



Acid property of Nb₂O₅/Al₂O₃ prepared by impregnation method by using niobium oxalate solution: Effect of pH on the structure and acid property



Tomoyuki Kitano^a, Tetsuya Shishido^{b,c,*}, Kentaro Teramura^{a,c,d}, Tsunehiro Tanaka^{a,c,**}

^a Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

^b Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

^c Elements Strategy Initiative for Catalysts & Batteries Kyoto University, Kyoto 615-8520, Japan

^d Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

ARTICLE INFO

Article history:

Received 15 June 2013

Received in revised form

11 September 2013

Accepted 25 September 2013

Available online 27 October 2013

Keywords:

Solid acid catalyst

Niobium oxide

Monolayer

Domain size

Brønsted acid site

Alumina

ABSTRACT

5 and 16 wt% Nb₂O₅/Al₂O₃ catalysts were prepared by impregnation method by using niobium oxalate solution with various pH values. The acid property of Nb₂O₅/Al₂O₃ was examined by benzylation of anisole and pyridine adsorbed Fourier transform infrared (FT-IR) spectra. The structure of domains of niobium oxide monolayer on 5 and 16 wt% Nb₂O₅/Al₂O₃ were characterized by means of X-ray diffraction (XRD), Raman spectroscopy, and pyridine adsorbed FT-IR spectra. The acid property of 16 wt% Nb₂O₅/Al₂O₃ strongly depended on the pH values of niobium oxalate solution. As increase of pH value of niobium oxalate solution, the size of domains of niobium oxide monolayer increased. Brønsted acidity on Nb₂O₅/Al₂O₃ increased with increasing in the domain size of niobium oxide monolayer. The structural analysis strongly suggests that the stress triggered by generation of the boundaries between domains is higher, as the domain size of niobium oxide monolayer increases. We proposed that the strong distortion of Nb–(OH)–Nb bond at the boundaries between domains of niobium oxide monolayer is necessary to generate Brønsted acid sites on Nb₂O₅/Al₂O₃ catalysts.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Recently, we demonstrated that Brønsted acid sites were generated on Nb₂O₅/Al₂O₃ calcined at high temperatures such as 1123 K. Most ordinal solid acid catalysts lose their acid property when these were calcined at high temperatures (>1000 K). Acid property of niobic acid (Nb₂O₅·nH₂O), which shows a solid acid catalyst exhibiting activity for water-relating reactions [1–5] and strong acid property ($H_0 < -5.6$) [1,2,6], also disappears by calcination at higher temperatures than 773 K due to phase transformation from amorphous to crystalline phases (TT- and T-phases) [7,8]. In contrast, Nb₂O₅/Al₂O₃ calcined at 1123 K maintains Brønsted acid sites despite of calcination at high temperature [9–11]. 16 wt%

Nb₂O₅/Al₂O₃ calcined at 1123 K exhibited the highest activity and Brønsted acidity among the Nb₂O₅/Al₂O₃ tested. Moreover, the Brønsted acid sites generated on Nb₂O₅/Al₂O₃ catalysts were thermally stable, no decline of the activity for isomerization of α -pinene was observed even after treatment at high temperatures such as 1173 K.

The acid property of Nb₂O₅/Al₂O₃ strongly depended on both calcination temperature and loading amount of Nb₂O₅ due to structural change of niobium oxide supported on alumina [12,13]. Based on structural characterization of Nb₂O₅/Al₂O₃ calcined at 1123 K, we revealed that niobium oxide was loaded as two-dimensional monolayer domains on alumina, and the number of domains increased without change in the domain size as Nb₂O₅ loading amount increased [12]. Furthermore, we proposed that Brønsted acid sites were generated at the boundaries between domains of niobium oxide monolayer.

Many researchers have widely investigated the size effect of supported metal particle on catalytic activity [14–18]. Gold is generally known as inert metal. However, Au nanoparticle supported on titania (Au/TiO₂) exhibited a reaction activity for various reactions such as selective oxidation and hydrogenation, and the reaction activity strongly depended on the particle size of gold

* Corresponding author at: Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan. Tel.: +81 42 677 2850; fax: +81 42 677 2850.

** Corresponding author at: Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. Tel.: +81 75 383 2558; fax: +81 75 383 2561.

E-mail addresses: shishido-tetsuya@tmu.ac.jp (T. Shishido), tanakat@moleng.kyoto-u.ac.jp (T. Tanaka).

[14–16]. Tsukuda et al. also reported that Au clusters stabilized by poly(*N*-vinyl-2-pyrrolidone), which was smaller than 1.5 nm, exhibited a high activity for selective aerobic oxidation, and that the activity strongly depends on the size of gold nanoparticle [17,18].

Catalytic performances and properties of supported metal oxides are affected by structure (crystal structure, anisotropic aspect, etc.). Two-dimensional domains of molybdenum oxide supported on alumina promote oxidative dehydration of propane, and polymeric molybdenum oxide on alumina is active for epoxidation of allyl alcohol. However, these reactions do not take place on monomeric molybdenum oxide well [19,20]. In the case of WO_3/ZrO_2 , no superacid site is generated on monomeric tungsten oxide. In contrast, superacid sites are generated on polymeric tungsten oxide [21–23].

