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Ammonia activation over catalysts for the selective catalytic reduction of NO_x and the selective catalytic oxidation of NH_3. An FT-IR study

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Abstract

The adsorption and transformation of ammonia over V_2O_5, V_2O_5/TiO_2, V_2O_5-WO_3/TiO_2 and CuO/TiO_2 systems has been investigated by FT-IR spectroscopy. In all cases ammonia is first coordinated over Lewis acid sites and later undergoes hydrogen abstraction giving rise either to NH_2 amide species or to its dimeric form N_2H_4, hydrazine. Other species, tentatively identified as imide NH, nitroxyl HNO, nitrogen anions N_2^- and azide anions N_3^- are further observed over CuO/TiO_2. The comparison of the infrared spectra of the species arising from both NH_3 and N_2H_4 adsorbed over CuO/TiO_2 strongly suggest that N_2H_4 is an intermediate in NH_3 oxidation over this active selective catalytic reduction (SCR) and selective catalytic oxidation (SCO) catalysts. This implies that ammonia is activated in the form of NH_2 species for both SCR and SCO, and it can later dimerize. Ammonia protonation to ammonium ion is detected over V_2O_5-based systems, but not over CuO/TiO_2, in spite of the high SCR and SCO activity of this catalyst. Consequently Brönsted acidity is not necessary for the SCR activity.

Keywords: Ammonia activation; Selective catalytic reduction of NO_x; NO_x; Selective catalytic oxidation of NH_3; NH_3; FT-IR study

1. Introduction

The oxidation of ammonia to NO_x is carried out industrially for the production of nitric acid [1,2]. The industrial catalysts are noble metals such as Pt-Rh gauzes. The same reaction has also been carried out over metal oxides as the catalysts, giving rise either to N_2 or to NO, with N_2O frequently as a byproduct [3,4]. The selective catalytic oxidation (SCO) of NH_3 to N_2, following the reaction:

$$2NH_3 + 3/2O_2 = N_2 + 3H_2O \quad (1)$$

has been proposed recently as an industrial process for the abatement of slip ammonia after selective catalytic reduction (SCR) reactors aimed at the NO_x abatement from waste gases of power stations [5,6]. In these plants NO_x is converted to nitrogen through the SCR of NO by NH_3, following the main stoichiometry:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \quad (2)$$

The industrial catalysts for SCR reaction are based on V_2O_5/TiO_2-anatase with addition of WO_3 or MoO_3 [5,6]. Other catalytic systems, like CuO/TiO_2, show higher activities but lower selectivities to N_2, with N_2O as the byproduct [7,8], with respect to industrial catalysts. Catalysts like MoO_3/SiO_2 [9,10], CuO/TiO_2 and

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$CuO\text{-}MnO_x/TiO_2$ [11] have been proposed for the SCO process. V_2O_5/TiO_2 [12] and WO_3/TiO_2 [13] are also more or less active and selective for SCO. So, most catalytic systems active for the SCR process are also active for the SCO process. This could imply that the mechanisms of these two reactions are related.

To have further information on the mechanisms of these reactions, we investigated spectroscopically ammonia adsorption, activation and oxidation in absence and in presence of oxygen or NO over different SCR and SCO active systems, like pure V_2O_5, V_2O_5/TiO_2, $V_2O_5\text{-}WO_3/TiO_2$ and CuO/TiO_2.

2. Experimental

V_2O_5/TiO_2, and $V_2O_5\text{-}WO_3/TiO_2$ model catalysts ($S \cong 50$ m^2/g) were prepared by impregnation of P25 TiO_2 from Degussa (Hanau, Germany) with ammonium metavanadate and/or ammonium tungstate in aqueous solution, followed by calcination at 723 K for 2 h. The nominal V_2O_5 content was in the range 1–5% w/w, while the WO_3 content was 9% w/w. For comparison, experiments were performed also on the bare support and on pure V_2O_5 (18 m^2/g, produced by Degussa). The copper-based catalyst used here (10% CuO w/w, 85 m^2/g) has been prepared by impregnation of Ti oxide TiO_2 (anatase with traces of brookite) with copper nitrate, and was characterized previously [14].

