



Dispersion states and acid properties of SiO₂-supported Nb₂O₅

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ABSTRACT

Nb₂O₅/SiO₂ samples were prepared by the incipient-wetness impregnation method using niobium oxalate aqueous solution. The microstructure and dispersion process of the niobia species supported on SiO₂ were characterized by means of power X-ray diffraction (XRD), laser Raman spectroscopy (LRS), and UV–vis diffuse reflectance spectroscopy (UV–vis DRS). The acid properties were investigated by the method of Hammett indicator and Pyridine adsorption infrared (Py-IR) spectroscopy. The results showed that the dispersion process of Nb₂O₅ was performed by consuming surface hydroxyl groups of the amorphous SiO₂ support. The aggregation of niobia species led to the formation of microcrystalline particles, so that there was no a clear monolayer dispersion capacity for Nb₂O₅ supported on amorphous SiO₂. Furthermore, the catalytic activities of the as-prepared samples were evaluated by the condensation reaction of iso-butene (IB) and iso-butyraldehyde (IBA) to form 2,5-dimethyl-2,4-hexadiene (DMHD). The catalytic activities of the as-prepared samples for the condensation and their acid properties were strongly affected by the dispersion states.

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1. Introduction

High-acidity and water-tolerant properties are the most interesting features for niobium-containing catalytic materials. As a family of important functional materials, bulk niobia-containing catalysts (mixed oxides of niobia, niobia loaded on various oxides, surface-modified niobia, mesoporous molecular sieves, and Nb-containing layered compounds) have been applied in different areas [1–4], such as dehydration [5], condensation [6], hydrolysis [7], and ketonization [8]. However, general oxides have almost no sufficient acidity and stability for these reactions.

For niobium-based catalysts, the local structure is a key factor to tune their catalytic activities, especially for the SiO₂-supported niobia catalysts. Up to now, many outstanding results have been achieved in the preparation of the supported niobia catalysts. Among them, the most effective way is to select a suitable support which could adjust the structure of the surface niobia species [9,10]. Moreover, the acid properties and catalytic activities of the niobia species are closely dependent on their dispersion states, which are closely related to the interaction between the niobia species and the support. Our group has reported that the niobia species was dispersed on some oxide supports such as TiO₂ [11], γ-Al₂O₃ [12] and t-ZrO₂ [13]. The results revealed that the dispersion states, structures and surface acid properties of niobia species were significantly affected or controlled by the nature of the

supports. However, it has not been well-established that the effect of the local structures on acid properties and catalytic activities of niobia species, especially for the amorphous supports such as SiO₂.

Here in, the dispersion states of niobia species supported on amorphous SiO₂ were characterized by means of X-ray diffraction (XRD), laser Raman spectroscopy (LRS), and UV–vis diffuse reflectance spectroscopy (UV–vis DRS). The acid properties were determined by the method of Hammett indicator and pyridine adsorption infrared (Py-IR) spectroscopy. The catalytic activities were evaluated by the condensation reaction of iso-butene (IB) and iso-butyraldehyde (IBA) to 2,5-dimethyl-2,4-hexadiene (DMHD). The aim of this work is to obtain the dispersion model, and further to explore the effect of the local structures on acid properties and catalytic activities of niobia species.

2. Experimental

2.1. Materials preparation

Porous silica microsphere was purchased from Qingdao Haiyang Chemical Co., Ltd., with $S_{\text{BET}}=408 \text{ m}^2 \text{ g}^{-1}$. Nb₂O₅/SiO₂ samples were prepared by incipient-wetness impregnation of the SiO₂ microspheres with stoichiometric aqueous solution of niobium oxalate. After drying the microspheres with a rotary evaporator at 333–343 K, then the samples were dried at 393 K for 12 h. At last they were calcined at 773 K for 24 h in air atmosphere. The sample denoted as mechanical mixture was obtained by grinding the mixture of Nb₂O₅ and SiO₂ at room temperature in air atmosphere.

