

The state of dispersed niobia species on γ -Al₂O₃ and their catalytic performance for condensation of isobutylene and isobutyraldehyde

Jie HE (✉)^{1,2} and Yining FAN²

Catalysts of Nb₂O₅/ γ -Al₂O₃ were prepared by aqueous solution impregnation. The state of niobia species on surface of γ -Al₂O₃ is characterized by using the technology of X-ray power diffraction (XRD) and analyzed using the “incorporation model”. The acidity and the nature of acid sites of the catalysts were evaluated by means of Fourier transform infrared (FT-IR) spectroscopy of adsorbed pyridine. The catalytic activity of Nb₂O₅/ γ -Al₂O₃ catalysts was evaluated by a condensation reaction from isobutene and isobutyraldehyde to 2,5-dimethyl-2,4-hexadiene. The results of XRD indicate that the dispersion capacity of niobia on γ -Al₂O₃ is about 0.76 mmol Nb per 100 m² γ -Al₂O₃, which is almost identical to the theoretical value (0.75 mmol Nb per 100 m² γ -Al₂O₃) calculated by the “incorporation model”. The results of Py-IR and catalytic activity evaluation indicate that the acidity feature is related to the state of dispersed niobia species as well as the loading of niobia onto the surface of γ -Al₂O₃ support.

Keywords niobia, alumina, dispersion capacity, acidity, olefin-aldehyde condensation

1 Introduction

Supported niobia catalysts have received much attention because of their unique catalytic properties for a wide variety

of reactions [1–5]. It has been verified that the catalytic properties of supported niobia are not only related to the type of used supports but also related to the niobia loading. γ -Al₂O₃ is one of the major supports because of its unique mechanical and chemical properties. For the Nb₂O₅/ γ -Al₂O₃ catalyst, in fact, Wachs et al. [6] have found that the dispersion capability of niobia is correlated to the amount of surface hydroxyl group of γ -Al₂O₃. Datka et al. [7] supposed that the formation of Brönsted acid sites on the Nb₂O₅/ γ -Al₂O₃ catalysts requires both Al and Nb atoms. It is related to bridging hydroxyl groups, Al-OH-Nb, on the catalyst surface. da Silva et al. [8] suggested that the amount of Brönsted acid sites should be related to the preparation methods and the treatment conditions in the process of catalyst preparation. However, at present the relationship between the surface Brönsted acid feature and the niobia loading for Nb₂O₅/ γ -Al₂O₃ has not been completely understood. In the present study, some experimental techniques, such as X-ray powder diffraction (XRD) quantitative analysis and infrared spectroscopy of adsorbed pyridine, are used to correlate the state of dispersed niobium oxide species to the surface acidity. The condensation reaction from isobutene (IB) and isobutyraldehyde (IBA) to 2,5-dimethyl-2,4-hexadiene (DMHD) is used to evaluate the catalytic activity of the catalysts. The “incorporation model”, which describes the interaction between the metal ion and oxide support, is used to discuss the dispersion state of niobium oxide species on γ -Al₂O₃ support.

2 Experimental

Nb₂O₅/ γ -Al₂O₃ catalysts were prepared by incipient wetness impregnation of γ -Al₂O₃ pellet (diameter ca. 2 mm, BET surface area is 232 m²·g⁻¹) with an aqueous solution containing the appropriate amount of niobium oxalate, followed by drying and calcinations [9].

The amount of bulk Nb₂O₅ was determined by X-ray diffraction (XRD) using a Shimadzu XD-3A diffractometer, with CuK α radiation at $\lambda = 0.15418$ nm, 35 kV, and 15 mA by using V₂O₅ as a reference.

The catalytic activities for the condensation reaction of IB with IBA to DMHD were evaluated. It was carried out in a fixed-bed catalytic reactor at atmospheric pressure and 493 K. A 30-ml catalyst sample was used for each test. The mixture of IB, IBA, and steam (IB/IBA/H₂O = 7800/1070/4480 (molar ratio)) was introduced into the reactor with GHSV = 445 h⁻¹. The products were analyzed online using a gas-chromatography with flame ionization detector (FID).

