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Ammonium complex of niobium as a precursor for the preparation of Nb_2O_5/Al_2O_3 catalysts

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Abstract

Ammonium oxalate complex of niobium was investigated as an aqueous precursor for the preparation of x% Nb_2O_5/Al_2O_3 ($x = 5$, 10, 20 and 30 wt.%) samples. Catalysts with the same Nb_2O_5 contents were also prepared from the traditional niobium oxalate/oxalic acid aqueous solution. The catalysts were characterized by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), temperature-programmed reduction (TPR), infrared spectroscopy of chemisorbed pyridine and X-ray photoelectron spectroscopy (XPS). A comparison with the preparation method using the niobium oxalate salt was performed. The results showed that the niobium precursor influence the species growing leading to phases with different reducibility. The XPS revealed the presence of multilayers of niobium oxide on the Nb_2O_5/Al_2O_3 samples prepared by using niobium ammonium oxalate complex, while the ones obtained from niobium oxalate led to Nb_2O_5 particles islands. The addition of niobium oxide decreased the fraction of Lewis acid sites and increased the fraction of Brønsted acid sites, independent of the precursor salt. However, the creation of BAS was more pronounced on the Nb_2O_5/Al_2O_3 samples prepared from niobium oxalate.

Keywords: Alumina-supported niobium oxide; Catalyst preparation; Catalyst characterization; Niobium oxalate precursor salt; Niobium ammonium oxalate complex precursor salt

1. Introduction

Supported metal oxides are extensively studied as heterogeneous catalysts in numerous reactions [1,2]. The catalytic properties of supported metal oxides such as niobium oxide are directly related to the molecular structure of the surface niobium oxide species, which depends on the nature of the support and the surface coverage [3].

Several surface species have been identified on supported niobium oxide. Raman studies showed the presence of NbO_4 and NbO_6 species on alumina-supported niobium oxide systems [4–6]. At low surface coverage, tetrahedral NbO_4 structures are present. At high surface coverage, polymerized NbO_6 species are typically found. On silica-supported niobium oxide systems, only isolated surface niobia species are present. XANES and EXAFS analysis reveal three surface species on alumina-supported niobium oxide: NbO_4 monomer, Nb_2O_7 dimer and niobic acid-like polymer [7]. At low niobium oxide contents, the results suggest the presence of monomer and dimer,

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whereas the niobic acid-like compound is the main surface at high loadings.

According to Wachs et al. [8], the preparation method and niobium precursors do not affect the molecular structures of surface niobia species, but they determine their dispersion. Different niobium oxide precursors and preparation methods have been used for the preparation of supported niobium oxide catalysts such as: (i) aqueous impregnation with niobium oxalate [4]; (ii) impregnation of niobium ethoxide using organic solvents [9,10]; and (iii) chemical vapor deposition of niobium ethoxide or niobium pentachloride [11]. The niobium oxalate possesses low solubility in aqueous solutions, which can be increased by the addition of oxalic acid. However, the niobium oxalate and the oxalic acid precipitate from solution at high oxalic acid concentrations. The use of niobium ethoxide or niobium pentachloride requires a controlled environment and special procedures to avoid the decomposition of the precursor in the presence of water and to control the density of surface hydroxyl groups.

The preparation of supported niobium oxide catalysts using an ammonium oxalate complex of niobium as a precursor is not so usual [12,13]. Recently, Nb_2O_5/Al_2O_3 systems prepared by impregnation of alumina with niobium ammonium oxalate complex were used as support of Co catalysts on the CO hydrogenation reaction. The niobium addition decreased the methane formation, whereas the selectivity towards long-chain hydrocarbons (gasoline and diesel fraction) strongly increased. This promoting effect of Nb_2O_5 on liquid hydrocarbon selectivity revealed the important role of supported oxide on the Fischer–Tropsch synthesis.

The aim of this work was to study the niobium ammonium oxalate complex as a precursor for the preparation of Nb_2O_5/Al_2O_3 catalysts. A comparison with the preparation method using the niobium oxalate salt as a precursor was performed.

2. Experimental

2.1. Catalyst preparation

Niobium oxalate and niobium ammonium oxalate complex were supplied by CBMM and alumina by Degussa. Nb_2O_5 was prepared by calcination of niobium ammonium oxalate complex and niobium oxalate precursor salts in air flow (50 ml/min) at 873 and 823 K, respectively. Al_2O_3 was calcined in air flow (50 ml/min) at 823 K for 16 h.

The Nb_2O_5/Al_2O_3 samples were prepared by using two different methods:

(i) Al_2O_3 impregnation with an aqueous solution of the desired amount of the niobium ammonium oxalate complex, labeled x% Nb_2O_5/Al_2O_3 (NAC) ($x = 5$, 10, 20 and 30 wt.%).
(ii) Al_2O_3 impregnation with an aqueous solution of niobium oxalate in oxalic acid at pH = 0.5, labeled x% Nb_2O_5/Al_2O_3 (NO) ($x = 5$, 10 and 20 wt.%).

