



New insights into the development of Brønsted acidity of niobic acid

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ABSTRACT

The development of Brønsted acidity and the relationship between acidity, catalytic performance and structure of niobium oxide were investigated for a series of samples prepared by calcination of niobic acid at temperatures between 423 and 823 K. All solids were active for propan-2-ol dehydration. The Brønsted acidity was monitored by adsorption of lutidine and CO followed by FT-IR. Low temperature CO adsorption measurements showed that all solids exhibit essentially the same medium Brønsted acid strength. A direct relationship between the abundance of Brønsted acid sites monitored by lutidine adsorption followed by desorption at 523 K and propan-2-ol dehydration activity was observed.

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1. Introduction

Solid acids catalysts were extensively investigated as an environmentally friendly alternative to liquid acids in refining units in petrochemistry and in the synthesis of fine chemicals [1,2]. They were also used in studies aimed at the development of renewable resources for the synthesis of fuel and chemical intermediates [2,3]. Specifically, niobic acid was shown to be an active solid for acid catalyzed reactions such as isomerization [4], polymerization [4], dehydration [4–7], hydration [8–10], alkylation [5,11,12] and esterification [8,13]. Recently, it has also found applications as a catalyst for the valorisation of the products of biomass conversion (biodiesel production [3,14,15], hydrolysis of cellulosic materials [3] and fructose dehydration [16,17]). This highlights the importance of detailed investigations of the development of the acidity of this solid as a function of pretreatment and its relation to the catalytic performance. Such studies were hindered by the fact that increasing the pretreatment temperature of niobic acid brings about drastic changes in the surface area, acidity and the nature of the phases present (amorphous niobic acid; hexagonal or orthorhombic niobium oxide) [4,6,7,18,19]. Thus, to date, only a limited number of studies have examined the evolution of the acidity of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ as a function of the calcination temperature

and attempted to establish a relationship between acidity and catalytic activity [4,6,7,20]. Using Hammett indicators, Iizuka et al. [4,21] reported that niobic acid thermally treated below 573 K exhibits strong Brønsted acidity ($H_0 \leq -5.6$) which decreases with increasing the calcination temperature up to 773 K. Similarly, strong acidity ($-8.2 \leq H_0 \leq -3.0$) was reported by Chai et al. [22]. Pyridine adsorption monitored by infrared spectroscopy indicated a progressive decrease in the abundance of Brønsted acid sites with increasing calcination temperature from 373 to 773 K [4]. The reported disappearance of Brønsted acid sites at 773 K was attributed to the crystallization of amorphous niobic acid into niobium oxide. The decrease in Brønsted acid sites concentration with increasing calcination temperature was associated with the observed decrease in catalytic activity for but-1-ene isomerization and butan-2-ol dehydration. Nevertheless, no direct relation between the abundance of Brønsted acid sites and the catalytic activity was established. Vedrine and coworkers [6,7] studied the influence of calcination temperature of niobic acid on the total amount of acid sites and their strength. No relationship between the total amount of acid sites (measured by NH_3 adsorption) and the catalytic activity for the reaction of propan-2-ol dehydration was evidenced. However, microcalorimetry results of NH_3 adsorption indicated that the most active solids exhibit the strongest acid sites.

The purpose of the present work was to study the development of Brønsted acidity of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ as a function of the calcination temperature and to investigate the relationship between Brønsted acid sites concentration and catalytic activity for the acid catalyzed reaction of propan-2-ol dehydration. Towards this end, a

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series of samples was prepared by calcination of niobic acid at various temperatures. The texture and structure of the solids were characterized by nitrogen adsorption, thermogravimetric analysis, X-ray diffraction (XRD) and Raman spectroscopy. The evolution of the Brønsted acidity was monitored by adsorption of probe molecules (CO, lutidine) followed by infrared spectroscopy (FTIR). The results were correlated with the catalytic activity for the reaction of decomposition of propan-2-ol (isopropanol).

2. Experimental

2.1. Samples preparation

Niobic acid, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (Niobia HY-340), was provided by CBMM. The major impurities were Cl (91 ppm) and Fe (113 ppm). The samples were prepared by heating $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in air for 2 h at 373 K and then for 16 h at temperatures between 423 and 823 K.

2.2. BET surface area

The BET surface areas of the samples were determined from nitrogen adsorption measurements at 77 K using an automatic adsorptiometer (Micromeritics ASAP 2000). The samples calcined at temperatures higher or equal to 623 K were pretreated at 573 K for 2 h under vacuum; those which were calcined at 423 and 523 K were pretreated, respectively, at 373 and 473 K, to avoid textural modification during this stage. The surface areas were determined from nitrogen adsorption values for five relative pressures (P/P_0) ranging from 0.05 to 0.2 using the BET method.

2.3. Thermogravimetric analysis

The combined thermogravimetric and differential scanning calorimetric analysis (TGA/DSC) was performed using a Netzsch STA 449 thermal analyzer with a heating rate of 10 K min^{-1} under helium flow.

