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Surface acidic properties of alumina-supported niobia prepared by chemical vapour deposition and hydrolysis of niobium pentachloride

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Abstract

Niobia–aluminas were prepared by chemical vapour deposition at 150°C of niobium pentachloride on the surface of γ-aluminas calcined at different temperatures and with controlled degrees of hydration, followed by hydrolysis with water vapour at 150°C and a thermal treatment with steam at 440°C aimed at removing surface chloride contamination. The samples were characterised with respect to chemical composition, surface area, acidity by temperature-programmed desorption of ammonia, nature of acid sites by infrared spectroscopy of adsorbed pyridine and catalytic activity at 370°C in the dealkylation of cumene.

The results showed that, for each alumina calcination temperature, the catalysts with the lowest niobium content have a higher density of acid sites than the alumina support, but the acidity decreased, within each series with an increase in the niobium content. Comparatively to the TPD results, catalytic activity in cumene dealkylation was much more sensitive to the history and composition of the samples. The niobia-alumina samples were much less active than the alumina support, but this was most likely due to the severe hydrothermal treatment for chlorine removal, since their activity was close to that of an alumina submitted to the same treatment. A strong decrease in the acidic activity was observed with increase in the niobium content. A sample of pure niobium oxide had a much higher activity than the niobia-alumina samples. Brønsted acidic sites could only be observed by the IR spectra of adsorbed pyridine on the surface of the pure niobium oxide sample.

Keywords: Alumina; Niobia; Chemical vapour deposition; Acidity; Cumene; Dealkylation

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1. Introduction

Supported transition metal oxides are of both fundamental and applied interest, since these oxides, such as niobia, when in the unsupported form, frequently have interesting catalytic and surface properties. They are, however, expensive and their textural properties are difficult to control. Depositing the oxide on the surface of a suitable support, with large surface area and easily controlled textural properties, is an attractive solution to these problems, but it is necessary to investigate the extent to which the surface properties of the oxide are modified and whether new

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surface properties appear due to interaction with the support.

The preparation of niobium oxide supported on silica or alumina has been described in the literature by several methods, such as: (i) aqueous impregnation of ammonium oxaloniobate or oxaloniobic acid [1,2]; (ii) impregnation of niobium ethoxide using organic solvents [3,4]; (iii) chemical vapour deposition of niobium ethoxide. We have recently described the preparation of alumina-supported niobium oxide by chemical vapour deposition (CVD) of niobium pentachloride, followed by hydrolysis in order to decompose the supported chlorides [5]. Niobium pentachloride has the potential advantage of being less expensive than other precursors such as niobium pentaethoxide or niobium allyl. It was shown that highly dispersed niobium species were obtained and the amount of niobium deposited in a single CVD step was limited by the concentration of anionic sites (oxide and hydroxyl anions) on the alumina surface and the size of the niobium pentachloride molecule. The mechanism of deposition of niobium pentachloride seemed to involve, not only reaction with surface hydroxyls, but also adsorption on oxide anionic sites.

In the present paper, we describe the surface acidic properties of alumina-supported niobia prepared by this method, as measured by temperature-programmed desorption of ammonia (TPD), infrared spectroscopy of adsorbed pyridine and catalytic activity in the cumene dealkylation reaction.

2. Experimental

2.1. Preparation of the materials

2.1.1. Preparation of the alumina supports

A commercial Condea Chemie Pural-SB high-purity pseudo-boehmite was extruded, oven-dried at 120°C and calcined at 550, 650 or 750°C in an oven, under static air for 3 h. Each of the calcined aluminas was ground and sieved to 0.15–0.30 mm pellet diameter. Each alumina was then exposed to air saturated with water vapour, at room temperature in a closed container, for about 32 h, in order to standardise their degree of hydration. The hydrated aluminas were stored in well stoppered bottles and were denominated AL550, AL650 and AL750, according to the respective temperatures of calcination.

