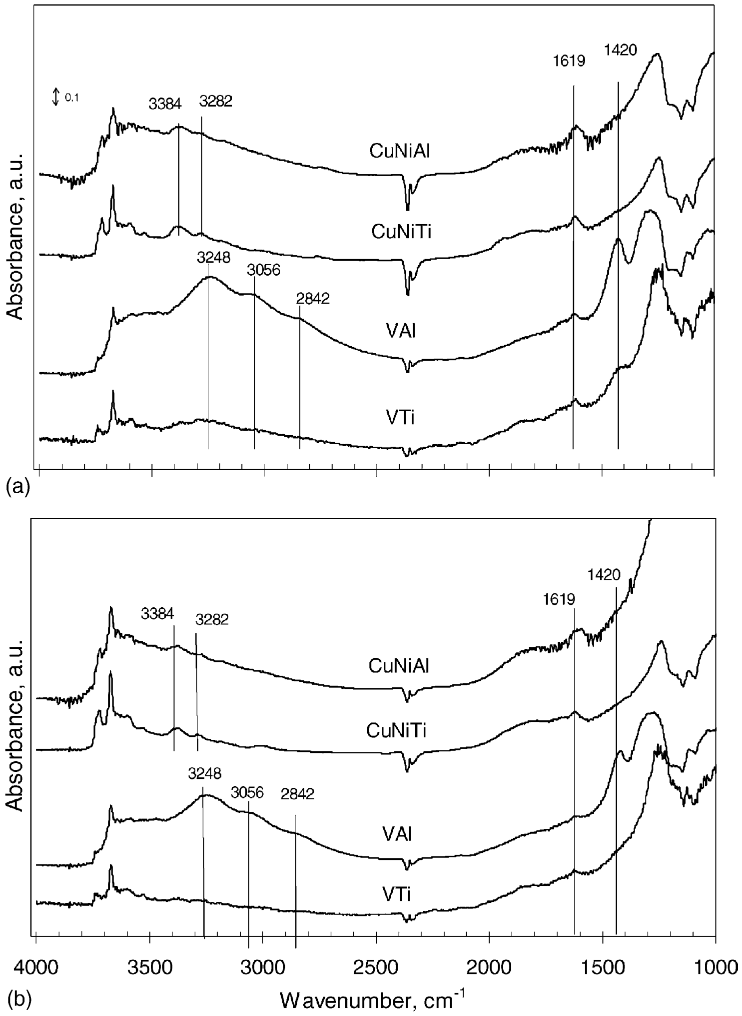

Fig. 4. In situ DRIFTS spectra at: (a) 180 °C; (b) 300 °C for VTi, VAl, CuNiTi, CuNiAl catalysts after ammonia oxidation reaction (30 min). Feed compositions: $[NH_3] = 1000$ ppm, $[O_2] = 3$ vol.%, [He]: balance.

the beginning of the 1980s revealed the important role of NO adsorption on the SCR mechanism on copper/nickel catalysts supported on alumina. CuNi systems selected for this work had a strong dependency of NO_x conversion with the NO_2:NO ratio [14]. The presence of NO_2 in the feed increased the N_2O formation for CuNi catalysts, while no increase was observed with V catalysts. Additionally, when only NO_2 (as NO_x) was on the feed, a significant increase of N_2O formation with temperature was detected in the temperature range from 250 ° to 350 °C.

The formation of NO_2 and N_2O during the NO oxidation reaction, could be explained by NO reacting with oxygen from the lattice to form NO_2 or being adsorbed and reacting with another NO molecule from the gas phase to produce N_2O. Thus, it can be suggested that even in the presence of O_2, NO could be adsorbed and NO_2 intermediate species could play an important role in