Preparation method has been widely investigated to control local structure of supported metal oxide. Tanaka et al. [24] reported that propene photo-oxidation on $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalysts prepared by an equilibrium adsorption method yields propene oxide selectively, formed on monomeric NbO_4 , whereas the photo-oxidation on the catalyst prepared by a conventional evaporation to dryness method with low-loading yields propanal selectively. They concluded that propanal is the product in decomposition of propene oxide on oligomeric NbO_4 tetrahedra. Changing in the pH value of the preparation solution is one of the most utilized methods to control the aggregation state of supported metal oxide. Yoshida et al. [25] reported that the dispersion of tetrahedral niobium oxide species (the size of niobium oxide cluster) supported on the silica surface can be controlled by changing the pH values of the niobium oxalate solution.

In the present study, we prepared a series of 5 and 16 wt% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ prepared by impregnation method by using niobium oxalate aqueous solution with various pH values to control the size of niobium oxide cluster. The acid property and structure of prepared $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ were investigated. To clarify the effect of pH value on the acid property and the structure of niobium oxide monolayer domains, the acid property of $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ was evaluated by benzylation of anisole and pyridine adsorbed FT-IR spectra. The structure of niobium monolayer domains on $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ was characterized by means of XRD, Raman spectroscopy, and pyridine adsorbed FT-IR spectra.

2. Experimental

2.1. Preparation

A series of 5 and 16 wt% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ were prepared by impregnation of γ -alumina (JRC-ALO-8) with an aqueous solution of niobium oxalate (CBMM) of various pH values (pH 0.7–4.1) as below. The constant volume (33 mL) of aqueous solution including the desired amount of the niobium ammonium oxalate was used. The pH value of the preparation solution was controlled at a pH range of 0.7–4.1 by addition of aqueous ammonium. The γ - Al_2O_3 was impregnated with the solutions and stirred for 2 h at 353 K. Then, the solution was dried up at 353 K. The precipitate was dried at 353 K for 12 h, and calcined at 1123 K for 3 h in a dry air.

2.2. Reactions

Benzylation of anisole (Friedel–Crafts alkylation of anisole with benzylalcohol) was examined in a liquid phase as follows: 0.2 g of the catalyst was pretreated in N_2 flow at 473 K for 1 h and then added to a mixture of benzyl alcohol (6.25 mmol) and anisole (92.5 mmol) in a 100 ml flask. The reaction was carried out at 413 K and products were determined by GLC (Shimadzu GC-14B with a

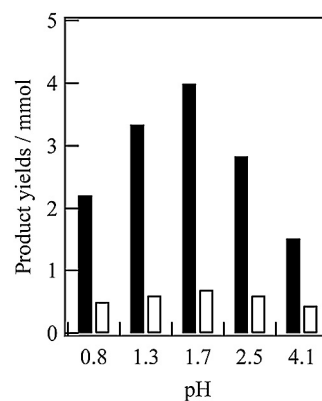


Fig. 1. Activity of 16 wt% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ prepared from niobium oxalate solution with various pH values. (■) Benzyl anisole and (□) dibenzyl ether. Calcination temperature: 1123 K.

flame ionization detector) and GC-MS (Shimadzu GC-MS QP-5050), by using a CBP10 column.

2.3. Characterizations

X-ray diffraction (XRD) patterns were obtained using a Multi-Flex DR powder X-ray diffractometer (Rigaku, Tokyo, Japan), using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$).

Laser Raman spectra were obtained using a NRS-2000 Raman Spectrometer (JASCO, Tokyo, Japan), using 514.5-nm line of an argon laser. The spectral resolution was 4 cm^{-1} .

Characterization was performed for the obtained catalysts by FTIR. FTIR spectra were recorded with Perkin-Elmer SPETROM ONE Fourier transform infrared spectrometer with the resolution of 4 cm^{-1} . Each sample (12.5 mg) was pressed into a self-supporting wafer (13 mm in a diameter). The catalysts were pretreated under 13.3 kPa of O_2 for 1 h at 673 K and then evacuated for 1 h at the same temperature. For the determination of the amount of Brønsted and Lewis acid sites over samples, the wafer was exposed to 0.667 kPa of pyridine at 298 K for 10 min followed by evacuation at 423 K for 10 min.

3. Results

3.1. Acid properties

Fig. 1 shows the activities for benzylation of anisole over 16 wt% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ prepared by using niobium oxalate solution with various pH values. The main products were *o*-benzyl and *p*-benzyl anisoles, and the minor was dibenzyl ether. No polymerized product appeared. Benzyl anisole is produced on Brønsted acid sites [26–32]. The yield of benzyl anisole remarkably depended on pH value. Increase of pH value up to 1.7 resulted in raise of the yield of benzyl anisole and the yield decreased above pH 1.7. On the other hand, the yield of dibenzyl ether slightly changed. In the previous papers, we showed that the yield of benzyl anisole well correlates with Brønsted acidity of $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ [11,33]. These results strongly suggest that the pH value of niobium oxalate aqueous solution affects Brønsted acidity of $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$, and that the largest number of Brønsted acid site was generated on 16 wt% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ prepared at pH 1.7 among the $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ tested.

Fig. 2 shows the Brønsted acidity of 16 wt% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ calcined 1123 K prepared from the solution of niobium oxalate with various pH values. The Brønsted acidity was estimated from the area of band at 1545 cm^{-1} , which is assignable to protonated pyridine (pyridine adsorbed on Brønsted acid site). The integrated molar adsorption coefficient value of $\epsilon = 1.67 \text{ cm} \mu\text{mol}^{-1}$

Download English Version:

<https://daneshyari.com/en/article/54513>

Download Persian Version:

<https://daneshyari.com/article/54513>

[Daneshyari.com](https://daneshyari.com)