After impregnation, the samples were dried at 373 K, under vacuum and calcined under air flow at 823 K for 16 h.

2.2. Catalyst characterization

The BET surface areas were determined from nitrogen adsorption isotherms at the liquid nitrogen temperature. The adsorption isotherms were obtained in a Micromeritics ASAP equipment, model 2000. The samples (280 mg) were pre-treated in situ under vacuum at 573 K for 3 h.

The X-ray diffraction measurements (DRX) were carried out in a Freiberger Prazisionsmechanik equipment, using Cu Kα radiation (40 kV, 30 mA).

The diffuse reflectance spectra were recorded between 200 and 800 nm in a UV-Vis NIR spectrometer (Cary 5—Varian) equipped with an integrating sphere (Harrick). Al_2O_3 was used as reference.

X-ray photoelectron spectroscopy (XPS) analyses were performed in a Perkin-Elmer 1257 spectrometer using Mg Kα (1253.6 eV) radiation. The vacuum in the spectrometer chamber was 10^{-9} Torr, and the charge correction was obtained by using the Al 2p emission at 74.0 eV line as reference. The Nb/Al surface ratios of the niobium oxide on the alumina support were calculated from photoelectron peak areas of the Nb 3d and Al 2p photoelectron lineshapes after correction of the photoionization cross-sections and photoelectron mean free paths [14].

Temperature-programmed reduction (TPR) was conducted using a conventional apparatus equipped with a thermal conductivity detector. Each sample was pre-treated in an argon flow at 423 K for 30 min, and cooled down to room temperature. The reduction was performed by heating the sample from 298 up to 1273 K at a rate of 10 K/min using a 1.65% H_2/Ar mixture flow.

Infrared spectroscopy analyses of adsorbed pyridine were carried out in an FTIR Perkin-Elmer spectrometer (model 2000) with 4 cm^{-1} resolution. A self-supported wafer, containing ca. 25 mg/cm^2 of sample, was evacuated at 698 K for 1 h, cooled down to room temperature and then a first spectrum was recorded. The sample was then heated up to 423 K and exposed to 1 Torr of pyridine. After evacuation at 423 K for 1 h, the spectrum of adsorbed pyridine was recorded at room temperature.

3. Results

Table 1 presents the niobium oxide content and the surface area of Nb_2O_5/Al_2O_3 samples prepared by using niobium ammonium oxalate complex and niobium oxalate as precursors. Comparing the surface areas of the Nb_2O_5/Al_2O_3 samples with that of the alumina support, it is observed that the increase of niobium oxide content decreased the surface area independently of the precursor used. The samples prepared from the niobium ammonium oxalate complex exhibited surface areas slightly higher than the ones prepared from niobium oxalate precursor.

The DRS spectra of Nb_2O_5 and Nb_2O_5/Al_2O_3 samples prepared by different precursors are shown in Fig. 1. All Nb_2O_5/Al_2O_3 samples exhibited a

Table 1
Chemical composition and BET surface area of the Nb_2O_5/Al_2O_3 samples prepared by using niobium ammonium oxalate complex (NAC) and niobium oxalate (NO)

Sample	Nb_2O_5 (wt.%)	Surface area (m^2/g)
Al_2O_3	–	196.9
5% Nb_2O_5/Al_2O_3 (NAC)	4.30	201.1
10% Nb_2O_5/Al_2O_3 (NAC)	9.45	195.9
20% Nb_2O_5/Al_2O_3 (NAC)	19.90	178.4
30% Nb_2O_5/Al_2O_3 (NAC)	31.30	149.6
5% Nb_2O_5/Al_2O_3 (NO)	4.51	198.8
10% Nb_2O_5/Al_2O_3 (NO)	10.83	186.7
20% Nb_2O_5/Al_2O_3 (NO)	17.24	167.8