FT-IR spectra were recorded at room temperature with Nicolet 5ZDX and Magna 750 Fourier transform spectrometers (4 cm^{-1} resolution) using self-supporting pressed disks of the pure catalyst powders calcined in the IR cell at 673 K for 2 h and outgassed in dynamic vacuum (10^{-4} torr) at 673 K for 30 min.

Ammonia was from commercial cylinders from SIAD (Milano, Italy) and hydrazine was from a water solution (85%) produced by Carlo Erba (Milano, Italy).

3. Results and discussion

3.1. Activation of ammonia on vanadia-based catalysts

The pure V_2O_5 material has been characterized previously [15]. It looks crystalline, without

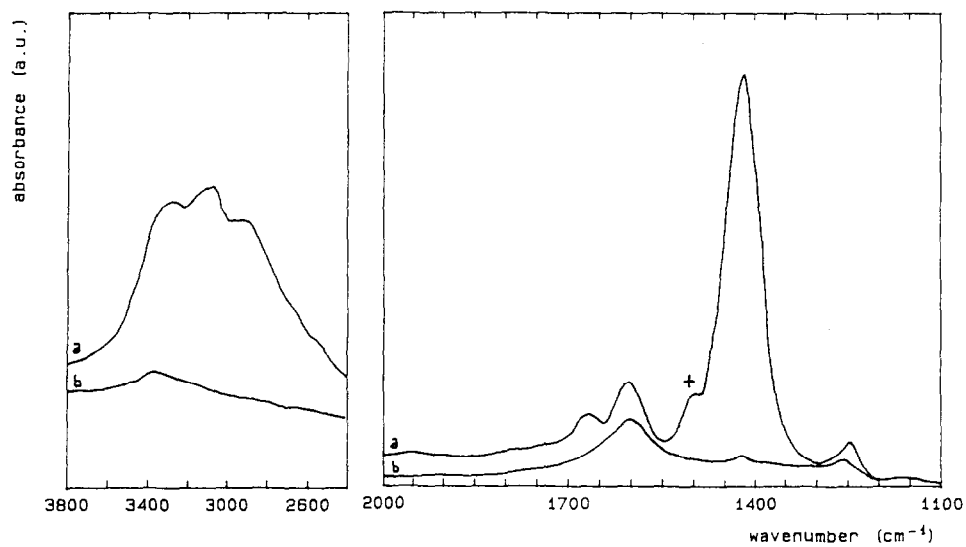

Fig. 1. FT-IR spectra of the adsorbed species on pure V_2O_5 activated in vacuum at 523 K and after contact with ammonia (20 torr), following evacuation at room temperature (a) and at 423 K (b). The symbol (+) indicates the band assigned to the amide group.

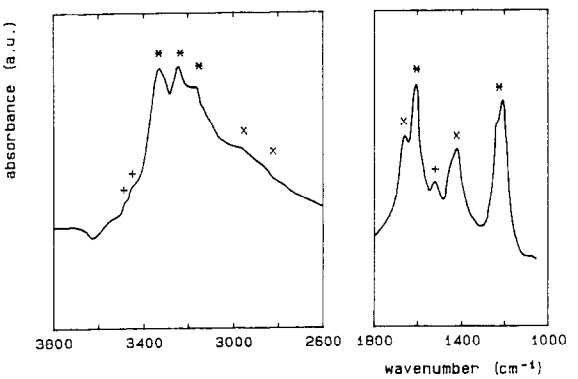

Fig. 2. FT-IR spectra of the adsorbed species arising from ammonia adsorption (50 torr) and following evacuation at 400 K on V_2O_5/TiO_2. The symbol (+) indicate bands due to the amide group; (*) bands due to coordinated ammonia; (×) bands due to ammonium ions.