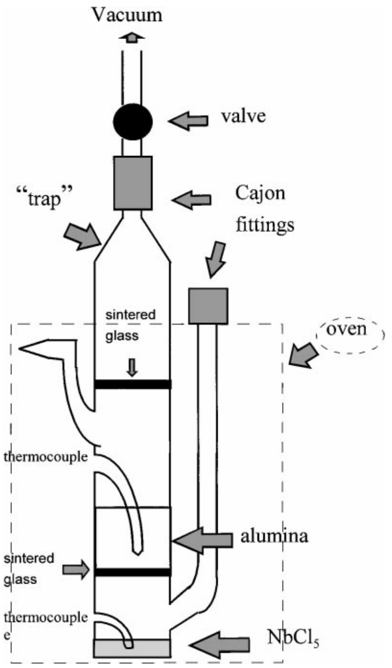


Fig. 1. Reactor used in the chemical vapour deposition of niobium pentachloride.

2.1.2. Chemical vapour deposition (CVD) of $NbCl_5$

About 10 g of an alumina support was placed in the CVD reactor shown in Fig. 1 and treated under a vacuum of 10^{-4}–10^{-5} Torr at 250, 350 or 450°C for 3 h, in order to control the degree of hydration of the surface. After this dehydration step, the reactor was sealed and transferred to a dry-box, where ca. 3.5 g of $NbCl_5$ were added to the bottom compartment of the reactor, under a nitrogen atmosphere. This amount of $NbCl_5$ is in great excess of the necessary for the deposition of a monolayer on the catalysts surface.

The reactor was again sealed and connected to a vacuum line, where it was heated to 150°C at a rate of 2°C/min and kept at this temperature for 15 h, under a vacuum of ca. 10^{-4} Torr. Under these conditions, the $NbCl_5$ sublimed and reacted with the alumina placed in the central compartment of the reactor. The excess of $NbCl_5$, which sublimed but did not react, condensed in the upper compartment, which was separated from the middle one by a porous glass plate. This avoided the contamination of the product with unreacted chloride.

After cooling down to room temperature, the glass seal shown in Fig. 1 was broken and the product was transferred to a tubular reactor under an inert atmosphere. The product was then hydrolysed, in order to decompose the $NbCl_5$, at 150°C under a 150 cm^3/min flow of synthetic air saturated with water vapour at 60°C (ca. 150 Torr water vapour pressure), for 5 h, after which acidic vapours could not be detected in the reactor effluent, using an universal indicator paper. The product was finally heated to 450°C at a rate of 3°C/min and kept at this temperature for 5 h, under a pure oxygen flow of ca. 100 cm^3/min.

The series of materials obtained with this procedure were denominated CNA*xy*, where *x* and *y* are numbers which correspond to the first figure, respectively, in the temperatures of calcination and dehydration of the alumina support. Thus, in a sample called CNA52, the alumina support was calcined at 550°C and dehydrated at 250°C before CVD.

With part of sample CNA52, a second CVD step was carried-out, after re-hydration under air saturated with water vapour at room temperature for 32 h, and dehydration at 250°C as described above, in order to obtain a sample with a higher niobium content. This sample was called CNA522.

Analysis of the CNA samples by XPS showed a considerable contamination of the surface with chloride anion, indicating that the hydrolysis treatment used was not enough for complete chloride removal. Thus, a second more severe hydrolysis was performed, in order to remove the residual chloride, as described in the next item.

2.1.3. Hydrothermal treatment for chloride removal

The samples were treated in a tubular reactor at 350°C for 9 h and further at 400°C for 9 h, under a flow of synthetic air saturated with water vapour at 70–80°C. Finally, they were treated at 440°C under a flow of oxygen saturated with water vapour at 70–80°C (water vapour pressure 233–355 Torr) for 8 h more. The treatment with oxygen aimed to guarantee the oxidation of any reduced niobium that might be present in the materials after the previous treatments, since the niobium sub-halides are considerably more resistant to hydrolysis than the corresponding penta-halides. At the end of this procedure, no silver chloride formation could be observed by bubbling the reactor effluent in a silver nitrate solution.

Only samples CNA52, CNA54, CNA522, CNA62, CNA64 and CNA72 were submitted to this treatment and the resulting materials constituted the NA series. No residual chloride could be detected by XPS on the surface of the NA samples.

As a control, a sample of alumina AL550 was submitted to the same severe hydrothermal treatment as the CNA samples and was called AL550T.

2.1.4. Impregnation of ammonium oxaloniobate

A sample containing ca. 6.5 wt.% niobium oxide was prepared by incipient wetness impregnation of alumina AL550 with ammonium oxaloniobate dissolved in an aqueous solution containing 0.3 mol/dm^3 oxalic acid. The alumina support was dried for 2 h at 150°C before the impregnation. The impregnated material was oven-dried at 120°C for 1 h and calcined under static air at 450°C for 2 h. This sample was denominated NAOX.