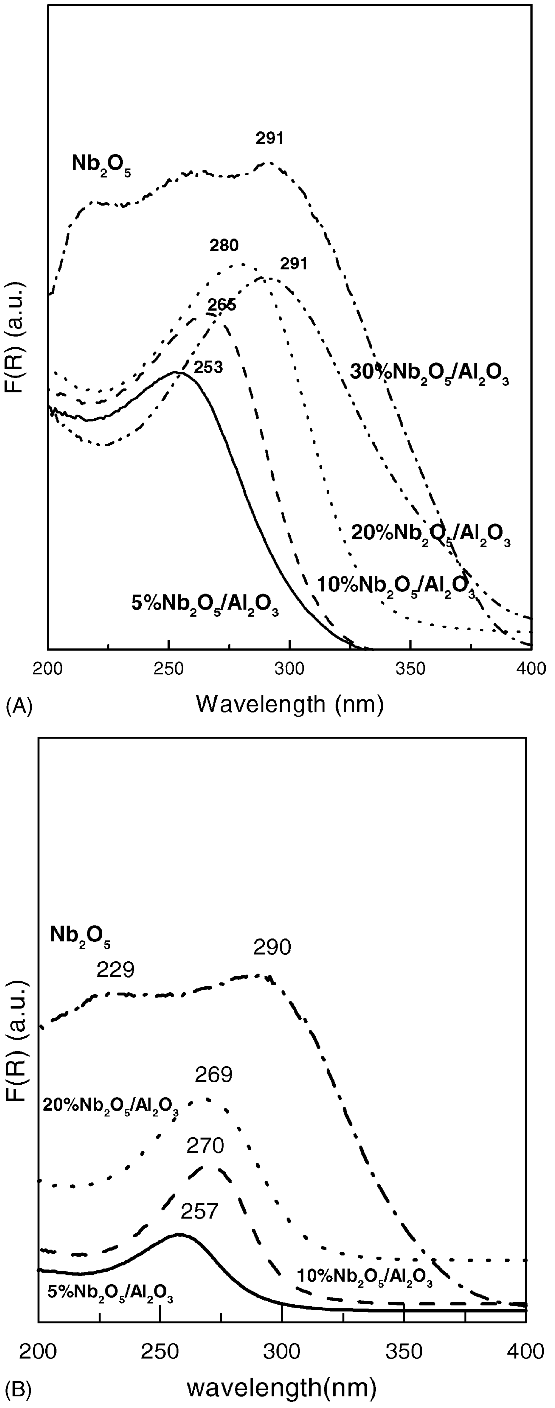

Fig. 1. DRS spectra of Nb_2O_5/Al_2O_3 samples prepared by using: (A) niobium ammonium oxalate complex; (B) niobium oxalate.