a definite predominance of particular morphologies. The spectra of the adsorbed ammonia (Fig. 1) show bands at 1680 and 1425 cm^{-1}, due to NH_4^+ cations (symmetric and asymmetric deformation modes, respectively), while the weaker bands at 1605 and 1249 cm^{-1} are due to ammonia adsorbed as such ($\delta_{as}NH_3$ and δ_sNH_3). Another shoulder is evident at 1505 cm^{-1}. It can be assigned, according to the literature [16], to the scissoring mode of an amide species, NH_2, formed by hydrogen abstraction from coordinated ammonia. In the NH stretching region, bands near 3250 cm^{-1} and at 3000 and 2850 cm^{-1} can be assigned to coordinated ammonia and to ammonium ions, respectively. The very high value of the $\delta_{as}NH_3$ mode, that is sensitive to the strength of the Lewis acid–base interaction [16], clearly indicates that this ammonia species is coordinated on Lewis sites of remarkable strength. Evacuation at 423 K (Fig. 1b) causes the almost complete disappearance of the bands of ammonium ions and of the amide species, while weak bands of coordinated ammonia are still detectable. Evolution of the adsorbed ammonia species upon further heat treatment under evacuation cannot be investigated on V_2O_5 because of the partial reduction of the sample under these conditions, with consequent loss of transmittance of the IR light by the sample.

The spectra of ammonia adsorbed on vanadia-titania (Fig. 2) show again the presence of both coordinated ammonia (1605 cm^{-1}, $\delta_{as}NH_3$; 1230 cm^{-1}, δ_sNH_3) and ammonium ions (1664 cm^{-1}, $\delta_sNH_4^+$; 1428 cm^{-1}, $\delta_{as}NH_4^+$). A comparison of the spectra relative to adsorbed ammonia on the TiO_2 support [17], on pure V_2O_5 (see above) and on the supported catalyst, leads

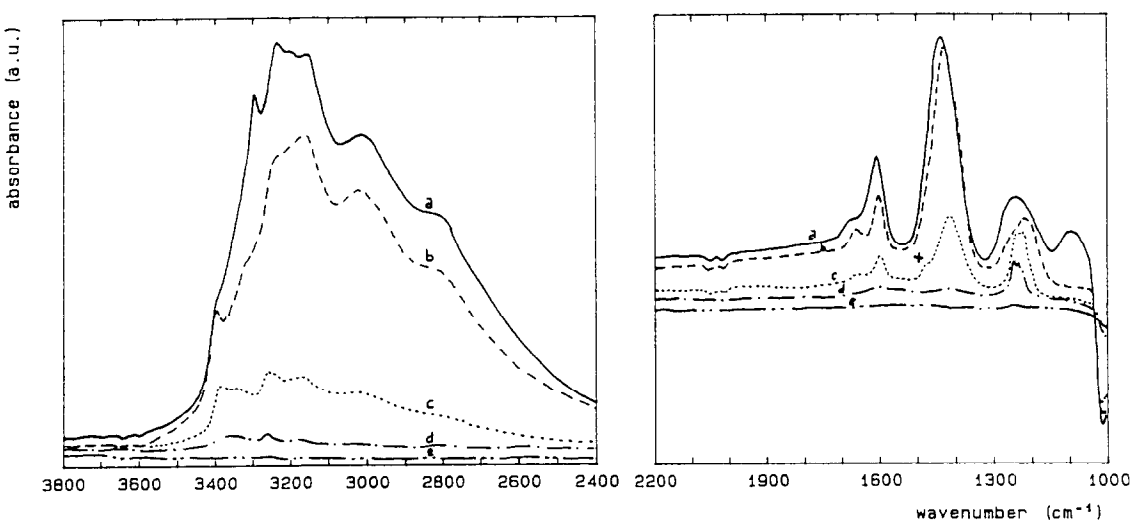

Fig. 3. FT-IR spectra of the adsorbed species arising from adsorption of ammonia (50 torr) over V_2O_5-WO_3/TiO_2 in the presence of gas (a), after outgassing at room temperature (b), 423 K (c), 523 K (d) and 623 K (e). The symbol (+) indicates the deformation mode due to the amide species.

us to the following conclusions: (i) protonation of NH_3 giving rise to ammonium ions involves V-OH centers, since it is not observed on pure TiO_2; (ii) coordination of NH_3, that is observed in all three cases, would involve both vanadium and titanium exposed cations; (iii) vanadium centers are slightly more Lewis acidic than titanium centers, since coordinated NH_3 is more perturbed on the V_2O_5-based catalysts than on TiO_2.