2.1.5. Calcination of niobic acid

A niobic acid sample obtained from Companhia Brasileira de Metalurgia e Mineração (batch AD-936) was calcined at 450°C for 3 h under static air and was designated NB450.

2.2. Characterisation

2.2.1. Elemental composition

The quantitative analysis of each metal in the samples was carried out by X-ray fluorescence spectroscopy (XRF) in a Phillips sequential spectrometer, model PW 1480, equipped with a rhodium tube. The samples were fused with lithium tetraborate in an 1:5 proportion and the mol% of each element was read from calibration curves especially constructed for matrices similar in composition to our samples.

2.2.2. Textural characterisation

The BET surface areas were determined from nitrogen adsorption isotherms at the normal boiling temperature of liquid nitrogen. The adsorption isotherms were obtained in a Micromeritics ASAP (Accelerated Surface Area and Porosimetry), model

2400. The samples were pre-treated in situ under a 50 mTorr vacuum, at 300°C, for 1 h.

2.2.3. Temperature-programmed desorption (TPD) of ammonia

A conventional flow-type TPD apparatus was used, with a thermal conductivity detector. About 350 mg of sample were placed in a quartz U-tube sample-holder. Each sample was pre-treated in situ, by heating under a flow of nitrogen at 350°C for 1 h. The system was then cooled to 175°C and adsorption of ammonia was carried out by injection of 35.8 μmol pulses into a helium flow of 50 cm^3/min. Saturation of the sample surface with ammonia was considered to be complete when pulses of constant height were seen to elute from the reactor. The sample was then kept under the helium flow at 175°C for 1 h.

Desorption of ammonia was performed by heating of the sample to 500°C at a linear rate of 15°C/min under a 50 cm^3/min flow of helium. Finally, the sample was kept at 500°C until the detector signal returned to the baseline level. The total amount of desorbed ammonia was determined by comparison of the integrated area of the TPD signal with the area obtained with standard 35.8 μmol pulses of ammonia.

2.2.4. Infrared spectroscopy of adsorbed pyridine

An FTIR spectrometer manufactured by Nicolet (60XR model) with 4 cm^{-1} resolution was used in the experiments.

A self-supported wafer, containing ca. 20 mg/cm^2 of sample, was placed in a glass cell and was evacuated at 480°C for 16 h, under a vacuum of 10^{-5} Torr. The sample was then brought to 150°C and exposed to 4 Torr of pyridine vapour for 10 min. The excess pyridine was removed by evacuation at 150°C until the vacuum returned to the level of 10^{-5} Torr. The spectra of adsorbed pyridine were recorded at room-temperature.

2.3. Catalytic ativity

Catalytic activity of the materials in the dealkylation of cumene was measured in a tubular flow glass micro-reactor at 370°C and atmospheric pressure. The samples were pre-treated in situ at 450°C for 30 min under a 38 cm^3/min (STP) flow of nitrogen. The temperature was then brought to 370°C and cumene vapour was fed to the reactor by bubbling the nitrogen carrier through a saturator kept at 30°C. The reaction products were analysed by means of an on-line gas-chromatograph equipped with a flame ionization detector.

The catalytic activities were calculated from the measured conversions, assuming zero-order reaction kinetics [6].

3. Results

Table 1 summarises the results for surface area, niobia content, total desorbed ammonia and catalytic activity in cumene dealkylation for the several samples.

Comparing the surface areas of the niobia–alumina samples with those of the corresponding alumina supports it is observed that no significant changes in the textural properties of the aluminas were caused by niobium incorporation. The small differences observed with the samples supported on AL650 and AL750 may be fully explained by the increase in density of the samples due to niobium incorporation, i.e., the surface areas expressed per mass of alumina are the same, within experimental error, as those of the aluminas themselves. With the samples supported on AL550, a larger difference is observed, but that is apparently due to the hydrothermal treatment for chloride removal rather than to the incorporation of niobium by CVD, since a significant loss of surface area was observed by submitting AL550 to the same thermal treatment as the niobia–aluminas (alumina AL550T).

The hydrothermal treatment does not seem to have influenced the density of acid sites, measured by desorption of ammonia, as the values were very similar for samples AL550 and AL 550T. Also the calcination temperature of the aluminas had only a small influence on the acid site density.