The acidity feature was analyzed by FTIR of adsorbed pyridine. The catalysts were pressed into self-supported wafers (ca. 6 mg) and placed into a quartz IR cell equipped with CaF₂ windows. Before the adsorption experiments, the

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1. School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, China

2. Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

E-mail: jhe@aust.edu.cn

samples were evacuated at 573 K and 1×10^{-3} Pa for 2 h, and then were contacted at 298 K for 30 min with 612 Pa of pyridine vapor. After evacuation for 1 h, the IR spectra were recorded using a Bruker Vector 22 spectrophotometer. The bands of adsorbed species were obtained by subtracting the spectra recorded before the introduction of the probe to the spectra taken after that. The amount of Lewis acid and Brönsted acid were quantified by the ratio of the integration area of the band at 1450 and 1540 cm^{-1} to surface area of the corresponding samples, respectively.

3 Results and discussion

The $\text{Nb}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ samples were calcined in air at 973 K for 24 h, then the amount of bulk Nb_2O_5 was determined by XRD quantitative analysis using V_2O_5 as a reference. We measured the area ratio of the diffraction peak of the crystalline Nb_2O_5 (202) plane at $2\theta = 24.9^\circ$ to V_2O_5 (001) plane at $2\theta = 20.2^\circ$ (denoted as $I_{\text{Nb}_2\text{O}_5(202)}/I_{\text{V}_2\text{O}_5(001)}$) in the $\text{Nb}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ samples with different Nb_2O_5 loading. From the dispersion, the capacity of Nb_2O_5 on $\gamma\text{-Al}_2\text{O}_3$ was evaluated. Figure 1 shows the relationship of the area ratio and niobium oxides loading. One straight line crossing one point of the x -axis was obtained. At this point, the value of x was 0.76 mmol Nb/($100 \text{ m}^2 \text{ Al}_2\text{O}_3$). This value was responsible for the amount of the Nb_2O_5 monolayer dispersion capacity on the $\gamma\text{-Al}_2\text{O}_3$, and it is almost identical to the value derived by Wachs et al. using the method of Raman spectroscopy [6]. When the Nb_2O_5 loading was lower than the dispersion capacity, no crystal Nb_2O_5 could be detected by XRD, indicating that niobia species are well dispersed on the surface of the support. Whereas the Nb_2O_5 loading exceeded the value, the crystal Nb_2O_5 was found, and its amount increased linearly as the total amount of Nb_2O_5 increased.

To discuss the interactions between dispersed oxide species

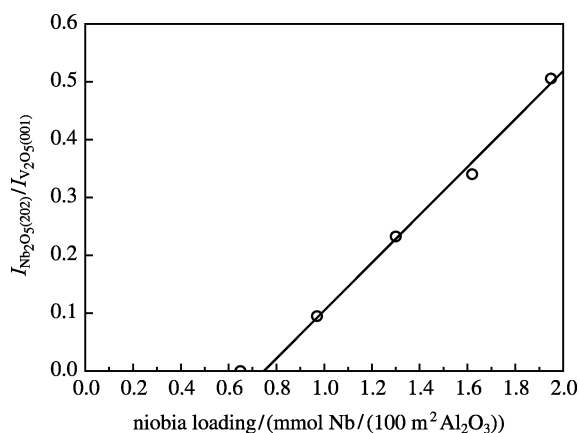


Figure 1 XRD quantitative analysis result of $\text{Nb}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$.