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2.2. Characterization

The X-ray diffraction (XRD) patterns were recorded using a XD-3 A diffractometer (Shimadzu Co., Japan) with a curved graphite-monochromatized Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) at 40 kV and 30 mA at room temperature. The Laser Raman spectra (LRS) were obtained on a RF-100 laser Raman spectrometer (Bruker Co., Germany) with an Nd-YAG laser ($\lambda=1.064 \text{ \mu m}$) at 300 mW laser power. The UV-vis diffuse reflectance spectra (UV-vis DRS) were determined by a UV-2401 PC UV-vis spectrophotometer (Shimadzu Co., Japan) equipped with an integrated sphere using BaSO $_4$ as the reference. The FT-IR spectra were acquired on a Bruker Vector 22 FT-IR spectrophotometer (DTGS detector) with a resolution of 4 cm $^{-1}$. Acid properties were investigated with Pyridine adsorption infrared spectroscopy and Hammett indicator, which had been described in our earlier works [11–13].

2.3. The catalytic activities of Nb $_2$ O $_5$ /SiO $_2$ samples

The catalytic activities of Nb $_2$ O $_5$ /SiO $_2$ catalysts were evaluated by the condensation reaction of iso-butene (IB) and iso-butyraldehyde (IBA) to form 2,5-dimethyl-2,4-hexadiene (DMHD), which had been described in our earlier work [12].

3. Results and discussion

3.1. The structure of Nb $_2$ O $_5$ /SiO $_2$ samples

The XRD patterns of Nb $_2$ O $_5$ /SiO $_2$ samples are shown in Fig. 1. When Nb $_2$ O $_5$ loading (Γ_{Nb}) was 3.54 $\mu\text{mol m}^{-2}$, the characteristic peaks of orthorhombic phase Nb $_2$ O $_5$ (JCPDS 30-0873) were observed. In addition, the characteristic peaks also appeared in the mechanical mixtures of Nb $_2$ O $_5$ and SiO $_2$ (corresponding to $\Gamma_{\text{Nb}}=3.54 \mu\text{mol m}^{-2}$). This result suggested that the niobia species were dispersed on the surface of the SiO $_2$ support and Nb $_2$ O $_5$ crystallite phase have not formed when Γ_{Nb} was less than 3.54 $\mu\text{mol m}^{-2}$. The intensity of diffraction peak corresponding to (0 0 1) plane in orthorhombic phase Nb $_2$ O $_5$ becomes stronger significantly with the increase of Γ_{Nb} . The ratio of the XRD peak intensity of Nb $_2$ O $_5$ (0 0 1) to V $_2$ O $_5$ (as an internal reference) (0 0 1) plane vs Γ_{Nb} is plotted in Fig. 2, so the monolayer dispersion

capacity of Nb $_2$ O $_5$ loaded on SiO $_2$ can be obtained (3.50 $\mu\text{mol m}^{-2}$) by the extrapolation method.

However, the monolayer dispersion capacity for SiO $_2$ -supported Nb $_2$ O $_5$ reported by Wachs [14] was 0.3 atoms nm $^{-2}$ (Nb/SiO $_2$), which was measured with the technology of Raman spectroscopy. This value is equal to 0.50 $\mu\text{mol m}^{-2}$ (Nb $_2$ O $_5$ /SiO $_2$). It has a considerable difference with our present value obtained through XRD quantitative phase analysis. In order to investigate this difference, the laser Raman spectroscopy has been employed to characterize the dispersion states of niobia species, and the result is shown in Fig. 3. For the sample with $\Gamma_{\text{Nb}}=0.11 \mu\text{mol m}^{-2}$, the Raman band located at about 943 cm $^{-1}$ is attributed to the highly distorted octahedral NbO $_6$ [15], and it is originated in niobia species with highly dispersion states. When Γ_{Nb} is 0.55 $\mu\text{mol m}^{-2}$, three typical Raman bands were observed, which were located at 972, 925 and 875 cm $^{-1}$. The band at 972 cm $^{-1}$ is the characteristic band of terminal Nb=O in NbO $_6$ octahedral unit of amorphous Nb $_2$ O $_5$, and the bands at 925 and 875 cm $^{-1}$ are attributed to crystalline phase Nb $_2$ O $_5$, as reported in the literatures [16,17]. The results indicated that the Nb $_2$ O $_5$ crystalline phase have been formed on the surface of the SiO $_2$ support at this loading ($\Gamma_{\text{Nb}}=0.55 \mu\text{mol m}^{-2}$), and it is in agreement with the result reported