With the niobia–aluminas supported on AL550 and AL650, the materials with the lowest niobium content had higher densities of acid sites than the corresponding alumina supports, but the acidity decreased, within each series, with an increase in the niobium content. A comparison of NAOX and NA54, with very similar niobia contents, shows that the method of niobium incorporation had little effect on the density of acid sites. The unsupported Nb_2O_5 sample (NB450) had a considerably higher acidity than the alumina-supported ones, on a surface area basis.

Table 1
Results for chemical composition, surface area, TPD of ammonia and catalytic activity in cumene dealkylation at 370°C

Szmple	Nb_2O_5 (wt.%)	Surface area (m^2/g)	Desorbed NH_3 (μmol/m^2)	Catalytic activity (μmol/m^2 h)
AL550	–	246	2.23	2.77
AL550T	–	212	2.18	0.95
NAOX	6.5	228	2.42	0.11
CNA54	6.5	212	n.a.[a]	2.28
NA54	6.6	212	2.38	1.09
CNA52	8.2	204	n.a.[a]	1.83
NA52	8.2	204	2.15	0.60
NA522	14.0	182	1.77	0.29
AL650	–	209	2.05	n.a.[a]
NA64	5.1	188	2.47	n.a.[a]
NA62	7.2	187	2.20	n.a.[a]
AL750	–	183	2.07	n.a.[a]
NA72	5.6	167	1.99	n.a.[a]
NB450	100.0	108	2.99	19.7

[a] Not available.

Fig. 2 shows the TPD profiles for samples AL550 and NB450, normalised on a basis of signal intensity per unit mass. Clearly, the profile for the alumina is displaced towards higher temperatures as compared to the niobia sample, indicating that stronger acidic sites are present on the alumina surface. In order to assess, semi-quantitatively at least, the effect of niobium deposition on the acid site strength distribution, the desorption curves were partitioned into arbitrarily chosen temperature ranges, assuming that the ammonia retained on stronger sites desorbs at higher temperatures. The results are shown in Fig. 3. It is apparent

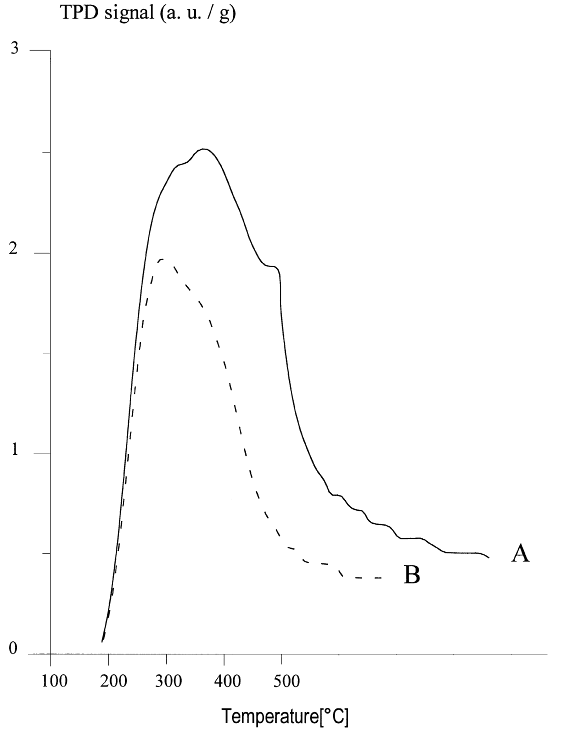


Fig. 2. Temperature-programmed desorption of ammonia from (A) γ-alumina calcined at 550°C and (B) niobic acid calcined at 450°C.

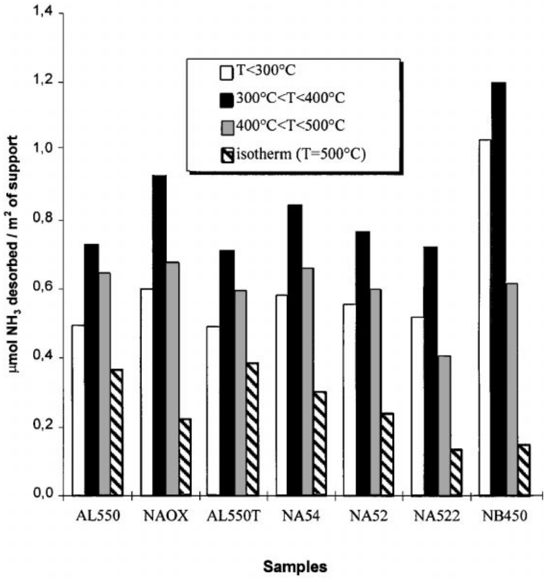


Fig. 3. Ammonia desorbed at different temperature ranges during temperature-programmed desorption.

