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Supported niobium catalysts for methanol dehydration to dimethyl ether: FTIR studies of acid properties

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ABSTRACT

A series of NbO_x/TiO_2 catalysts (0.9–9.0 at Nb nm^{-2}) was prepared by incipient wetness impregnation of niobium (V) oxalate aqueous solutions on TiO_2. Spectroscopic data reveal that NbO_x phase is highly dispersed and relatively large Nb_2O_5 crystallites are not detected; highly distorted NbO_6 octahedral structures are exclusively identified by Raman spectroscopy. Surface acidity measurements by NH_3-temperature-programmed desorption experiments indicate that the overall number of Lewis acid sites in the solids decreases with Nb-loading, although their strength follows the opposite trend. A minor fraction of Brønsted acid sites is also detected for the sample with the highest Nb surface coverage used here (9.0 at Nb nm^{-2}). The catalytic activity of NbO_x/TiO_2 in methanol dehydration to dimethyl ether is found to be determined mainly by the strength of the acid sites and the presence of Brønsted acid sites, being more active those catalysts with stronger acid sites and with a higher number of Brønsted acid sites.

1. Introduction

Dimethyl ether (DME, CH_3OCH_3) is a non-toxic, non-carcinogenic and non-corrosive important chemical. It is also envisioned as an environmentally friendly compound because of its low global warming potentials for short and long time horizons [1]. Unlike other homologous ethers, DME does not form explosive peroxides, allowing its safe storage and handling. Although DME is a gas at ambient conditions, it forms a liquid phase when pressurized above 0.5 MPa, and therefore, it is commonly handled and stored as a liquid [2]. DME vapor pressure is similar to that of liquefied petroleum gas (LPG); then, DME can be used in the existing infrastructures for transportation and storage.

At present, DME is mainly used as an aerosol propellant to replace chlorofluorocarbons (CFCs) and as a key intermediate for producing many important chemicals, such as methyl acetate [3], ethylidene diacetate [4], and light olefins [5]. In the recent years, the interest for DME use in compression ignition engines as an additive or replacement of diesel fuel have increased considerably, in part because of its high cetane number, high oxygen content (smokeless combustion), and low boiling point (rapid evaporation in the engine cylinder) [1]. DME is also a convenient substitute fuel used for electric power generation as well as for domestic heating and cooking applications [6]. DME is also envisioned as a promising H_2 source for fuel cells applications [7,8].

DME can be produced from biomass, natural gas, and/or coal. First, the feedstock is transformed into synthesis gas or syngas ($H_2/CO/CO_2$ mixtures) via steam reforming or partial oxidation reactions. Next, syngas is converted into CH_3OH with Cu-based catalysts. Finally, CH_3OH forms DME via acid-catalyzed bimolecular dehydration reactions [2]. A myriad of solid acid catalysts has been explored for the conversion of CH_3OH into DME, including γ-Al_2O_3, modified alumina with silica, TiO_2–ZrO_2, and zeolite and zeotype materials (HZSM-5, HY, $AlPO_4$, SAPOs, etc.) [9–14]. An important drawback of these materials is the excessive formation of CH_4 and coke deposits, which are responsible for catalyst deactivation phenomena. Some authors have proposed that Brønsted acid sites present in HZSM-5 and $AlPO_4$ materials catalyze CH_3OH conversion to DME [9,12], although some reports did not find a relationship between CH_3OH dehydration rates and the number of Brønsted acid sites in HZSM-5 [15]. Other researchers have claimed that Lewis acid–base pairs catalyze more efficiently CH_3OH dehydration reactions to DME [16].

Bulk hydrated niobium pentoxide, $Nb_2O_5 \cdot nH_2O$, exhibits strong Lewis and Brønsted acid sites [17]. In particular, niobic acid containing large amounts of H_2O has been reported to show high rates in acid-catalyzed reactions involving the participation or removal of H_2O molecules [18]. Interestingly, supported niobium oxides show remarkable differences when compared to bulk Nb_2O_5 [19]. Thus, highly distorted NbO_6 octahedra are usually formed at low niobium

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surface coverages on acid supports, while slightly distorted NbO_6, NbO_7, and NbO_8 species are developed for high surface densities [19,20]. Highly distorted NbO_6 octahedral structures possess Nb=O bonds that yield Lewis acid sites. In contrast, the slightly distorted NbO_6 octahedra as well as the NbO_7 and NbO_8 groups possess only Nb—O bonds, which are associated to Brønsted acid sites [20].

Here, we report on the acid properties of a series of NbO_x/TiO_2 catalysts with different Nb surface densities and on their influence in the CH_3OH dehydration reaction to DME. We have found that NbO_x/TiO_2 are active and selective catalysts for CH_3OH reaction to give DME. Measured rates and selectivities increase with the Nb content as a result of the increasing strength of the acid sites formed over these solids.

2. Experimental

2.1. Preparation of catalysts

TiO_2 (Degussa P25, 20% rutile, 80% anatase) was first treated in ambient air at 823 K for 4 h. NbO_x/TiO_2 samples with different Nb contents were prepared by incipient wetness impregnation at room temperature of the TiO_2 substrate with aqueous solutions of niobium (V) oxalate. The impregnated solids were dried at 393 K overnight and subsequently treated in ambient air at 773 K for 4 h. The prepared samples are referred as xNb/TiO_2, where x denotes the surface metal density (at Nb nm^{-2}). Table 1 summarizes the nomenclature and chemical composition of the samples studied in this work.