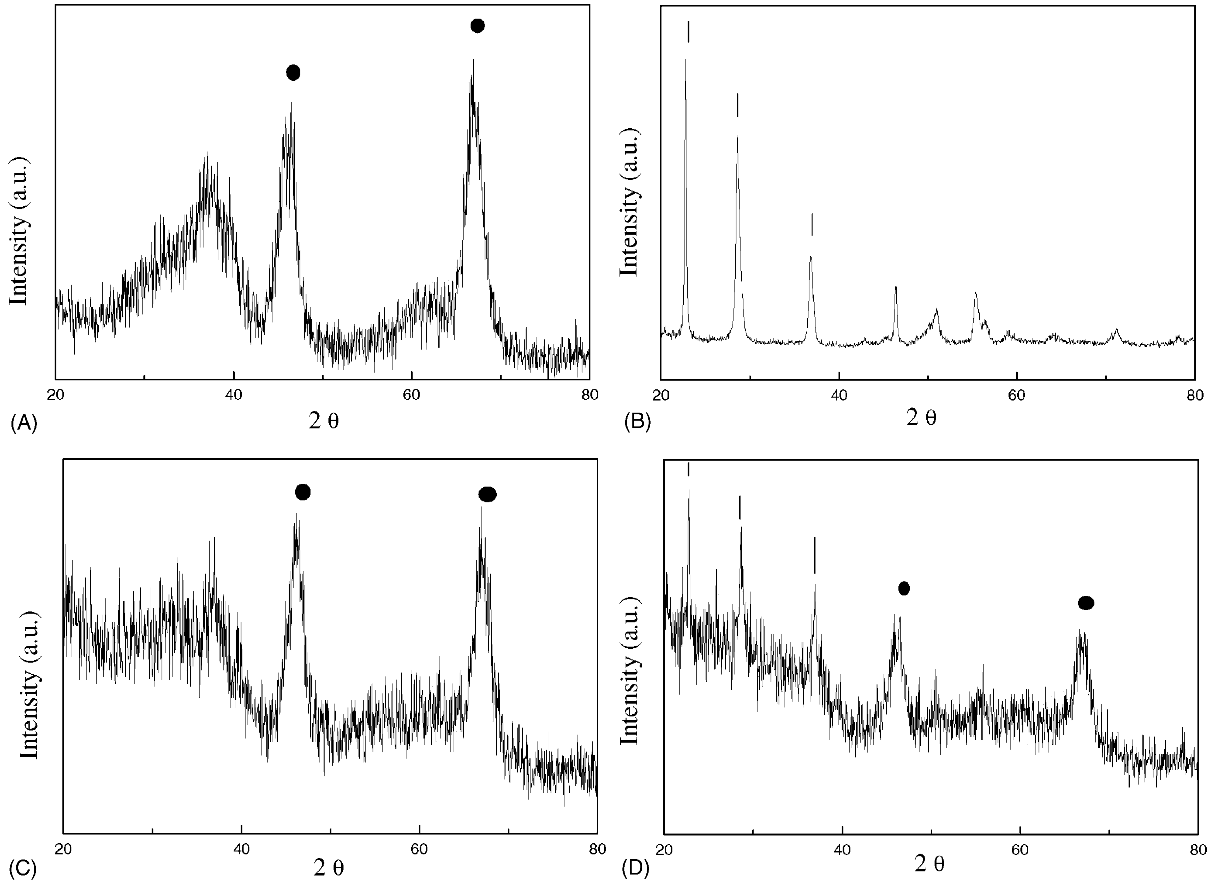

Fig. 2. XRD patterns of (A) Al_2O_3; (B) Nb_2O_5; (C) 20% Nb_2O_5/Al_2O_3 (NAC); (D) 30% Nb_2O_5/Al_2O_3 (NAC). Points and straight lines corresponds to diffraction lines characteristic of Al_2O_3 and Nb_2O_5.

Table 2
Binding energies of Al 2p, O 1s and Nb 3d levels and Nb/Al surface atomic ratios of the niobium alumina systems

Sample	Binding energy (eV)			Atomic ratio	
	Al 2p	O 1s	Nb 3d	$(Nb/Al)_{surface}$	$(Nb/Al)_{bulk}$
Al_2O_3	74.0	531.1	–	–	–
5% Nb_2O_5/Al_2O_3 (NAC)	74.0	530.8	206.8	0.184	0.020
10% Nb_2O_5/Al_2O_3 (NAC)	74.0	530.8	206.8	0.138	0.043
20% Nb_2O_5/Al_2O_3 (NAC)	73.8	530.6	206.8	0.208	0.096
30% Nb_2O_5/Al_2O_3 (NAC)	74.0	530.8	207.0	0.548	0.164
5% Nb_2O_5/Al_2O_3 (NO)	74.0	530.6	206.6	0.307	0.026
10% Nb_2O_5/Al_2O_3 (NO)	74.0	530.4	206.6	0.536	0.056
20% Nb_2O_5/Al_2O_3 (NO)	74.0	530.5	206.7	0.310	0.127
Nb_2O_5 (NAC)	–	530.0	207.0	–	–

metal–ligand charge transfer band. This band was shifted to higher wavelength as the niobium content increased. The 30% Nb_2O_5/Al_2O_3 (NAC) sample showed a band at 291 nm, which was also observed on bulk Nb_2O_5, suggesting the presence of this species on this sample.

The X-ray diffractogram of samples prepared by using niobium ammonium oxalate complex are shown in Fig. 2. The 20% Nb_2O_5/Al_2O_3 presented only the alumina lines (Fig. 2C), while the 30% Nb_2O_5/Al_2O_3 showed also the lines of Nb_2O_5 (Fig. 2D).

Table 2 presents the binding energies of Al 2p, O 1s and Nb 3d levels and the Nb/Al surface ratios calculated by XPS analysis. No significant changes were observed on the Nb 3d binding energy as a function of both niobium oxide content and precursor salt. The Nb_2O_5/Al_2O_3 samples presented approximately the same binding energy of bulk Nb_2O_5. The Nb/Al surface atomic ratios were higher than the calculated Nb/Al bulk atomic ratios for both precursor salts. However, the samples prepared using niobium oxalate precursor presented higher Nb/Al surface ratio than the ones obtained with niobium ammonium oxalate complex.

Fig. 3 showed the curve of Nb/Al surface atomic ratio versus Nb/Al bulk atomic ratio of the Nb_2O_5/Al_2O_3

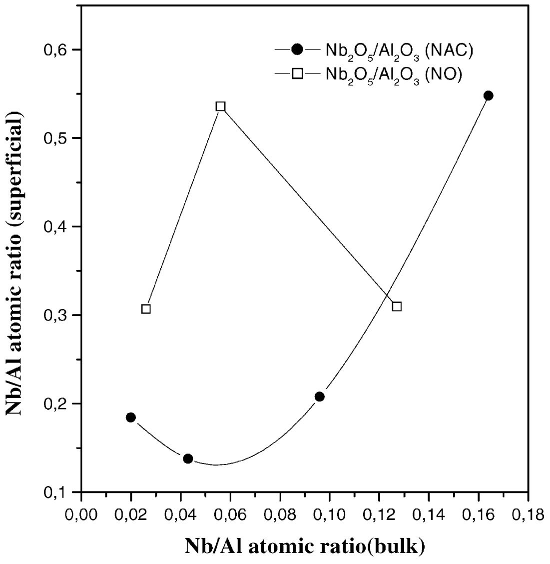

Fig. 3. Nb/Al surface atomic ratios as a function of Nb/Al bulk atomic ratios of Nb_2O_5/Al_2O_3 samples.