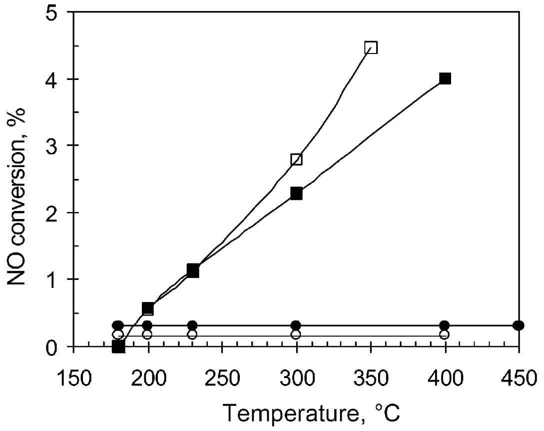

Fig. 5. NO conversion as a function of the operating temperature: (■) CuNiTi; (□) CuNiAl; (●) VTi; (○) VAl. Feed compositions: [NO] = 1000 ppm, $[O_2] = 3$ vol.%, [He]: balance. Operating conditions: total flow $F = 100\,\text{ml}\,\text{min}^{-1}$, GHSV (NTP) $= 15{,}000\,\text{h}^{-1}$, $P = 1$ atm.

the SCR reaction mechanism and in N_2O formation.

4. Summary

As a result, the difference in the behaviour of NO and NH_3 oxidation, could explain the different catalytic activity in the SCR reaction between vanadia and copper–nickel oxide catalysts. The chemistry of NO reduction by ammonia in the absence of catalyst is known as the following [28]:

$$NH_3 + OH \Leftrightarrow NH_2 + H_2O \quad (5)$$

$$NH_2 + NO \Leftrightarrow N_2 + H_2O \quad (6)$$

$$NH_2 + OH \Leftrightarrow NH + H_2O \quad (7)$$

$$NH + O_2 \Leftrightarrow NO + OH \quad (8)$$

When the temperature is high enough (800 °C), a H/O radical pool is built due to the presence of O_2 and H_2O, which results in appreciable amounts of OH radicals that are the key radicals for the conversion of NH_3 to NH_2, since NH_2 radicals are mainly responsible for the reduction of NO (Eq. (6)). In the presence of catalysts, the ultimate mechanism is similar. Janssen et al. [29,30] suggested that intermediate V–O–NH_2 species formed on O=V–O–V=O are responsible of the SCR reaction. Ramis et al. [31] proposed that the breaking of the N–H bond of coordinated ammonia is the first reaction step and a radical-like amide species is expected to react with the radical NO molecule to give NH_2NO. At higher temperature, the formation of NH due to subsequent reaction of NH_2 with OH (Eq. (7)) radicals leads to ammonia oxidation through the reaction with O_2 (Eq. (8)).

Based on SCR mechanisms, the formation rate of NH_x species on vanadia and copper/nickel catalysts, may have a higher correlation with the reaction rate of SCR and ammonia oxidation. In other words, as compared with vanadia-based catalysts, species M–NH responsible for the NH_3 oxidation as well as the N_2O formation could, dominate on the catalytic surface of CuNi at low temperature.

The different formation rates of NH_x species could be explained by the different electron properties of the catalysts studied. V_2O_5 is an n-type semiconductor whereas NiO and some copper oxides are considered to be p-type semiconductors. These semiconductors show different trends when they react with oxygen and a reductant. n-Type semiconductors lose oxygen by reaction with a reductant like NH_3 and the oxygen site is replenished by gas phase oxygen. On the contrary, p-type semiconductors gain oxygen to form species O_2^- and O^-, which have strong reducing properties. Thus, copper/nickel-based catalysts can show higher ammonia oxidation than vanadia-based catalysts. In addition, the species of O_2^- and O^- produced by p-type semiconductors may also interact with NO to form NO_2 and in the presence of NH_3 adsorbed on Lewis acid sites leads to SCR reaction.

The following main conclusions have been obtained in the present study over copper/nickel and vanadia catalyst:

(i) There was a relationship between the ammonia oxidation ability and the initial reduction temperature of the catalytic systems.
(ii) The presence of NH_3 adsorbed on Brønsted acid sites was not necessary for the ammonia oxidation reaction to take place.
(iii) The trend observed in the N_2O formation was: CuNiTi > CuNiAl > VTi > VAl for the SCR and ammonia oxidation reaction.
(iv) The different behaviour of copper/nickel compared with vanadia catalyst when NO oxidation

takes place, indicated the important role of NO adsorption on the SCR mechanisms for copper/nickel catalysts.

(v) An SCR reaction mechanism could be proposed for copper/nickel catalysts based on: (a) NO adsorption and formation of NO_2 adsorbed species on the surface; (b) reaction of these species with ammonia adsorbed on Lewis acid sites.

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