that, with respect to the alumina surface, addition of ca. 6.5% Nb_2O_5 (NAOX and NA54) had the effect of decreasing the amount of strongly acidic sites (ammonia desorbed between 400 and 500°C and during the isothermal step at 500°C) and increasing the amount of sites with weak to medium acidity (175–300°C and 300–400°C ranges, respectively). Further addition of niobia resulted in a decrease in amount of all sites, but the effect on the stronger sites was more pronounced.

Fig. 4 shows the infrared spectra of adsorbed pyridine in the wave number range of 1400–1700 cm^{-1}, where bands due to skeletal vibrations of the pyridine ring can be observed [7]. The band most characteristically associated with pyridine adsorbed on Brønsted acid sites (pyridinium ions, $C_5H_6N^+$) [7,8] occurs at ca. 1580 cm^{-1} and could not be observed, neither in the spectra of the alumina supports, nor in the ones of the niobia–aluminas. The bands at ca. 1450, 1490, 1575, and 1620 cm^{-1} can be associated with pyridine coordinatively bonded to Lewis acid sites [8]. In contrast, in the spectrum of pyridine adsorbed on NB450, shown in Fig. 5, bands at 1542 and 1636 cm^{-1}, both characteristic of pyridinium ions, are clearly apparent. Datka et al. [9] claim to have found small but growing amounts of Brønsted acid sites on niobia–aluminas with increasing niobium contents in the range of 8–19 wt.% of niobia. However, from their spectra, it is difficult to ascertain whether these sites were really present in the samples containing 8–12% niobia.

In the cumene dealkylation reaction at 370°C, the only significant reaction products were benzene and