Heating under vacuum causes the decrease of the bands of ammonium species adsorbed on vanadia-titania, more than those of coordinated ammonia, showing that also in this case coordinated species are more strongly bonded than the protonated species. The spectrum of the adsorbed species, still present after heating under evacuation at 400 K, is shown in Fig. 2. Besides the bands cited above new weak features at 3490, 3430 and 1535 cm^{-1} are observed. They are assigned [18] to NH_2 amide species (ν_{as}, ν_s and δ modes). This reaction does not occur on pure titania [17] and would consequently involve vanadium centers. This behaviour parallels that outlined above concerning ammonia adsorbed at room temperature on V_2O_5 (Fig. 1a) and could be due to a similar amide species.

In Fig. 3 the FT-IR spectra of the species arising from the contact of the V_2O_5-WO_3/TiO_2 catalysts with ammonia gas are reported. As above, the sharp band at 1609 cm^{-1} is assigned to the asymmetric deformation mode $\delta_{as}NH_3$ of ammonia coordinatively adsorbed over Lewis acid sites, whose corresponding symmetric mode δ_sNH_3, rather broad, shows a main maximum at 1249 cm^{-1}. The bands, observed at 1676 and 1442 cm^{-1}, are assigned to symmetric and asymmetric deformation modes of ammonium ions respectively. The corresponding stretching modes are found in the region 3400–3100 cm^{-1} for coordinated ammonia and at 3020 and 2820 cm^{-1} for ammonium ions. A further broad absorption centered near 1100 cm^{-1} in the presence of ammonia gas is due to hydrogen-bonded ammonia, whose corresponding N–H stretchings are also evident at 3305 and 3247 cm^{-1}.

The strong negative peaks at 2049 and 2017 cm^{-1} in Fig. 3a–c correspond to bands observed over the clean surface, that disappear upon ammonia adsorption. These bands are associated to the first overtones of the V = O and W = O stretchings of surface vanadyl and wolframyl species, respectively, as discussed previously [18–20]. The fundamental V = O stretching also appears as a negative band at 1025 cm^{-1} while the fundamental W = O is cut-off by the skeletal absorptions. The perturbation of these bands can be interpreted assuming that the vanadyl and wolframyl groups are active in ammonia coordination.

Evacuation at increasing temperature causes the progressive disappearance of the bands due to ammonium ion and, later, of those corresponding to coordinated ammonia, indicating that protonated species are thermally less stable than coordinated ones. At 523 K only ammonia on Lewis acid sites is detected, but it appears composed of two different species, according to the splitting of the δ_sNH_3 mode and of some νN–H modes. At an intermediate temperature of evacuation (423 K), a shoulder near 1500 cm^{-1} is also evident, as observed above, in similar conditions, also on pure V_2O_5 and V_2O_5/TiO_2. This absorption is assigned to the scissoring mode of a surface amide species NH_2.

3.2. Activation of ammonia on the CuO/TiO_2 catalyst

In Fig. 4A the FT-IR spectra of the species arising from the contact of the CuO/TiO_2 catalyst with ammonia gas are reported. The spectrum recorded in presence of gas shows a sharp band at 1602 cm^{-1} and a doublet at 1225 and 1160 cm^{-1}. These bands are due to the asymmetric and symmetric deformation modes of ammonia coordinated on surface Lewis acid sites [16]. The splitting of the symmetric deformation mode, most sensitive to the acidic strength of the surface sites, shows that two different adsorbing centers are active. The posi-