and an oxide support, we take the surface structure of the support as one of the key factors into consideration. For $\gamma\text{-Al}_2\text{O}_3$, the (110) plane is preferentially exposed plane with the octahedral and tetrahedral vacant [10]. Moreover, $\gamma\text{-Al}_2\text{O}_3$ can be assumed to consist of particles formed by one-dimensional stacking of C- and D- layers. The exposure possibilities of these two layers are equal [11,12]. Figure 2 shows the surface lattice vacant with the tetrahedral and octahedral structures on both C and D layers. From this figure, one can estimate that the vacant density for C and D layers on the (110) plane is 3.12 mmol sites/($100 \text{ m}^2 \text{ Al}_2\text{O}_3$) and 3.42 mmol sites/($100 \text{ m}^2 \text{ Al}_2\text{O}_3$), respectively, and the vacant density for octahedral is 0.75 mmol sites/($100 \text{ m}^2 \text{ Al}_2\text{O}_3$) for these two layers. Based on the consideration of the incorporation model [13], the dispersion process of ionized compounds on oxide support was proposed that metal cation is located on vacant sites on the oxide support. In order to compensate the extra positive charge, anions associated with the metal ions will stay at the top of the occupied sites as capping anions. Therefore, we can propose the dispersion process of the niobia on the $\gamma\text{-Al}_2\text{O}_3$ surface. The dispersed niobia could be tentatively described as the incorporation of Nb^{5+} ions into the surface vacant sites on $\gamma\text{-Al}_2\text{O}_3$ surface with accompanied oxygen anions positioning on the top for charge compensation. Considering that the stable octahedral coordination structure of Nb^{5+} in Nb_2O_5 is stable on the surface of $\gamma\text{-Al}_2\text{O}_3$, as suggested by Wachs [14], we suggest that the Nb^{5+} ions might preferentially be incorporated into the surface octahedral vacant sites of $\gamma\text{-Al}_2\text{O}_3$ surface under current experimental conditions, as shown in Figure 2. It could be calculated that the dispersion capacity of niobia on $\gamma\text{-Al}_2\text{O}_3$ is about 0.75 mmol Nb/($100 \text{ m}^2 \text{ Al}_2\text{O}_3$), which is almost identical to the value from XRD quantitative analysis, as shown at Figure 1. The result suggests that the dispersion capability of transition metal ions on oxide support is correlated to the amount of specific surface vacant sites of the support with different vacant sites.

In order to explore the relationship between the dispersion state of the niobia species and their catalytic properties, the catalytic properties of the $\text{Nb}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts (calcined in air at 773 K for 6 h) with different Nb_2O_5 loading for the vapor phase condensation reaction from IB and IBA to DMHD are measured. The catalytic activity was denoted by turnover frequency (TOF) of the DMHD yield per unit time for each Nb^{5+} ion. The results were shown in Figure 3. The catalytic activity to produce DMHD is almost zero on pure $\gamma\text{-Al}_2\text{O}_3$. The catalytic activity for the supported $\text{Nb}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts is sensitive to Nb_2O_5 loading. This observation indicates that niobia species on $\gamma\text{-Al}_2\text{O}_3$ are active component for catalyzing the condensation reaction. Two approximate linear relationships that corresponded to the catalytic activity

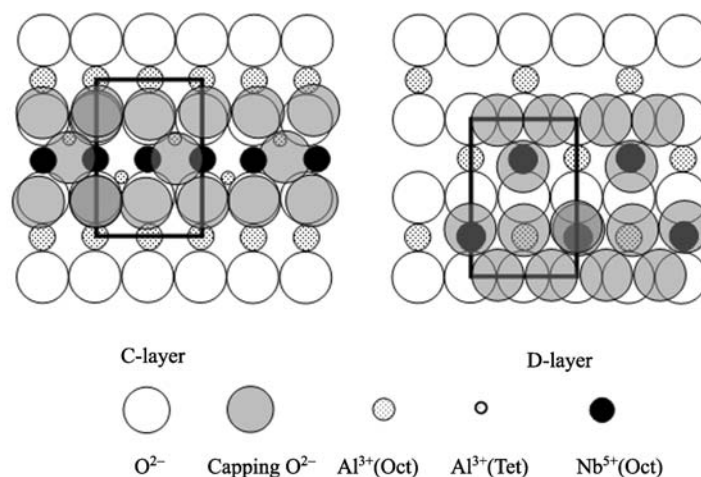


Figure 2 The schematic diagram of the incorporated Nb⁵⁺ cations in the surface octahedral vacant sites of the (110) plane of γ -Al₂O₃.