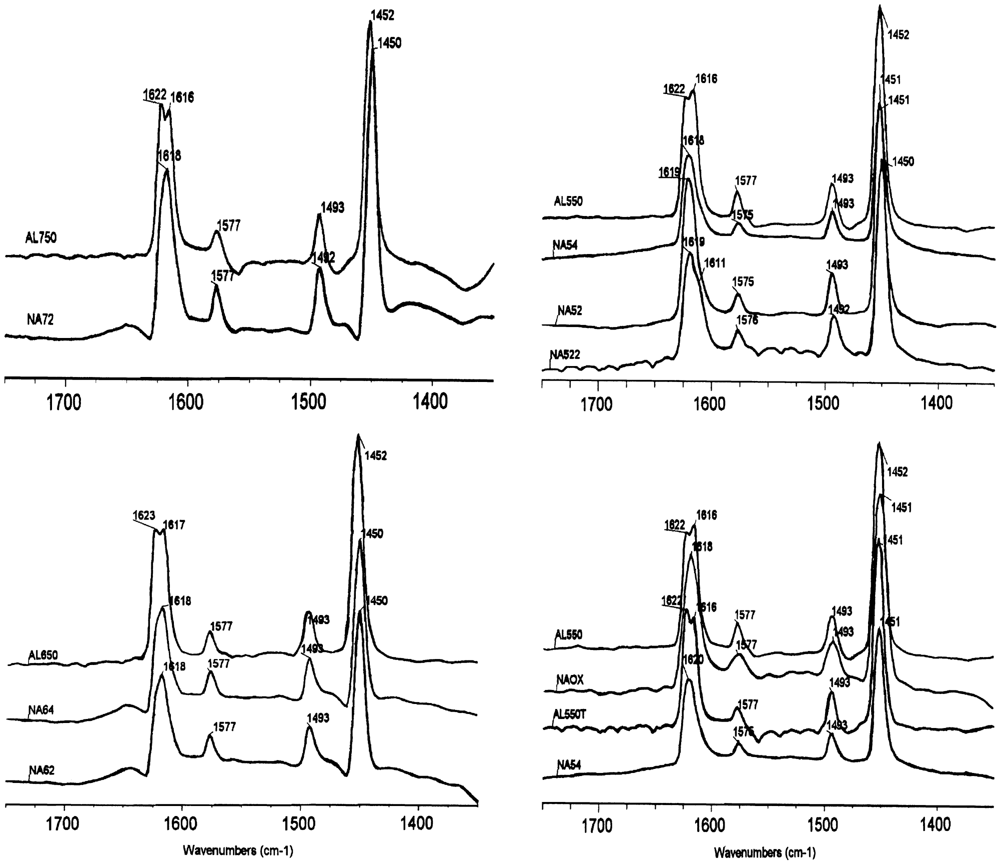


Fig. 4. Infrared spectra of adsorbed pyridine in the wave number range 1350–1750 cm^{-1} for the niobia–aluminas and respective supports.

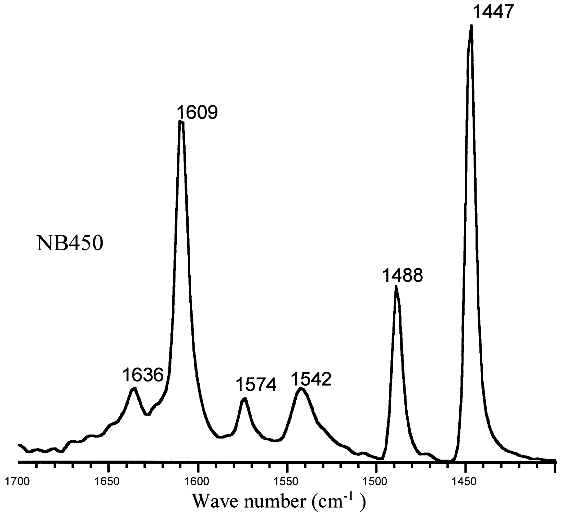


Fig. 5. Infrared spectrum of adsorbed pyridine (150°C) in the wave number range 1400–1700 cm^{-1} on niobic acid calcined at 450°C.

propene. The catalysts suffered a slow deactivation over the 40–80 min duration of each experiment and the activity results reported in Table 1 correspond to values extrapolated to zero time-on-stream (initial activity).

Comparatively to the TPD results, catalytic activity in cumene dealkylation was much more sensitive to the history and composition of the samples. The niobia–aluminas of the NA series, NA52 and NA54, had an activity considerably smaller than either alumina AL550 or the corresponding niobia–aluminas of the CNA series. At the same time, alumina AL550T had an activity similar to that of NA54. Therefore, the strong loss in dealkylation activity after the severe hydrothermal treatment was apparently a consequence of the effects of the treatment itself, rather than of chloride removal from the surface of the niobia–aluminas.

Within the NA series, there was a strong decrease of activity with increasing niobia content (NA54> NA52>NA522), but catalyst NAOX, with composition similar to NA54, had a much lower activity.

By comparison with the aluminas and niobia–aluminas, the Nb_2O_5 sample was more active by 1–2 orders of magnitude. This is in line with expectations, since cumene dealkylation is generally thought to occur on Brønsted sites [6,10] and those were visible by pyridine adsorption only on the pure niobia.

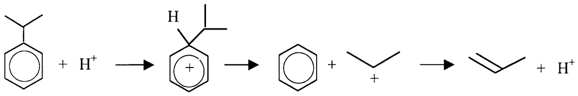
4. Discussion

The results for TPD of adsorbed ammonia indicate a small increase in acid site density with incorporation of ca. 6.5 wt.% of niobia, followed by a decrease with increasing niobium content. This behaviour has been reported before for niobia–aluminas prepared by impregnation [11].

Several studies [12,13] use the concept of cation electronegativity in order to explain the increase in acid strength of oxides with addition of a dopant: the acid strength of the oxide is thought to be increased upon addition of a more electronegative cation, due to inductive effects. Using the method proposed by Tanaka and Ozaki [14] for the calculation of electronegativities, values of 17.6 and 10.5 are obtained for Nb^{5+} and Al^{3+}, respectively. The increase in the number of acid sites when a small amount of niobia is added to the alumina may therefore be related to the increase in acid strength of otherwise very weakly acidic sites on the alumina surface, caused by the inductive effects of neighbouring niobium atoms. According to our former results [5], niobium pentachloride adsorbs indistinctly on surface oxide and hydroxyl sites and then looses an average of two chlorine atoms by reaction with neighbouring surface hydroxyls. After hydrolysis, highly dispersed NbO_x species are obtained, linked to the surface by bridging Nb–O–Al bonds. The effect on neighbouring coordinatively unsaturated Al^{3+} sites probably occurs very much in the same way as proposed by Tanabe et al. [15] for the effect of sulphate on the acidity of oxides. Further addition of niobium then results in a decrease of acid site density, due to physical blockage of the sites. This interpretation is consistent with the acid strength distributions shown in Fig. 3: while the addition of 6.5% niobia resulted in an increase in number of weak to medium acidity sites, further niobium addition caused a non selective decrease in site density of all acid strengths.