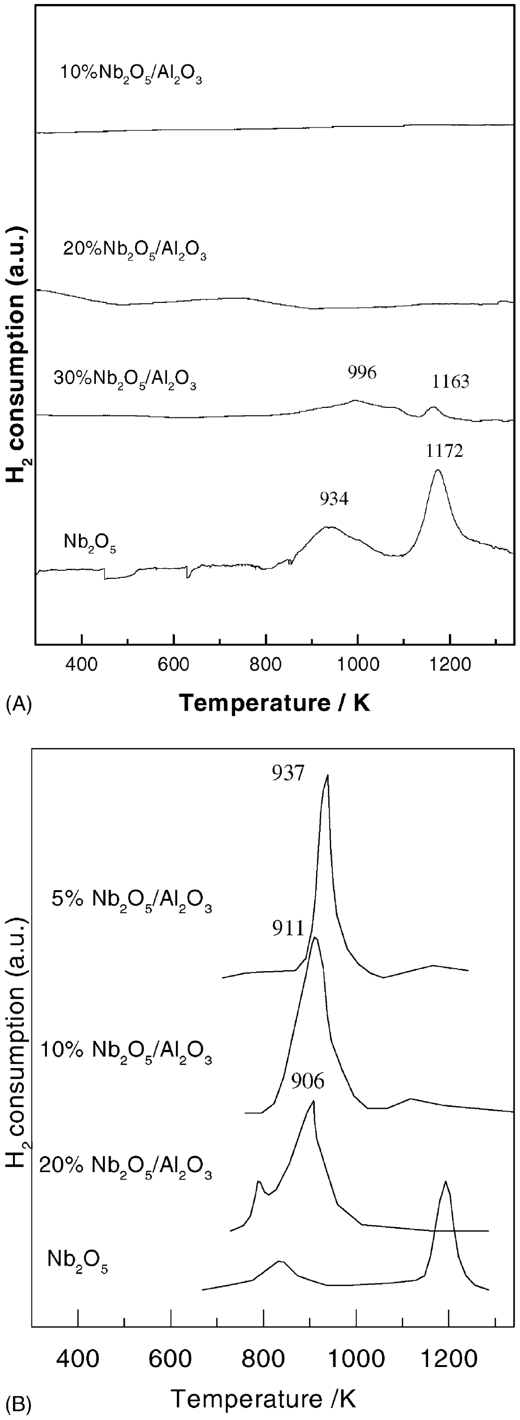

Fig. 4. TPR profiles of the Nb_2O_5/Al_2O_3 samples prepared by using: (A) niobium ammonium oxalate complex; (B) niobium oxalate.

samples. The Nb/Al surface ratio was strongly influenced by the nature of the precursor. The $(Nb/Al)_{surface}$ values of the samples prepared from niobium ammonium oxalate complex exhibited an exponential growth as the niobium content increased. On the other hand, $(Nb/Al)_{surface}$ values of the systems obtained by using the niobium oxalate as precursor showed a maximum around 10 wt.% of niobium oxide.