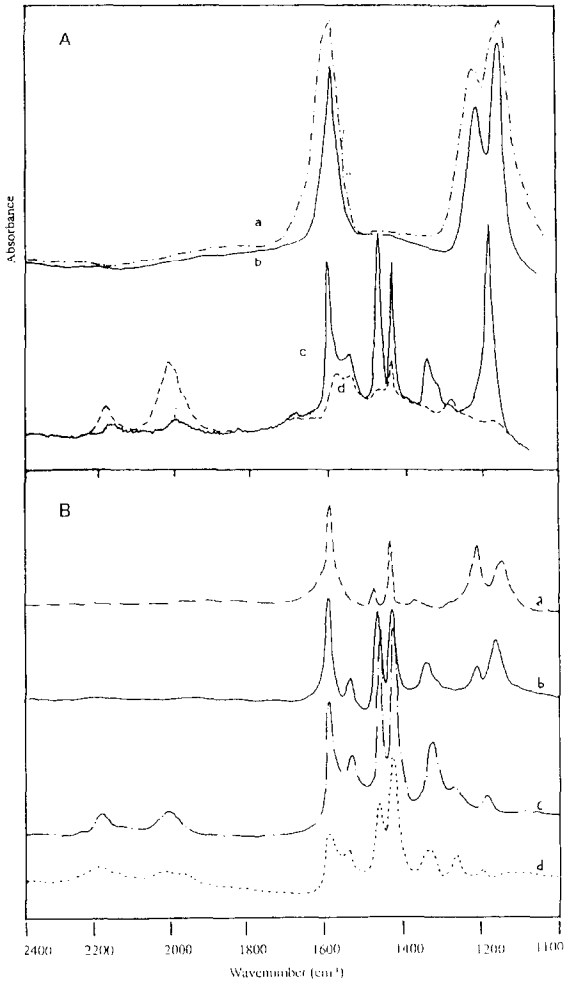

Fig. 4. FT-IR spectra of the adsorbed species on CuO/TiO_2 arising from contact of ammonia (50 torr) (A) and vapours obtained from an hydrazine solution (85%) degassed at 10^{-3} torr at room temperature (B); in the presence of vapours (a) and after degassing at room temperature (b), 423 K (c), 523 K (d) and 623 K (e).

tion of this mode only slightly differs from that measured on the bare support at 1215 and 1170 cm^{-1} [17]. The absence of bands near 1450 cm^{-1}, typically formed when ammonia is protonated over Brönsted acidic solids, indicates that this catalyst, in contrast to those based on vanadia, does not show any appreciable Brönsted acidity. By outgassing at room temperature (Fig. 4A,b) the spectrum does not change significantly.

After evacuation at 423 K the bands due to coordinated ammonia decrease in intensity, while new absorptions can be detected (Fig. 4A,c). In fact, in the region of the symmetric N–H deformations only a single sharp band at 1187 cm^{-1} is now observed; moreover the band at 1602 cm^{-1} is strongly sharpened and shifted to 1611 cm^{-1}, while bands at 1480 and 1440 cm^{-1} (both strong and sharp), and 1555 and 1340 cm^{-1} (both weak) are detected. The bands at 1440 and 1480 cm^{-1} apparently correspond to two different species one of which (1440 cm^{-1}) is formed first and disappears later. The band at 1480 cm^{-1} instead forms and disappears quickly, so being possibly associated to a species intermediate with respect to the formation of other species. Finally, the bands found at 1612, 1560, 1345, 1325 and 1187 cm^{-1}, apparently behaving similarly each other, should correspond, according to the multiplicity, to a species formed by 'aggregation' of more than one ammonia fragment. These features suggest that ammonia is decomposed by heating before desorption, in contrast to what is observed on the pure support, where no ammonia transformation is found [17], and indicate that the reaction of ammonia occurs over the surface CuO_x phase.

To better understand the above spectra, hydrazine adsorption experiments have been performed, thinking this molecule to be a possible intermediate in the transformation of ammonia. The spectra obtained after contact of hydrazine at room temperature and following evacuation at increasing temperature are shown in Fig. 4B. After evacuation at room temperature the spectrum of adsorbed hydrazine is very similar to those obtained after ammonia adsorption and outgassing at 423 K. The similarity becomes even more evident after outgassing adsorbed hydrazine at 423 K. For liquid hydrazine and for metal–hydrazine complexes six infrared bands are observed in the 1800–1000 cm^{-1} region as shown in Table 1. The presence of these bands in the conditions of Fig. 4B shows that hydrazine adsorbed as such is one of the oxidation products of ammonia over our cata-

Table 1
Wavenumbers (cm^{-1}) of the IR absorption bands spectra of hydrazine species

$CuTiO_2$	$ZnCl_2 \times 2N_2H_4$ Ref. [21]	N_2H_4 liquid Ref. [22]	Assignment Refs. [21–23]
1611	1610	1608	NH_2 scissoring
1560	1570	1608	NH_2 scissoring
1350	1345	1324	NH_2 wagging
1280	1310	1283	NH_2 wagging
1180	1170	1098	N–N stretching
	1150	1042	NH_2 rocking

lyst. However, the two prominent bands observed at 1480 and 1450 cm^{-1} after both ammonia and hydrazine adsorption and heating do not arise from hydrazine adsorbed as such, and are certainly due to two different species because they behave independently each other. Tentative assignments can be given at this step, to NO stretching of a nitroxyl HNO species (1480 cm^{-1}) and NH deformation of an imido = N-H species (1450 cm^{-1}). At higher temperatures the bands discussed above disappear, while both ammonia and hydrazine adsorption give rise to prominent bands at 2190 and 2030 cm^{-1}, that, according to previous data [24], can be assigned to N_2^- and N_3^- species, respectively. It is worth mentioning that the main product of ammonia SCO over this system, N_2, cannot be detected by IR. However, the N_2^- ions can be taken as an adsorbed form of nitrogen.

