Characterization of $AlNbO_4$ and Vanadium Oxide Catalysts supported on $AlNbO_4$ by ^{27}Al and ^{51}V Solid State NMR Spectroscopy

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^{27}Al Solid state NMR spectroscopy of Al_2O_3–Nb_2O_5 mixtures (Al/Nb = 1) reveals three types of aluminium centres corresponding to tetrahedral, pentagonal and octahedral coordination;^{51} V solid state NMR spectra of vanadium oxide, dispersed on Al–Nb oxides at a coverage lower than a monolayer reveal two types of vanadia species, one due to a symmetric tetrahedral environment and the other due to a distorted or octahedral coordination (different from V_2O_5).

Vanadium oxide-supported catalysts are well known for the selective oxidation of hydrocarbons.[1] In recent years, many studies have been devoted to the modifications in the catalytic properties induced by the degree of dispersion of V_2O_5 on different supports like Al_2O_3, SiO_2 or TiO_2 (anatase). The V_2O_5–anatase system is a classical example of support enhancement of the vanadium oxide active phase for the oxidation of *o*-xylene to phthalic anhydride. A key concept used to rationalize the behaviour of the supported V_2O_5 is the idea that there is a close epitactic match between V_2O_5 and the anatase support.[2] Currently many studies are being directed towards the modification of physicochemical and catalytic properties induced by vanadium coverages lower than monolayer. These studies involve techniques which approach the local structure of the V–O_x clusters, for example X-ray absorption spectroscopy, EXAFS, XANES,[3] high-resolution electron microscopy (HREM),[4,5] radial electron distribution (RED)[6] or the combination of laser-Raman and Fourier transform IR spectroscopy (FTIR).[7]

Aluminium niobate, $AlNbO_4$, which crystallizes in the monoclinic system,[8] has a structure similar to that of TiO_2(B).[9] As a consequence, it can be used as a support for vanadium oxide species at low coverage[10] and thus to promote interesting catalytic results especially for hydrogen oxidation. The present communication reports the characterization by solid state NMR spectroscopy of the $AlNbO_4$ support (^{27}Al) and of the VO_x species (^{51}V) on $AlNbO_4$.

The Al-Nb oxides were prepared, as previously described,[11] by drying aluminium and niobium solutions initially adjusted at pH 1.5–2.0 with ammonia. The solid was then calcined under air at different temperatures (500, 600, 650 and 750 °C) in order to get different specific areas and different surface OH densities (Table 1). A series of VO_x/Al-Nb-O catalysts with low vanadium loadings of *ca.* 0.4–1.2 wt% (expressed as metallic vanadium) were prepared by grafting the niobium-based support with a tetrahydrofuran (THF) solution of $VOCl_3$ by reaction with surface OH groups. Before each operation of grafting, the Al-Nb-O support was outgassed at 200 °C *in vacuo* ($<10^{-2}$ torr). All the operations were conducted under dry argon. After filtration and subsequent washing with dry THF, the material was calcined at 500 °C under wet air [$P(H_2O)$ 23.3 torr]. A strong decrease of the Brunauer–Emmett–Teller (BET) area of the solids was observed after grafting as shown in Table 1.

^{27}Al and ^{51}V NMR spectra were recorded with a Bruker MSL-300 spectrometer by using a single pulse sequence. For the ^{27}Al experiments, the conditions were chosen in order to obtain quantitative spectra (small pulse angle, long delay between the pulses) and all the samples were spun at the magic angle with the same frequency (3000 Hz). Under these conditions, comparisons between the spectra are quantitative and subtractions can be performed. However, as for all NMR

Table 1 Characteristics of the niobium-based support and of the VO_x/Al-Nb-O catalysts

T/°C[a]	BET surface area/ m^2 g^{-1} Support	Catalyst	VO_x/Al-Nb-O catalyst (V, wt %)
500	168	90	1.2
600	115	53	0.6
650	95	57	0.5
750	53	33	0.4

[a] Temperature of calcination of the niobate support.