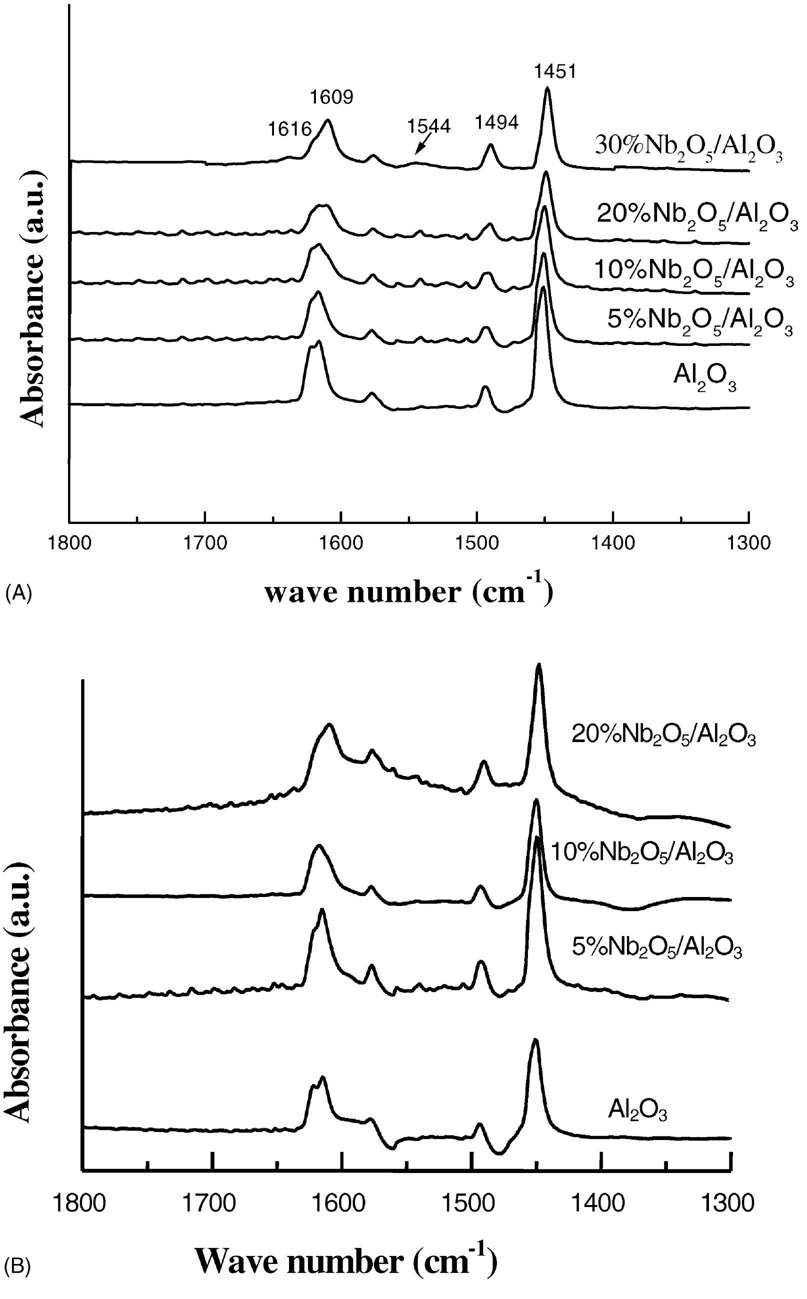

Fig. 5. Infrared spectra of adsorbed pyridine on the (A) Nb_2O_5/Al_2O_3 (NAC) samples; (B) Nb_2O_5/Al_2O_3 (NO) samples.

The reduction profile of Nb_2O_5/Al_2O_3 samples are shown in Fig. 4. For the sample prepared using niobium ammonium oxalate complex as precursor, only the 30 wt.% Nb_2O_5/Al_2O_3 sample exhibited a significant hydrogen consumption, presenting a reduction profile similar to the one obtained for bulk Nb_2O_5. On the other hand, for the Nb_2O_5/Al_2O_3 (NO) samples, a hydrogen uptake was already observed on the sample containing just 5 wt.% of Nb_2O_5.

Fig. 5 shows the infrared spectra of adsorbed pyridine in the range between 1300 and 1800 cm^{-1}, where bands due to skeletal vibrations of the pyridine ring can be observed. According to the literature, the band associated to pyridine adsorbed on Brønsted acid sites (BAS) appears at 1535–1550 cm^{-1}, while those related to pyridine coordinatively bonded to Lewis acid sites (LAS) are observed at 1440–1460 and 1600–1635 cm^{-1} [15,16]. The band at 1493 cm^{-1} corresponds to σ_{19a} vibrational mode, which occurs for Lewis and BAS, simultaneously [17]. The IR spectra of chemisorbed pyridine revealed Lewis acidity in all Nb_2O_5/Al_2O_3 samples, independent of the precursor salt. However, it was not clearly detected from the spectra the band attributed to BAS.

The LAS were quantified by integration of the band at 1453 cm^{-1}. Since the band associated to BAS around 1544 cm^{-1} is hardly identified, they were estimated through the ratio of the integrated areas of the bands at 1453 and 1493 cm^{-1} (LAS/(LAS + BAS)) as previously described [17]. The calculated values are presented in Table 3. An increase of niobium oxide content caused a decrease in the LAS concentration of Nb_2O_5/Al_2O_3 (NAC) samples. The concentration of the LAS increased with niobia loading up to 5 wt.% of niobium oxide on the Nb_2O_5/Al_2O_3 (NO) samples and then decreased. Furthermore, the addition of niobia led to the appearance of BAS, mainly on the samples prepared from oxalate precursor.

Table 3
LAS concentration and intensity ratios of the bands at 1451 and 1494 cm^{-1}

Sample	LAS[a]	(LAS/LAS + BAS)[b]
Al_2O_3	1	1
5% Nb_2O_5/Al_2O_3 (NAC)	0.673	0.859
10% Nb_2O_5/Al_2O_3 (NAC)	0.628	0.775
20% Nb_2O_5/Al_2O_3 (NAC)	0.641	0.730
30% Nb_2O_5/Al_2O_3 (NAC)	0.535	0.466
5% Nb_2O_5/Al_2O_3 (NO)	1.208	0.806
10% Nb_2O_5/Al_2O_3 (NO)	0.827	0.672
20% Nb_2O_5/Al_2O_3 (NO)	0.839	0.562

[a] Obtained by integration of the band at 1453 cm^{-1} and normalized with respect to alumina.