Conversely, no adsorbed ammonia transformation species (i.e. hydrazine, NHO and NH species) are found in presence of gaseous NO, while water is formed at the expense of coordinated ammonia [8]. These data suggest strongly that NO reacts with coordinated ammonia or with an earlier intermediate giving rise to adsorbed water, together with nitrogen, that desorbs and cannot be detected by IR in the gas phase. It is remarkable that in the presence of NO the multiple bands observed when ammonia alone interacts and is oxidized, are not found at all.

3.3. On the mechanism of ammonia oxidation

The data reported above show that ammonia adsorbs differently over the surfaces of different SCR and SCO catalysts. In particular over vanadia-based catalysts, that are very selective for SCR, both ammonium ions formed by protonation over Brönsted acid sites, and coordinated ammonia species over Lewis acid sites are observed. Instead, over CuO/TiO_2 that is even more active although less selective in SCR, and very active in SCO too, only species coordinated on Lewis acid sites are apparent. According to the similarity of the catalytic behavior of these materials in the SCR reaction (8), this indicates that Brönsted acidity is not a necessary requirement for SCR and SCO activity, that needs, instead, oxidation catalysts able to perform redox cycles.

In all cases ammonia adsorption gives also rise to transformation products. In particular, amide NH_2 species are observed over vanadia-based catalysts and hydrazine N_2H_4 species over CuO/TiO_2. These intermediates, that are only detected in the absence of NO, suggest the following mechanism for the main path of ammonia oxidation by oxygen over these catalytic systems:

$$NH_3(g) = NH_3(ads) \quad (3)$$

$$NH_3(ads) = NH_2(ads) + H^+ + e \quad (4)$$

$$2NH_2(ads) = N_2H_4(ads) \quad (5)$$

$$N_2H_4(ads) = N_2 + 4H^+ + 4e \quad (6)$$

The electrons produced during these steps reduce V and Cu cationic centers that are later reproduced by oxidation by O_2 so closing a redox-type (Mars–van Krevelen type) catalytic cycle. The detection of hydrazine over CuO/TiO_2 and of amide species on vanadia-based catalysts could only be due to the different relative rates of the reaction steps (4), (5) and (6): over CuO/TiO_2 step (5) could be the faster, while it could be the slowest over V_2O_5-based systems.

As proposed previously by us [18,8] the NH_2

intermediate is likely common to the SCR and SCO pathways, because it can react with gas-phase or weakly adsorbed NO through the following step:

$$NH_2(ads) + NO = NH_2NO(ads) = N_2 + H_2O \quad (7)$$

This can explain the competition of SCR and SCO, that is very important because it tends to limit the conversion of NO and the selectivity to N_2 upon the SCR reaction.

These results strongly imply that ammonia is activated in a similar way (i.e. through coordination and hydrogen abstraction) over different SCO and SCR catalysts. So, the same mechanism proposed previously [18] for industrial vanadia-titania-based catalysts [based on reaction (7)] is likely also active over CuO/TiO_2 catalysts.

According to our interpretation, the lack of selectivity in SCR catalysis, with the formation of N_2O as the byproduct, is essentially related to a deep oxidation of ammonia. In fact, N_2O formation appears or strongly grows when NO conversion starts to decrease, due to its formation by ammonia oxidation [8,20]. It seems reasonable to hypothesize that the NH fragment (imide) is involved in the formation of N_2O (through its reaction with NO) and in NO formation (through its further oxidation to HNO). According to our data, in contrast to the opinion of Topsøe [25], we do believe that Brönsted acidity has no direct effect on the SCR reaction. However, it is possible that, when present, it can favour the coordination of ammonia through reaction (8):

$$NH_3(gas) + H^+(surf) = NH_4^+(ads) = NH_3(ads) + H^+(surf) \quad (8)$$

4. Conclusions

The main conclusion of the present investigation can be summarized as follows.

