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NH_3 adsorption over lanthanide doped V_2O_5/Al_2O_3 catalysts

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Abstract

A diffuse reflectance FTIR spectroscopy (DRIFTS) study of the NH_3 adsorption from room temperature to 400°C have been carried out over vanadia–alumina and vanadia–lanthanide-doped alumina catalysts. A shift of the ammonia adsorption bands to lower wavenumbers as well as a change in the geometry of the adsorption at room temperature is detected due to the presence of the lanthanide cation. On the other hand, lanthanide doped catalysts present new acid Lewis sites associated to the Ln^{3+} species and an enhancement of their Lewis acidity, as compared with the undoped sample.

Keywords: NH_3 adsorption; V_2O_5/Al_2O_3 catalysts; In situ DRIFTS

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1. Introduction

The selective catalytic reduction (SCR) of NO with ammonia is the most used process to abate NO from gaseous emissions [1]. Among the catalysts active in such reaction, vanadium oxide supported on γ-Al_2O_3 is one of the most efficient. In recent papers we have shown that lanthanide doped vanadia–alumina catalysts are also active in the SCR reaction [2,3]. As function of the vanadium loading and lanthanide dopant used, an alteration of the electronic density of support cations and supported vanadium ions is detected, thus producing a change in the Lewis acid–base character of the solids [3]. The role of the acid sites on the surface of the catalyst is determinant in the SCR mechanism. In this sense, the lanthanide doped vanadia/alumina solids present a specific SCR activity which can be directly related with their Lewis acidity [2,3].

Ammonia is often used as a basic probe molecule in infrared spectroscopy to characterise acid sites in catalysts. Besides this, NH_3 itself is a reactant of the SCR reaction and the adsorbed ammonia species play a predominant role in the reaction mechanism.

In this work we present a diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) study of the NH_3 adsorption, from room temperature to 400°C, over 10% w/w V_2O_5 catalysts supported on Al_2O_3 and lanthanide (La, Sm, and Ce) doped Al_2O_3.

2. Experimental

In this study 10 wt.% Ln_2O_3–Al_2O_3 (Ln=Sm, La, Ce) supports and 10% w/w V_2O_5 loaded catalysts were prepared by impregnation. A detailed description of the preparation procedure is given elsewhere [3]. We denote 10VAl as the vanadia–alumina catalyst and 10VLnAl (Ln=Sm, La, Ce) as the lanthanide doped ones. All the catalysts present the same specific surface BET area of the starting support (γ-Al_2O_3 Degussa type C, 82 ± 5 m^2 g^{-1}), subjected to the same process for comparative purposes, and the number of theoretical monolayers of vanadium oxide on the support was calculated to be 0.85.

DRIFTS spectra of pure samples were obtained using a Nicolet 510P Infrared Spectrometer, with KBr optics and a DTGS detector. A controlled environment reflectance cell (Spectra-Tech 0030-101) equipped with ZnSe windows was coupled to the spectrometer. Before introduction of the adsorbate, the catalyst (40 mg) was activated at 500°C for 2 h in 20 ml min^{-1} of synthetic air (99.999% pure, Sociedad Española del Oxígeno (SEO)), cooled down to room temperature (RT) in nitrogen and the reflectance spectrum collected. This spectrum was taken as reference for the adsorption experiment. Then, a flow of 30 ml min^{-1} of NH_3 (3000 ppm in N_2, Abelló Oxígeno Linde)

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was passed through the catalyst for 1 h at, respectively, 25°C, 100°C, 200°C, 300°C and 400°C. Spectra were obtained by coadding 200 scans at 4 cm^{-1} of resolution, and they are presented in Kubelka–Munk mode without any other manipulation.

3. Results and discussion

Fig. 1 shows the DRIFTS spectra of the catalysts studied after NH_3 adsorption at the temperatures indicated.