The results for catalytic activity in the cumene dealkylation reaction followed the same general trend as the TPD results (the very low activity of sample NAOX being a notable exception), but the sensitivity to sample composition and history was much more pronounced. This is not surprising, since the TPD technique measures all sites capable of adsorbing ammonia and only a fraction of these is likely to be active in the dealkylation reaction.

Cumene dealkylation is generally thought to be a reaction catalysed by Brønsted acid sites, according to the following mechanism [10]:



The fact that the pure niobia catalyst was much more active in this reaction than the aluminas and niobia–aluminas is in line with the proposed mechanism, as only on NB450 could Brønsted acid sites be observed in the infrared spectra of adsorbed pyridine. Still, the activity of the remaining catalysts, although small, was measurable at 370°C and followed some definite trends.

The existence of Brønsted sites on the γ-alumina surface has been the object of much debate and it has been proposed [16] that a small Brønsted acidity may be developed by adsorption of traces of water vapour on coordinatively unsaturated Al^{3+} ions (Lewis acidic sites), where the water molecules are polarised to produce acidic protons:

$$Al^{3+}\text{-}\Box + H_2O \rightarrow Al^{3+} \leftarrow OH_2^{\delta+}$$

The slight increase in Brønsted acidic activity upon addition of a small amount of niobium may be due to the inductive effect discussed above on neighbouring sites. The strong decrease in dealkylation activity with further addition of niobium may be attributed to physical blockage of the sites capable of generating the Brønsted acidity.

The effect of the hydrothermal treatment on the activity of the alumina and niobia–aluminas was striking. It may be expected that the strongest Lewis sites will also give rise to the strongest Brønsted sites when water vapour is adsorbed. The strongest sites are likely to occur on surface defects, such as anionic vacancies and crystallographic imperfections, which may be healed due to the steam-treatment. Some evidence for that is the significant loss of surface area observed when AL550 was steam-treated to produce AL550T, indicating that some sintering has occurred. Sintering is expected to affect most strongly the high energy sites associated with surface defects. In our previous work, we demonstrated by infrared spectroscopy that the steam treatment also had a significant effect on the hydroxyl structure of the alumina surface: by reference to the model proposed by Knözinger and Ratnasamy [17], it increased the proportion of basic, monocoordinated hydroxyls at the expenses of the acidic, tricoordinated ones.

The very low activity of the sample prepared by impregnation of ammonium oxaloniobate, NAOX, is difficult to explain at the light of available experimental evidence. The XPS analysis showed this sample to have a higher surface carbon content than the remaining samples. With the samples that were prepared by CVD of niobium pentachloride, the surface carbon comes mostly from adsorption of carbon dioxide and hydrocarbons, both from the atmosphere and from the XPS vacuum chamber. In contrast, some of the carbon on the NAOX may have come from decomposition of oxalate during calcination. This may have led to deactivation of the sites responsible for generation of Brønsted acidity.

5. Conclusion

Niobia–aluminas with no residual chlorine detectable by XPS analysis were prepared by chemical vapour deposition of niobium pentachloride on γ-alumina followed by treatment with water vapour. Addition of niobia up to a level of ca. 6.5 wt.% resulted in a slight increase both in the ammonium adsorption capacity and in the catalytic activity for cumene dealkylation of most samples. Further deposition of niobia, however, resulted in a decrease in both properties.

Brønsted acidic sites strong enough to protonate pyridine could only be observed on the surface of the pure niobium oxide, but they may be formed under reaction conditions on the surface of the alumina and niobia–aluminas, presumably by adsorption of traces of water vapour from the carrier gas stream, as these materials had a non-negligible activity in cumene dealkylation.

The steam treatment had a strongly negative effect on the cumene dealkylation activity of both the alumina support and the niobia–aluminas.

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