with Nb₂O₅ loading were observed. They come across at 0.76 mmol Nb/(100 m² Al₂O₃). The value is close to the dispersion capacity measured by XRD and calculated by the incorporation model. It is noteworthy that the TOF values increase with the increase of Nb₂O₅ loading, and decrease after its dispersion capacity.

Based on the reaction results, it could be concluded that the catalytic activity for Nb₂O₅/ γ -Al₂O₃ catalysts is closely related to the state of niobia species. For Nb₂O₅/ γ -Al₂O₃ catalyst with Nb₂O₅ loading far lower than its dispersion capacity, the niobia species might be highly dispersed (or isolated) bridging to the surface of the γ -Al₂O₃ through Nb-O-Al bonds. For example, at the loading lower than 0.17 mmol Nb/(100 m² Al₂O₃), the catalytic activity (TOF) for isolated niobia species is low. With the increase of Nb₂O₅ loading, the isolated niobia species interact with their nearest neighbors

(either isolated or polymerized niobia) through bridging Nb-O-Nb at the expenses of Nb-O-Al bonds, resulting in the increase of the ratio of polymerized to isolated niobia species. And the activity increases with loading to reach a maximum value. The catalytic activity (TOF) is consistent with the aggregation level of niobia species. In contrast, the TOF decreases with the increase of Nb₂O₅ loading after the loading exceeds its dispersion capacity. This result can be attributed to the formation of three-dimensional polymerized niobia species, which causes a decrease of Nb atom utilization. The TOF is $2.1 \times 10^{-5} \text{ s}^{-1}$ when Nb₂O₅·nH₂O is used as the catalyst for its highest polymerized.

To investigate the relationship between acid feature and state of niobia species on the γ -Al₂O₃, the acidity development as a function of Nb₂O₅ loading was monitored by the adsorption of pyridine molecule followed by infrared spectroscopy at

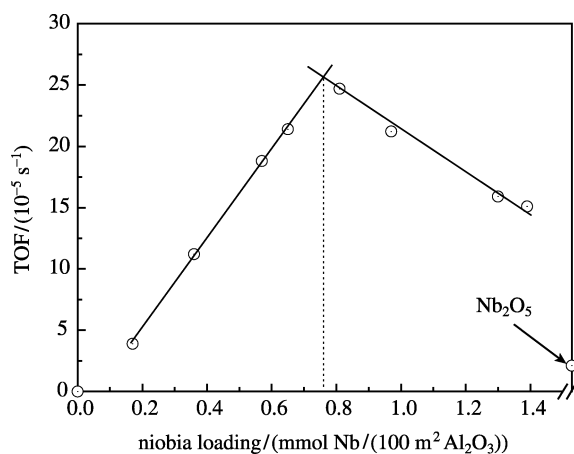


Figure 3 TOF for DMHD on Nb₂O₅/ γ -Al₂O₃ catalysts with Nb₂O₅ loading.

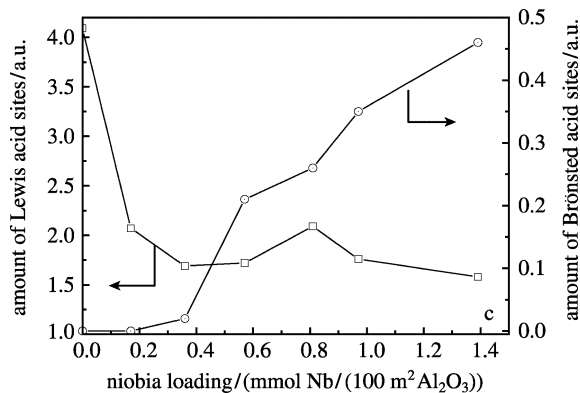


Figure 4 Surface acidity of the Nb₂O₅/ γ -Al₂O₃ catalysts with Nb₂O₅ loading.