[b] Obtained by the ratio of integrated bands at 1453 cm^{-1} (LAS) and 1493 cm^{-1} (LAS + BAS) and normalized with respect to alumina.

4. Discussion

The position of the charge transfer band was approximately the same on the Nb_2O_5/Al_2O_3 samples containing the same niobium oxide content and prepared using either niobium ammonium oxalate complex or niobium oxalate. This result suggests the presence of the same niobium oxide species on both systems. Moreover, the charge transfer band shifted towards high wavelength as the niobium oxide content increased, regardless of the nature of precursor salt.

Tanaka et al. [18] also used the DRS analysis to characterize Nb_2O_5/SiO_2 samples containing different niobium oxide loadings. The UV-Vis spectra showed that the charge transfer band around 260 nm on the 10% Nb_2O_5/SiO_2 sample shifted to low wavelength as the niobium content decreased to 0.1 wt.% of niobium oxide. According to the authors, the samples containing low niobium oxide loading had monomeric and oligomeric NbO_4 tetrahedra species, whereas the high-loading catalysts contained Nb_2O_5 particles.

In the literature [19–23], the shift of the UV-Vis band position as the metal oxide content increase is generally attributed to the enhance of polymerization degree. Therefore, the DRS analysis of Nb_2O_5/Al_2O_3 samples in this work suggested that the increase in niobium oxide content led to an increase in the degree of polymerization of niobium oxide species. According to the literature [4–7], the Nb_2O_5/Al_2O_3 samples containing low niobium oxide loading could be represented by monomer or dimer species, whereas the high niobium oxide loading samples could have the presence of Nb_2O_5 particles. These results are in agreement with DRX analysis, which identified bulk Nb_2O_5 particles on the high-loading Nb_2O_5/Al_2O_3 (NAC) samples. However, no significant effect of the nature of the precursor salt on both the molecular structure of niobium oxide and the extent of the polymerization degree could be observed. This result agrees very well with Wachs et al. [8], who reported that the preparation method does not influence the molecular structures of the surface niobium species.

The curve of $(Nb/Al)_{surface}$ versus $(Nb/Al)_{bulk}$ of Nb_2O_5/Al_2O_3 samples prepared using niobium ammonium oxalate complex as precursor was completely different from the ones obtained from niobium oxalate (Fig. 3).

XPS technique has been used in order to determine the monolayer coverage of Nb_2O_5/Al_2O_3 samples [4,24]. Jehng and Wachs [4] investigated the use of niobium oxalate as a precursor for the preparation of a series of alumina-supported niobium oxide samples. Nb_2O_5/Al_2O_3 samples were prepared by incipient wetness impregnation of alumina with an aqueous solution of niobium oxalate and oxalic acid. They observed a linear increase of the Nb/Al surface atomic ratio up to 19 wt.% of niobium oxide, and this ratio remained constant for higher loadings. According to them, this result suggested that the monolayer coverage was achieved at this niobium oxide concentration. Noronha et al. [24] reported that the intensity ratios and the Nb/Al surface ratio exhibited a maximum around 10 wt.% of niobium oxide on $Pd/Nb_2O_5/Al_2O_3$ catalysts containing different loading of niobium oxide. Nb_2O_5/Al_2O_3 samples were prepared by alumina impregnation with an aqueous solution of niobium oxide in acid oxalic ($pH = 0.5$).

Electron spectroscopy analysis can also be used for the characterization of the modes of film growth. According to the literature [25], there are different modes of film growth, which the most common are:

(i) *Layer by layer*. In this, the deposited film completes one monolayer of coverage, then the second, etc. This mode is commonly referred to as Frank–van der Merwe growth.
(ii) *Layer plus islanding*. In this, the first layer completely covers the surface of the substrate and subsequent layers form islands of deposited material. This mode is referred to as Stranski–Krastanov growth.
(iii) *Complete islanding*. In this, the material immediately forms islands on the surface. This mode is commonly referred to as Volmer–Weber growth.

The characteristic shape of the curve of intensity ratios versus niobium oxide content, corresponding to the first mode of oxide film growth should be represented by an exponential growth. The second and the third modes should be described by a linear growth of intensity ratios until a finite value is reached, since some fraction of the support is not covered by the overlayer.