2.4. X-ray diffraction

X-ray powder diffraction patterns were recorded using a Philips X'pert diffractometer equipped with a copper anode ($K\alpha_1 = 0.15405 \text{ nm}$). The diffractograms were recorded in the 2θ range of $20\text{--}70^\circ$ with steps of 0.05° and a count time of 2 s for each step.

2.5. Raman spectroscopy

Raman spectra were recorded with a Jobin-Yvon LabRam 300 spectrometer between 30 and 1500 cm^{-1} (power: 13 mW; acquisition time: 3 s). The instrument was equipped with a He–Ne laser source (633 nm) and a CCD detector. The samples were analyzed in a powder form under ambient conditions.

2.6. Infrared spectroscopy

2.6.1. Pretreatment

The samples, pressed into pellets ($\sim 20 \text{ mg}$ for a 2 cm^2 pellet), were first heated under vacuum at 373 K (ramp 5 K min^{-1}) for 1 h and then for 0.5 h at the calcination temperature or at 723 K for the sample calcined at 823 K (ramp 5 K min^{-1}). This was followed by a treatment in O_2 ($P_{\text{equilibrium}} = 13.3 \text{ kPa}$) for 0.5 h and evacuation for 0.5 h at the calcination temperature or at 723 K for the sample calcined at 823 K, before cooling down to room temperature.

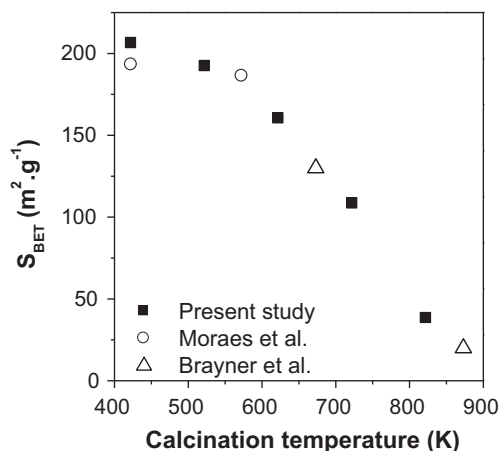


Fig. 1. Evolution of the BET surface area of Nb-based solids with increasing the calcination temperature (■: present study; ○: Moraes et al. [11]; △: Brayner and Bozon-Verduraz [19]).

2.6.2. CO adsorption

Following thermal treatment, the samples were cooled down to 77 K. CO was introduced in increasing amounts up to an equilibrium pressure of 133 Pa. Infrared spectra were recorded using a Bruker Vector 22 spectrometer (resolution 2 cm^{-1} , 64 scans). The spectra were obtained after subtraction of the spectrum recorded after calcination and prior to CO adsorption. When necessary, the contribution of CO in the gas phase was removed by subtraction of the gas-phase spectrum.

2.6.3. 2,6-Dimethylpyridine adsorption–desorption

2,6-Dimethylpyridine (lutidine) was introduced at room temperature ($P_{\text{equilibrium}} = 133 \text{ Pa}$) after pretreatment. The spectra were then recorded following desorption from 423 to 623 K with a Bruker Vector 22 spectrometer (resolution 4 cm^{-1} , 64 scans). To avoid altering the texture or structure of the sample during the thermo-desorption stage, the desorption temperature did not exceed that of the calcination. The reported spectra were obtained after subtraction of the spectrum recorded before lutidine adsorption. The amount of Brønsted acid sites titrated by 2,6-dimethylpyridine was obtained using a molar extinction coefficient value of $\epsilon = 6.8 \text{ cm}^2 \cdot \mu\text{mol}^{-1}$ for both the ν_{8a} and ν_{8b} vibrations of protonated lutidine (DMPH^+) at ~ 1644 and $\sim 1628 \text{ cm}^{-1}$ [23].

2.7. Catalytic activity

The catalytic conversion of propan-2-ol (isopropanol) was measured in a fixed bed flow reactor. 100 mg of sample were pretreated at the calcination temperature, for the samples calcined up to 723 K and at 723 K for the sample calcined at 823 K, under N_2 flow for 2 h (ramp 5 K min^{-1} ; $60 \text{ cm}^3 \text{ min}^{-1}$). The reaction was performed at atmospheric pressure with N_2 as carrier gas ($P_{\text{isopropanol}} = 1.23 \text{ kPa}$; $\text{WHSV} = 17.3 \text{ mmol h}^{-1} \text{ g}^{-1}$; total flow rate = $60 \text{ cm}^3 \text{ min}^{-1}$) and $P_{\text{isopropanol}} = 1.23 \text{ kPa}$; $\text{WHSV} = 34.6 \text{ mmol h}^{-1} \text{ g}^{-1}$; total flow rate = $120 \text{ cm}^3 \text{ min}^{-1}$) at 403, 423 and 443 K. The reactants and products were analyzed with an on line G.C. (HP 5890 Series II) equipped with a capillary column (CP WAX 52 CB) and a FID detector.

3. Results

3.1. Nitrogen adsorption

Fig. 1 depicts the evolution of the BET surface area of Nb-based solids as a function of calcination temperature. It can be readily

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