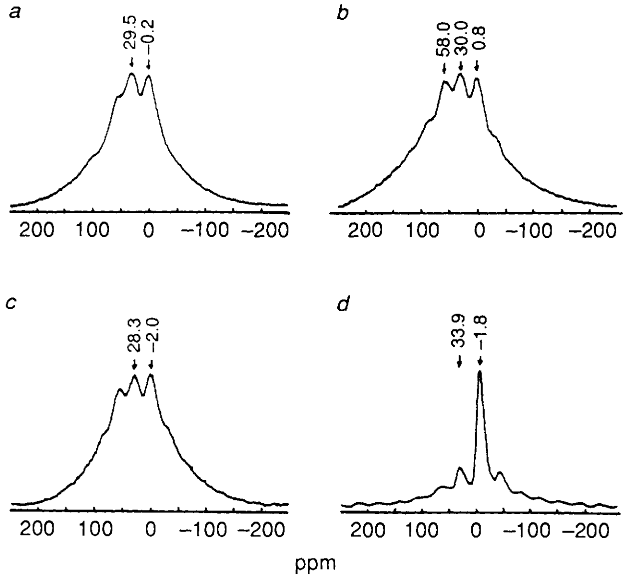

Fig. 1 ^{27}Al MAS NMR spectra of Al–Nb–O calcined at various temperatures: *a*, 500; *b*, 600; *c*, 650; *d* 750 °C [chemical shift referred to $Al(H_2O)_6{}^{3+}$ aq.]

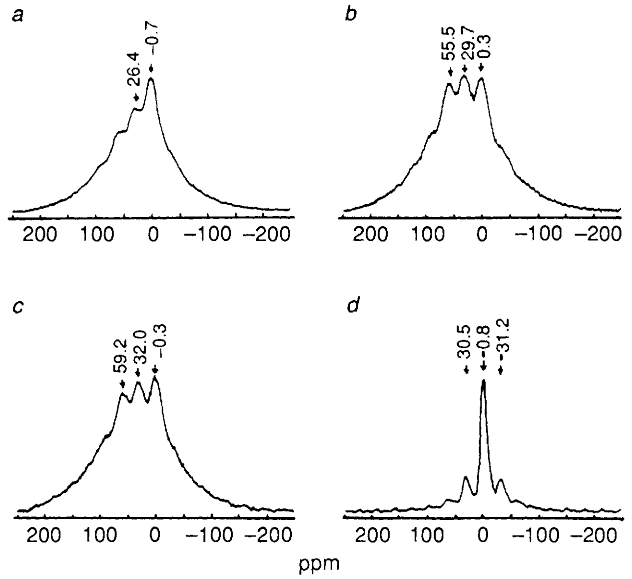

Fig. 2 ^{27}Al MAS NMR spectra from the VO_x-grafted Al–Nb–O calcined at various temperatures: *a*, 500; *b*, 600; *c*, 650; *d*, 750 °C [chemical shift referred to $Al(H_2O)_6{}^{3+}$ aq.]

experiments on quadrupolar nuclei, a small number of the aluminium atoms can give rise to a very broad signal which cannot be detected. The ^{51}V NMR spectra were recorded under both static and MAS conditions in order to study the symmetry of the environment around the vanadium nuclei.

The spectra of the niobium-based supports and of the vanadium-supported catalysts as a function of the temperature of calcination of the support are given in Figs. 1 and 2 for ^{27}Al and Fig. 3 for ^{51}V.

The ^{27}Al MAS NMR spectra of the niobium-based supports (Fig. 1) and of the VO_x-grafted niobate catalysts (Fig. 2) are identical except for the two solids calcined at 500 °C (Fig. 1*a* and 2*a*). As the technique is more sensitive to the bulk than to the surface, this proves that no transformation of the structure of the bulk of the support occurred during the operations of grafting of vanadium and during the further calcination. The spectrum of the support calcined at 750 °C (Fig. 1*d*), the temperature which corresponds to the crystallization of $AlNbO_4$ as observed by XRD,[12] shows only one peak at −1.8 ppm, which can be attributed to octahedral aluminium cations, in agreement with the crystallographic data.[8] When the support is calcined at lower temperatures, the ^{27}Al NMR spectra are more complex, and at least three peaks at about 0, 30 and 60 ppm can be detected. The signal at 0–2 ppm is attributed to aluminium in the same octahedral environment as in the crystalline $AlNbO_4$ phase, while the peak at 58–60 ppm corresponds to tetrahedral aluminium cations as in zeolites.[13] The attribution of the signal at 28–30 ppm is more controversial, having been attributed by different groups to five-coordinated atoms or to aluminium in a tetrahedrally distorted coordination.[13–16] However, it seems more probable that in this case it corresponds to five-coordinated atoms.