298 K. Figure 4 shows the amount of the acidity as a function of niobia loading on $\text{Nb}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts. As shown in Figure 4, the formation of the surface niobia species on the $\gamma\text{-Al}_2\text{O}_3$ is accompanied by a decrease in the amount of Lewis acid sites and an increase in the amount of Brönsted acid sites. A decrease in the amount of Lewis acid sites could be resulted from the incorporating of Nb^{5+} into vacant sites on $\gamma\text{-Al}_2\text{O}_3$ support. It will compensate the loss of Lewis acid sites on the surface of $\gamma\text{-Al}_2\text{O}_3$ support when new Lewis sites are generated with the formation of polymerized niobia species. There are hardly any surface Brönsted acid sites that can be determined on the catalyst when the Nb_2O_5 loading is lower than $0.17 \text{ mmol Nb}/(100 \text{ m}^2 \text{ Al}_2\text{O}_3)$. Brönsted acid sites are developed after the niobia loading is higher than this value, and the amount increases with the Nb_2O_5 loading. A threshold for developing Brönsted acid site may be considered. The results suggest that the formation of Brönsted acid sites requires polymerized niobia associated with Nb-O-Nb bonds. It could be correlated to the catalytic activities for the olefin-aldehyde condensation reaction, which is generally thought to be a reaction catalyzed by Brönsted acid sites.

4 Conclusions

From XRD quantitative analysis, the dispersion capacity of niobia on the surface of $\gamma\text{-Al}_2\text{O}_3$ is acquired to be approximately $0.76 \text{ mmol Nb}/(100 \text{ m}^2 \text{ Al}_2\text{O}_3)$, which is almost in agreement with the value predicted by the “incorporation model” ($0.75 \text{ mmol Nb}/(100 \text{ m}^2 \text{ Al}_2\text{O}_3)$). The results suggest that Nb^{5+} ions were preferentially incorporated into the surface octahedral vacant sites of $\gamma\text{-Al}_2\text{O}_3$ support. There is a loading threshold for Nb_2O_5 on $\gamma\text{-Al}_2\text{O}_3$ to develop Brönsted acid site, which is correlated to the formation of polymerized niobia species. The amount of Brönsted acid site increases with the ratio of polymerized to dispersed niobia species. The catalytic activity of the $\text{Nb}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts for the condensation from isobutene and isobutyraldehyde to 2,5-dimethyl-2,4-hexdiene is correlated to the state of niobia species on the $\gamma\text{-Al}_2\text{O}_3$ support. The catalytic activity (TOF) acquires the maximum value when the niobia species is in the state of monolayer dispersion on the $\gamma\text{-Al}_2\text{O}_3$ support.

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Jie HE was born in Anhui in 1962. He is a Professor at Anhui University of Science and Technology. Dr. He got his B.S. degree from Anqing Teachers College in 1984 and M.S. degree from Nanjing University in 1990. He got his Ph.D. degree in Physical Chemistry from Nanjing University in 2004. He worked as a postdoctoral on desulfurization

processes for fuel cells systems at University of Yamanashi, Japan in 2005–2006. His current research interests include (1) heterogeneous catalysis: in particular, solid acid catalysis, and environmental catalysis, and (2) surface/interface chemistry: surface modification of natural minerals. In recent years, Dr. He has been actively involved in heterogeneous catalysis. He was involved in studying the reaction of olefin-aldehyde condensation and nitration of aromatics by solid acid catalysts, especial in niobium compounds, such as supported niobia, layered and nanosheet niobate etc. He has also focused on adsorption and photocatalytic oxidation for removing organic sulfides from gas.

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