The introduction of ammonia into the DRIFTS cell at

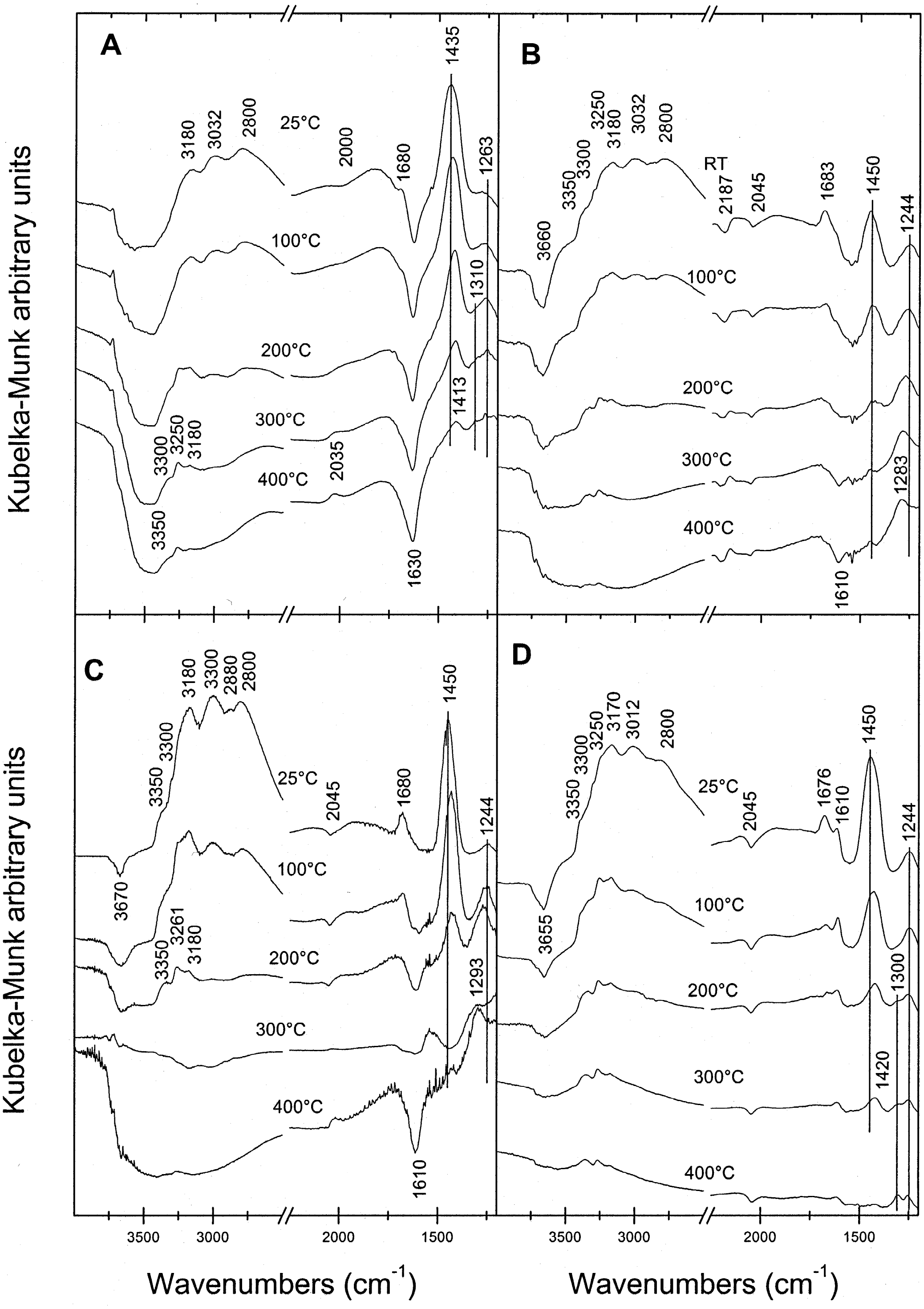

Fig. 1. 'In situ' DRIFTS spectra of the NH_3 adsorption over the studied catalyst at the temperatures indicated. The spectra are ratioed to that of the fresh catalyst before adsorption at room temperature. (A) Undoped catalyst, 10VAl; (B) Lanthanum doped catalyst, 10VLaAl; (C) Samarium doped catalyst, 10VSmAl; and (D) Cerium doped catalyst, 10VCeAl.

25°C induces the appearance of bands ascribed to ammonia species adsorbed on both Lewis (3350, 3300, 3250, 3180, 1610 and 1250 cm^{-1}) and Bronsted (3100, 3032, 2800, 1680 and 1450 cm^{-1}) acid sites of the surface of the solids [2,4]. Simultaneously, negative bands at 2045 (2000 for the undoped sample), 3660 and 1630 cm^{-1}, indicative of disappearing species, are also noticed. For the 10VLaAl sample, a band at 2187 cm^{-1}, due to an electronic transition of the lanthanide cation, allowed through crystal field effects, is also observed [2]. The elimination of this mode on adsorbing NH_3 might indicate that the acid sites responsible of the ammonia adsorption are associated to the presence of Ln^{3+} species on the surface [2]. The band of 2045 cm^{-1} is assigned to the first overtone of the stretching vibration of the V^{5+}=O bond ($2\nu(V^{5+}=O)$), and its disappearance is indicative of the reduction of the vanadium atoms by the ammonia [2]. The band around 3660 cm^{-1} is characteristic of surface hydroxyl groups bonding vanadium atoms (V–OH) and its disappearance is related with the adsorption of ammonia as NH_4^+ ions. The wideness of this band indicates the existence of any others overlapped, assigned to hydroxyl groups bonding Al and lanthanide cations, and ν(OH) of adsorbed water. This suggests the existence in the catalysts of different Bronsted acid sites, V–OH, Al–OH and Ln–OH groups, and the replacement of part of the water adsorbed on the surface of the solid by the ammonia adsorbed species. This is confirmed by the negative band at 1630 cm^{-1}, characteristic of the δ(HOH) of adsorbed water. The intensity of the negative 1630 cm^{-1} band and the wideness of the negative bands circa 3660 cm^{-1} are higher in the undoped sample than in the lanthanide-doped ones, suggesting the higher water coverage of its surface, which is also responsible of the observed wideness and shift to lower wavenumbers of the $2\nu(V^{5+}=O)$ band in this sample, due to the hydration of the V^{5+}=O bond.