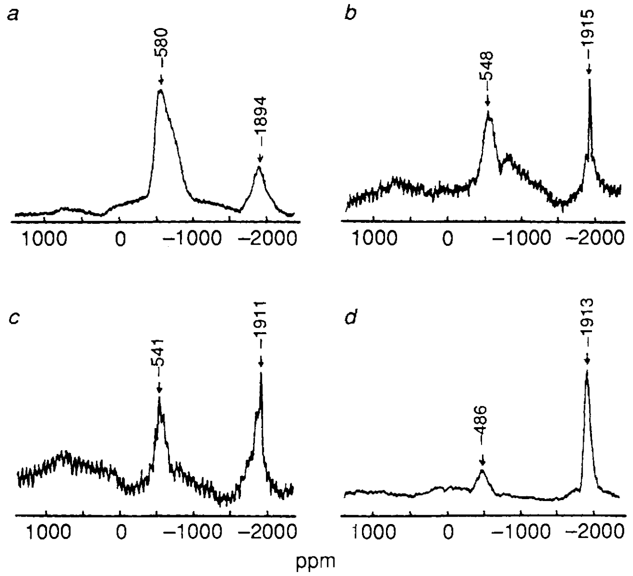

Fig. 3 ^{51}V NMR spectra of vanadium supported on Al–Nb–O as a function of the calcination temperature of the support: *a*, 500; *b*, 600; *c*, 650; *d* 750 °C. Spectra *a* and *d* were recorded under static conditions, while *b* and *c* were obtained with rotation of the sample at the magic angle (chemical shift referred to $VOCl_3$)

The ^{51}V NMR spectra of the catalysts (Fig. 3) show two signals, the relative amounts of which depend on the calcination temperature of the supports. The first signal (−486 to −580 ppm) is broad and quite similar to that observed by Chary *et al.* for vanadium oxide deposited on γ-Al_2O_3.[17] It is attributed to vanadium in a very distorted octahedral environment, and probably bonded to amorphous Al_2O_3.[12] Note a progressive displacement of the position of the signal on increasing the temperature of calcination. The second signal at (−1910 to −1915 ppm) gives a narrow peak corresponding to more shielded atoms. The MAS NMR spectrum proves that these atoms are in a symmetrical environment, the line width being very small compared to that of the first signal. It is attributed to tetrahedrally coordinated vanadium, by analogy with data on the VMgO system.[18,19] In addition, the chemical shift between these species can be explained if it is assumed that vanadium is bonded, *via* O-bridges, to metallic centres with different environments.

The solid state NMR spectra have provided original information on the following points: (*i*) Below the temperature of crystallization of $AlNbO_4$ (<750 °C), three coordination modes for aluminium have been observed: tetrahedral, pentagonal and octahedral. Above 750 °C, only the octahedral coordination is observed. (*ii*) For V coverages below the monolayer, two different coordination modes for vanadium have been observed on the VO_x catalysts grafted on Al–Nb–O: highly distorted tetrahedral or octahedral on the one hand, and tetrahedral on the other. The relative distribution of these two VO_x species is dependent on the structure of the support which is determined by the temperature of calcination. The coordination usually observed for vanadium on vanadium oxide catalysts, responsible for total oxidation, is octahedral as in V_2O_5.[19] The possibility of controlling this coordination by the choice of the temperature of calcination of the Al–Nb–O support makes the VO_x/Al–Nb–O series good potential catalysts for the mild oxidation of hydrocarbons. This aspect is currently under study.

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