Based on these modes of growth, it can be proposed that the niobium alumina systems prepared using the niobium ammonium oxalate complex are well described by the mode of growth like layer by layer. On the other hand, the system prepared using niobium oxalate as precursor has a mode of growth like layer plus islanding or complete islanding. These differences could be probably related to the preparation method. The excess of oxalic acid could modify the support surface and lead to another mode of growth.

In spite of the use of the same precursor (niobium oxalate), the curve of Nb/Al surface ratio of Nb_2O_5/Al_2O_3 samples as a function of niobium content presented on this work are different from the one obtained by Jehng and Wachs [4]. This result could be explained by the differences in the preparation method. Vuurman and Wachs [6] used an incipient wetness impregnation, while the impregnation was carried out in excess of solution in this work. The excess of acid solution could led to the formation of higher amounts of bulk Nb_2O_5 since the pH of the solution becomes more concentrated as water is evaporated.

The nature of precursor salt also affected significantly the reduction of niobium oxide species (Fig. 4). The systems prepared using niobium oxalate exhibited a higher reducibility than the Nb_2O_5/Al_2O_3 (NAC) samples. This result is in agreement with the XPS analysis, which revealed the island formation, probably represented by bulk Nb_2O_5 particles. This niobium oxide species have low interaction with the support, justifying the reduction at low temperature. The layer by layer growth, characteristic of the Nb_2O_5/Al_2O_3 (NAC) samples, results in a higher interaction between niobium oxide species and support and, consequently, lower reducibility. In this case, a hydrogen uptake was observed only on the Nb_2O_5/Al_2O_3 (NAC) sample containing 30 wt.% of niobium oxide. Moreover, DRX analysis identified the presence of bulk Nb_2O_5 only on this sample. These results agreed very well with the proposed model.

The acid properties of niobium alumina systems prepared using both precursors (niobium ammonium oxalate complex and niobium oxalate) were investigated by infrared spectroscopy of adsorbed pyridine. The niobium oxide addition decreased the fraction of LAS. This can be observed by the decrease of both the intensity of the band at 1451 cm^{-1} and the LAS/(LAS + BAS) ratio upon the niobium addition. Datka et al. [16] observed the same behavior, which was attributed to the disappearance of LAS of alumina and the creation of new LAS of niobium.

Datka et al. [16] reported the creation of BAS on Nb_2O_5/Al_2O_3 samples containing high niobium oxide content. On the other hand, da Silva et al. [11] did not observed the formation of BAS on Nb_2O_5/Al_2O_3 samples prepared by chemical vapor deposition of niobium(V) chloride, since the band at 1544 cm^{-1} was not detected. In our work, the appearance of BAS was detected through the LAS/(LAS + BAS) ratio, indicating the creation of BAS. This result is in agreement with the work of Datka et al. [16]. Furthermore, the fraction of BAS was higher on the Nb_2O_5/Al_2O_3 (NO) samples. For instance, the LAS/(LAS + BAS) ratio for the 20% Nb_2O_5/Al_2O_3 (NAC) was 0.730 and for the 20% Nb_2O_5/Al_2O_3 (NO) was 0.562. According to Datka et al. [16], the Brønsted acidity is associated with the creation of bridging hydroxyl groups formed between the surface niobium oxide species and the alumina support (Nb–OH–Al). These bridging hydroxyls should be more acidic when there are more Nb atoms around the Nb atom of the bridging group. This means that the presence of multilayered niobia species at high niobium oxide loading favors the creation of BAS. Therefore, the presence of islands of niobium oxide particles on the Nb_2O_5/Al_2O_3 (NO) samples could explain the higher fraction of BAS on this system.

5. Conclusions

DRS analysis revealed that the increase of niobium loading enhanced the polymerization degree of niobium oxide species on both series of Nb_2O_5/Al_2O_3 systems.

The nature of the precursor had a strong effect on the distribution of the niobium oxide species over the alumina. The XPS results revealed the presence of multilayers of niobium oxide on the Nb_2O_5/Al_2O_3 samples prepared using niobium ammonium oxalate complex. On the Nb_2O_5/Al_2O_3 samples obtained using niobium oxalate as precursor, the addition of niobium oxide led to the formation of islands of Nb_2O_5 particles even at low loadings. Consequently, the nature of the precursor affected significantly the reduction of niobium oxide species. The Nb_2O_5/Al_2O_3 (NO) samples exhibited a high reducibility due to the lower interaction between the niobium oxide species of the islands and the support.

The addition of niobium oxide decreased the fraction of LAS and increased the fraction of BAS, independent of the precursor salt. However, the creation of BAS was more pronounced on the Nb_2O_5/Al_2O_3 samples prepared from niobium oxalate. This result could be attributed to the presence of islands of niobium oxide on the Nb_2O_5/Al_2O_3 (NO) samples.

Acknowledgements

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