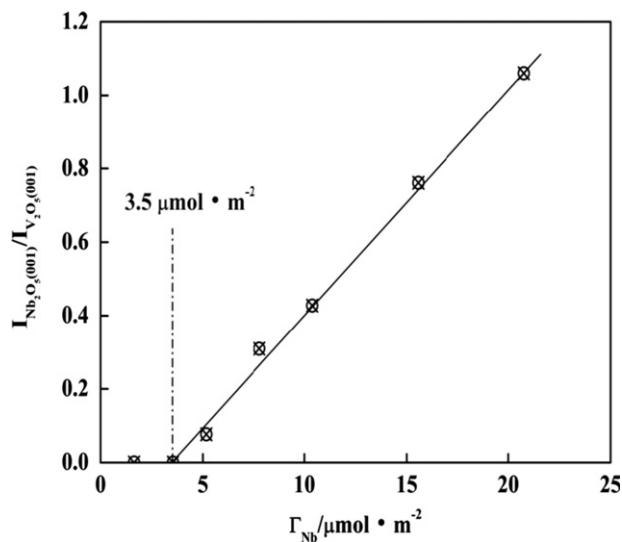


Fig. 2. The line obtained by XRD quantitative phase analysis of Nb $_2$ O $_5$ /SiO $_2$ samples.

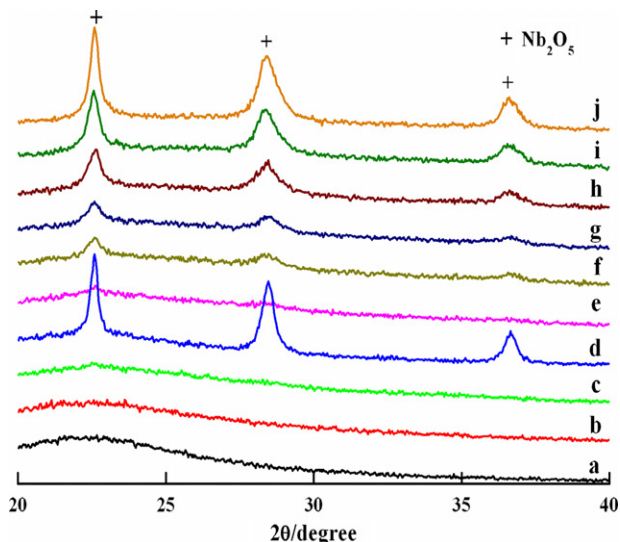


Fig. 1. XRD patterns of Nb $_2$ O $_5$ /SiO $_2$ samples. $\Gamma_{\text{Nb}}/\mu\text{mol} \cdot \text{m}^{-2}$: (a) 0.0, (b) 1.64, (c) 3.54, (d) 3.54 (Nb $_2$ O $_5$ +SiO $_2$ mixture), (e) 5.20, (f) 7.79, (g) 10.4, (h) 15.6, (i) 20.8 and (j) 31.1.

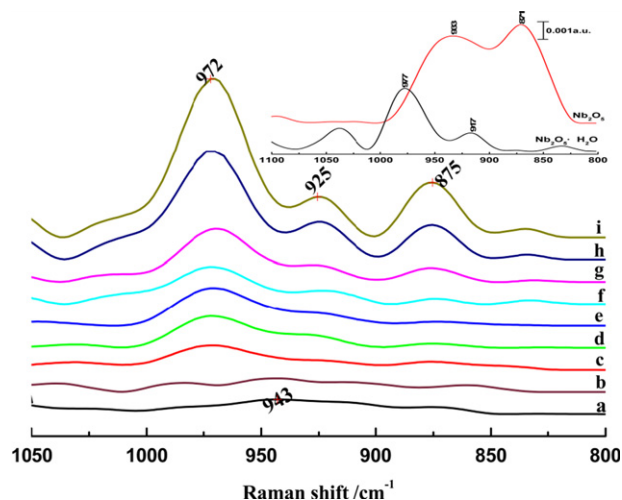


Fig. 3. Raman spectra of Nb $_2$ O $_5$ /SiO $_2$ samples. $\Gamma_{\text{Nb}}/\mu\text{mol m}^{-2}$: (a) 0.11, (b) 0.26, (c) 0.55, (d) 1.10, (e) 1.64, (f) 3.46, (g) 5.19, (h) 10.4 and (i) 15.6.

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