A change in the nature of the ammonia adsorption site induced by the presence of the lanthanide cation can be easily deduced from the position of the $\delta(NH_4^+)$ and $\delta(NH_3)$ IR adsorption bands (Table 1). The undoped alumina supported catalyst, 10VAl, presents a $\delta_{as}(NH_4^+)$ band at 1435 cm^{-1} and a $\delta_s(NH_3)$ one at 1263 cm^{-1}, however, the all three lanthanide doped catalysts have those adsorptions at 1450 and 1244 cm^{-1}, respectively. A decrease in the position of the $\delta_s(NH_3)$ band of ammonia adsorbed on Lewis acid sites and an increase in that of the $\delta_{as}(NH_4^+)$ band of ammonia adsorbed on Bronsted acid sites of V_2O_5/Al_2O_3 catalysts have been reported to occur when decreasing the oxidation state of the vanadium ions [5,6]. For instance, Davidov [5] assigns bands at 1260, 1245 and 1220 cm^{-1} to $\delta_s(NH_3)$ of coordinatively adsorbed ammonia on V^{5+}, V^{4+} and V^{3+} cations, respectively, and bands at 1425 and 1460 cm^{-1} to $\delta_{as}(NH_4^+)$ of ammonium ions adsorbed on, respectively, V^{5+} and V^{4+}. Sobalik et al. [6] find a similar sequence, but they considered that the Lewis acid sites for ammonia adsorption are not the vanadium atoms, but the aluminium ones. In this case, ammonia adsorptions on Al^{3+} Lewis acid centres close to oxidised vanadium species give bands in the 1250–1260 cm^{-1} region, those close to reduced vanadium species appear in the 1230–1250 cm^{-1} region, and, if the Al^{3+}centres are far enough from any vanadium atom, at wavenumbers higher than 1280 cm^{-1}.

Table 1
Position of the ammonia adsorption DRIFTS bands observed at 25°C (cm^{-1})

	10VAl	10VSmAl	10VLaAl	10VCeAl
$\delta_s(NH_4^+)$	1677	1680	1681	1678
$\delta_{as}(NH_3)$	1610	1618	1620	1615
$\delta_{as}(NH_4^+)$	1435	1450	1450	1450
$\delta_s(NH_3)$	1263	1244	1244	1244

On the basis of these data, the differences in the position of the ammonia adsorption bands between the undoped and lanthanide-doped catalysts could be explained assuming differences in the oxidation state of the vanadium atoms. A recently published detailed characterisation study by means of EXAFS-XANES, UV-Vis, XPS and TPR techniques reveals no differences in the average oxidation state of vanadium atoms in all catalysts [3]. However, from this wok is deduced that the presence of the lanthanide dopant induces an increase in the electron density of the vanadium 3d levels thus altering the Lewis acid–base character of the solid [3]. The higher electronic density of the vanadium atoms in the lanthanide doped samples would have a similar effect than a reduction of the vanadium atoms and explain the observed shift in the ammonia adsorption IR bands.

On the other hand, the separation between the symmetric and antisymmetric bending vibration bands of NH_3 adsorbed on Lewis acid sites is related with the ammonia adsorption geometry [7]. The different value observed for the undoped (347 cm^{-1}) and for the lanthanide doped catalysts (375 cm^{-1}) could indicate a change in the NH_3 adsorption geometry.

When the adsorption temperature increases, the ammonia adsorption bands decrease in intensity and shift in position. The decrease in the intensity means a decrease in the amount of the ammonia adsorbed. In good agreement with this, a lower reduction of the vanadia phase, as deduced from the lower intensity of the negative band at 2045 cm^{-1}, is detected. The intensity loss is higher in the bands of adsorbed ammonium ions while those of coodinatively adsorbed NH_3 remain practically unchanged, thus pointing to a higher thermal stability of the ammonia adsorbed on Lewis acid centres than on Bronsted acid ones. At the higher temperature tested, 400°C, the adsorption of ammonia is essentially on Lewis acid sites, except for the undoped catalysts, 10VAl, where an important presence of ammonium species is detected.