1. Ammonia is activated for SCR and SCO catalysis by coordination over Lewis acid sites.
2. Ammonia activated by coordination easily transforms by hydrogen abstraction giving rise to amide NH_2 species.
3. NH_2 species react with NO upon the SCR reaction, giving rise to nitrogen and water.
4. NH_2 species dimerize to hydrazine N_2H_4 that later dehydrogenates to nitrogen upon the SCO reaction.
5. Brönsted acidity is not a necessary requirement for SCR and SCO activity, although it can favour it, when present, by favouring the adsorption of ammonia on the coordinative sites.

Acknowledgements

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References

[1] W. Buchner, R. Schliebs, G. Winter and K.H. Buchel, Industrial Inorganic Chemistry, VCH, Weinheim, 1989, p. 55.
[2] P. Davies, R.T. Donald and N.H. Harbord, in M.T. Twigg (Editor), Catalyst Handbook, 2nd ed., Wolfe, London, 1989, p. 469.
[3] J.E. Germain and R. Perez, Bull. Soc. Chim. France, (1972) 2042.
[4] N. Giordano, E. Cavaterra and D. Zema, Chim. Ind. (Milan), 45 (1963) 15.
[5] H. Bosch and F. Janssen, Catal. Today, 2 (1988) 369.
[6] S.C. Wood, Chem. Eng. Progr., 90(1) (1994) 32.
[7] T. Iizuka, H. Ikeda and S. Okazaki, J. Chem. Soc., Faraday Trans. 1, 82 (1986) 61.
[8] G. Ramis, Li Yi, G. Busca, M. Turco, E. Kotur and R.J. Willey, J. Catal., in press.
[9] M. deBoer, H. Huisman, R.J.M. Mos, R.G. Leliveld, A.J. van Dillen and J.W. Geus, Catal. Today, 17 (1993) 189.
[10] J.J.P. Biermann and F.J.J.G. Janssen, Appl. Catal. A General, 86 (1992) 165.
[11] A. Wollner, F. Lange, H. Schmelz and H. Knozinger, Appl. Catal. A General, 94 (1993) 181.
[12] F. Cavani and F. Trifirò, Catal. Today, 4 (1989) 253.
[13] M. deBoer, A.J. van Dillen, D.C. Koningsberger, F.J.J.G. Janssen, T. Koerts and J.W. Geus, in New Developments in Selective Oxidation by Heterogeneous Catalysis, Elsevier, Amsterdam, 1992, p. 133.

[14] J.M. Gallardo Amores, V. Sanchez Escribano, G. Busca and V. Lorenzelli, J. Mater. Chem., 4 (1994) 965.
[15] G. Busca, G. Ramis and V. Lorenzelli, J. Mol. Catal., 50 (1989) 231.
[16] A.A. Tsyganenko, D.V. Pozdnyakov and V.N. Filimonov, J. Mol. Struct., 29 (1975) 299.
[17] G. Ramis, G. Busca, V. Lorenzelli and P. Forzatti, Appl. Catal., 64 (1990) 243.
[18] G. Ramis, G. Busca, F. Bregani and P. Forzatti, Appl. Catal., 64 (1990) 259.
[19] G. Ramis, G. Busca and P. Forzatti, Appl. Catal. B, Environ., 3 (1993) 13.
[20] L.J. Alemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello and F. Bregani, J. Catal., 155 (1995) 117.
[21] D.N. Sathyanarayana and D. Nicholls, Spectrochim. Acta, 34A (1978) 263.
[22] J.R. Durig, S.F. Bush and E.E. Mercer, J. Chem Phys., 44 (1965) 4238.
[23] L. Sacconi and A. Sabatini, J. Inorg. Nucl. Chem., 25 (1963) 1389.
[24] G. Martra, E. Borello, E. Giamello and S. Coluccia, in H. Hattori, M. Misono and Y. Ono (Editors), Acid–Base Catalysis II, Elsevier, Amsterdam, 1994, pp. 169–175.
[25] N.Y. Topsøe, Science, 265 (1994) 1217.