2.2. Characterization techniques

The Brunauer–Emmett–Teller (BET) specific surface area, pore volume, and pore size distribution of the samples were obtained from N_2 adsorption–desorption isotherms measured at 77 K with a Micromeritics ASAP 2000 apparatus. The samples were degassed at 413 K for 16 h prior to the physisorption measurements.

X-ray diffraction patterns were recorded using Cu Kα radiation in a Seiffert 3000 XPert X-ray diffractometer. Diffractograms were recorded within the $2\theta = 15–90°$ diffraction angles. The relative contents of anatase (A) and rutile (R) of the TiO_2 support were determined from the intensities of the $(1\,0\,1)_A$ plane of anatase and the $(1\,1\,0)_R$ plane of rutile located, respectively, at $2\theta = 24.3°$ and 27.4°, using the following equation [21]:

$$A = \frac{1}{1 + 1.26(I(1\,1\,0)_{Rutile}/I(1\,0\,1)_{Anatase})} \quad (1)$$

where A designates the fraction of the anatase phase.

Temperature-programmed desorption (TPD) of NH_3 was carried out with a Micromeritics TPR/TPD 2900 instrument in a quartz U-tube microreactor with He as carrier gas. Prior to the measurements, the sample was pretreated in flowing He at 493 K for 1 h. Subsequently, the sample was cooled down to 393 K, and then, a 5 vol.% NH_3/He flow was passed over the sample for 0.5 h. Physisorbed NH_3 was removed by flowing He at 393 K for 0.5 h. Finally, the sample was heated up to 1243 K at a heating rate of 15 K min^{-1}.

Raman spectra (1 cm^{-1} resolution) of hydrated (ambient conditions) and dehydrated samples (10 vol.% O_2/N_2, 723 K, 1 h) were recorded with a Renishaw in Via Raman Microscope spectrometer (equipped with a laser beam emitting at 532 nm, at 100 mW output power). The photons scattered by the sample were dispersed by an 1800 lines/mm grating monochromator and simultaneously collected on a CCD camera; the collection optic was set at 50× objective.

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200 R spectrometer in the pulse-count mode at a pass energy of 50 eV using a Mg Kα ($h\nu = 1253.6$ eV) X-ray source. Kinetic energies of photoelectrons were measured using a hemispherical electron analyzer working at a constant pass energy (20 eV). The powder samples were pressed into stainless steel holders and then mounted on a support rod placed in the pretreatment chamber. The XPS data were signal averaged for at least 200 scans and were taken in increments of 0.1 eV with dwell times of 50 ms. Binding energies were calibrated relative to the Ti $2p_{3/2}$ peak at 459.0 eV to correct the contact potential differences between the sample and the spectrometer.

Fourier transform infrared (FTIR) spectra of adsorbed CO or pyridine were recorded with a Nicolet Nexus instrument, using a conventional cell connected to a gas handling system. All spectra were obtained after subtraction of the spectrum corresponding to the degassed sample. Prior to adsorption, pressed disks of sample powders (ca. 20 mg) were thermally treated within the cell at 573 K under vacuum (0.01 Pa) for 1 h. CO adsorption (0.13 kPa) experiments were performed at 133 K, and spectra were recorded in the range 133–278 K while degassing. Pyridine (0.40 kPa) was introduced at 298 K, and spectra were recorded after desorption from 298 to 573 K.

2.3. In situ infrared spectroscopy studies of CH_3OH adsorption and reaction

CH_3OH interaction with the catalysts was studied by in situ infrared spectroscopy experiments. IR spectra were recorded in the instrument described above. The sample pellets (~20 mg) were heated under vacuum at 573 K for 1 h. Then, CH_3OH (0.13 kPa) was admitted into the IR cell at room temperature. Desorption was performed by evacuation from 323 to 573 K in intervals of 50 K. A spectrum was recorded at room temperature after desorption at each temperature.

The gas phase resulting from CH_3OH contact (1.2–1.5 kPa) with TiO_2 and 9.0Nb/TiO_2 at 523 and 573 K was also analyzed by FT-IR spectroscopy. Previously, the solids (ca. 20 mg) were pressed into wafers and treated at 573 K for 1 h in vacuum (0.01 Pa).

2.4. Catalytic activity

The catalytic conversion of CH_3OH to DME was determined in a fixed bed reactor (573 K, 6.1 kPa CH_3OH, 13.9 mmol h^{-1} $g_{cat}{}^{-1}$). The catalytic bed was prepared by mixing the catalyst (0.5 g, 0.25–0.30 mm pellet size) with SiC (2.0 g, 0.25–0.30 mm pellet size) to avoid hot spots. Reactants and products concentrations were determined with a gas chromatograph (Varian CP-3800)

Table 1
Nomenclature, chemical composition, textural properties, and NH_3 desorption measured for the xNb/TiO_2 solids.

Sample	Nb density (at nm^{-2})	Nb_2O_5 (wt.%)	Surface area (m^2 g^{-1})	Pore size (nm)	NH_3 desorption (mmol $g_{cat}{}^{-1}$)
TiO_2	0.0	0.0	53	50	1.63
0.9Nb/TiO_2	0.9	0.9	52	41	1.33
2.3Nb/TiO_2	2.3	2.2	52	41	1.40
4.5Nb/TiO_2	4.5	4.4	53	40	1.46
9.0Nb/TiO_2	9.0	8.4	53	37	1.57