Concerning the shift in the position of the adsorption bands, a different behaviour between the undoped and the

Table 2
Position of the ammonia adsorption DRIFTS bands observed at 300°C (cm^{-1})

	10VAl	10VSmAl	10VLaAl	10VCeAl
$\delta_s(NH_4^+)$	1662	–	–	–
$\delta_{as}(NH_3)$	1608	–	–	1614
$\delta_{as}(NH_4^+)$	1410	1423	1450	1419
$\delta_s(NH_3)$	1263	–	–	1249
$\delta_s(NH_3)$	1300	1293	1283	1300

lanthanide doped samples is also detected (Table 2). Thus, the $\delta_s(NH_3)$ band shifts to higher wavenumbers with temperature in 10VSmAl and 10VLaAl catalysts (from 1244 to 1290 cm^{-1}) while in the undoped sample the band remains at 1263 cm^{-1} at 400°C. The simultaneous presence at 300°C of two bands at 1249 and 1300 cm^{-1} in 10VCeAl, indicates that the band at 1300 cm^{-1} corresponds to an ammonia adsorption over a different Lewis acid centre than that responsible for the adsorption at low temperatures. A band at such position has been ascribed in vanadia/alumina catalysts to NH_3 adsorbed on Lewis centres of the free alumina that appear on the surface of reduced catalysts as resulting of a partial elimination of the vanadium compounds from the surface support [5,6]. However, this band is very weak in the undoped 10VAl catalyst, and its position depends on the nature of the lanthanide cation (1283 cm^{-1}, La; 1293 cm^{-1}, Sm; 1300 cm^{-1}, Ce). This allows us to tentatively assign it to ammonia coordinatively adsorbed on the lanthanide cation or aluminium cations close to them. This agrees with the decrease in the electronic density of the aluminium levels observed in the lanthanide doped catalyst due to the presence of the lanthanide cation [3]. It is important to note that in the lanthanum-doped sample, the intensity of the lanthanum electronic transition band at 2187 cm^{-1} remains negative and practically constant, suggesting that, in good agreement with the upper arguments, lanthanum cations are implied in the Lewis acidity of the catalyst.

On the other hand, the adsorption on Bronsted acid sites also change with temperature (Table 2). Thus, although for the 10VLaAl catalyst, the $\delta_{as}(NH_4^+)$ band remains at about 1450 cm^{-1}, for 10VAl, 10VSmAl and 10VCeAl ones it shifts to 1410–1420 cm^{-1} at high temperatures. This position matches rather well with the one observed for ammonia adsorption on bulk V_2O_5 [5,8], suggesting that the acid Bronsted sites responsible of the ammonia adsorption at high temperature are essentially associated to vanadium atoms not perturbed by the presence of the lanthanide cation. The shift to lower wavenumbers indicates a lower strength of the H–N–H vibration, that is meaning a stronger NH_4^+ adsorption and/or a higher Bronsted acidity of the ammonia adsorption centres. On the other hand, the intensity of the $\delta_{as}(NH_4^+)$ band for 10VAl and 10VCeAl solids at high temperature is higher than that for 10VSmAl and 10VlaAl, thus meaning a higher number of Bronsted centres capable of adsorbing ammonia. The comparison of these two factors, shift and intensity of the $\delta_{as}(NH_4^+)$ band, allows us to state the higher Bronsted acidity of 10VAl and 10VCeAl solids as compared with 10VSmAl and 10VlaAl ones. This enhanced Bronsted acidity can be responsible of the higher activity observed for such catalysts in the SCR deNOx reaction [2,3].

Finally, although the nature of the adsorption centre changes, the adsorption geometry of the ammonia molecules does not change with temperature, as deduced from the no change in the separation between de symmetric and antysymmetric deformation bands of adsorbed ammonia species.

4. Conclusions

Ammonia is adsorbed over undoped and lanthanide-doped vanadia–alumina catalysts in both Lewis and Bronsted acid sites of the surface associated essentially to the vanadia phase. The presence of the lanthanide cation produces an increase in the electronic density of the vanadium levels thus leading to a shift of the ammonia adsorption bands to lower wavenumbers, as well as a change in the geometry of the ammonia adsorption. When increasing the adsorption temperature, the amount of ammonia adsorbed, decrease. At high temperatures, coordinatively adsorbed ammonia species are preferentially adsorbed on Lewis acid sites associated to the support, in particular, the lanthanide cation, whereas ammonium ions are adsorbed over the vanadia phase. The presence of the lanthanide dopant induces a decrease in the electronic density of the aluminium atoms enhancing the Lewis acidity of the solid as well as generates new Lewis acid sites responsible of the adsorption band observes circa 1300 cm^{-1}. A shift of the bands of adsorbed ammonium species to lower wavenumbers in the case of the most active catalysts in the SCR denoX reaction is detected, thus pointing to a relationship between the Bronsted acidity of the solids and their activity in such reaction.

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