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Brønsted Acid Generation over Alumina-Supported Niobia by Calcination at 1173 K

**Tetsuya Shishido · Tomoyuki Kitano ·
Kentaro Teramura · Tsunehiro Tanaka**

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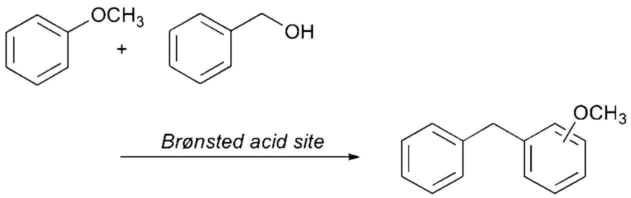
Abstract Alumina-supported niobium oxide promotes Friedel–Crafts reaction of benzyl alcohol and anisole effectively. The optimized condition of the catalyst was 16 wt% as Nb_2O_5 and calcination temperature of 1173 K. The catalyst exhibits the Brønsted acidity despite calcination at such high temperatures.

Keywords Alumina-supported niobia · Brønsted acid catalyst · Fridel–Crafts reaction

1 Introduction

Niobic acid ($Nb_2O_5 \cdot nH_2O$, hydrated niobium oxide) is known as a water-tolerant solid acid catalyst exhibiting strong Brønsted acidity and effective for the reaction relating to aqueous media like esterification, olefin hydration, alcohol dehydration, etc. [1–6] But due to the dehydration of niobic acid, it loses the acidity when heating at higher temperatures than 673 K in contrast to other usual metal oxide solid acids. On the other hand, previous XAFS study [7] of supported niobium oxide showed that a niobic acid-like compound is stabilized on Al_2O_3 surface at higher temperatures than 673 K at somewhat high loading of niobium oxide and predicted that highly loaded Nb_2O_5/Al_2O_3 would act as a stable Brønsted acid. In the present paper, we prepared a series of Nb_2O_5/Al_2O_3 with various loading of Nb_2O_5 and examined its unique acid property using a so-called Friedel–Crafts reaction of anisole and benzyl alcohol to be promoted on Brønsted acid [8–14].



2 Experimental

A series of Nb_2O_5/Al_2O_3 were prepared by impregnation of γ-alumina (JRC-ALO-8) with an aqueous solution of niobium oxalate and calcined at various temperatures.

Rigaku MultiFlex DR Powder X-ray diffractometer (XRD) and JASCO NRS-2000 Raman Spectrometer were employed for the identification of the compounds formed on the catalyst samples [15, 16]. Specific surface area was evaluated by BET method using liquid nitrogen with BEL Japan BELSORP28 28A.

Infrared spectra of adsorbed pyridine recorded with Perkin-Elmer SPETRUM ONE Fourier transform infrared spectrometer were used for determination of the amounts of Brønsted and Lewis acid sites over Nb_2O_5/Al_2O_3 using adsorbed pyridine with IR bands at 1550 and 1450 cm^{-1} due to pyridinium ion and pyridine coordinated to Lewis acid site [17].

T. Shishido · T. Kitano · T. Tanaka (✉)
Department of Molecular Engineering, Kyoto University
Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
e-mail: tanakat@moleng.kyoto-u.ac.jp

T. Shishido
e-mail: shishido@moleng.kyoto-u.ac.jp

K. Teramura
Kyoto University Pioneering Research Unit for Next Generation,
Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

The reaction between benzyl alcohol and anisole in the presence of Nb_2O_5/Al_2O_3 was adopted as a catalytic test. The 1.0 g of Nb_2O_5/Al_2O_3 was added to the mixture of 6.25 mmol benzyl alcohol and 92.5 mmol anisole in a flask. The reaction solution was stirred at 413 K. Products were determined by GLC and GC–MS. The main product was benzyl anisole presumably formed on Brønsted acid site and the byproduct, dibenzyl ether produced mostly on Lewis acid site.

3 Results and Discussion

Figure 1 shows the reaction selectivity to benzyl anisole over the catalyst with various Nb_2O_5 loadings calcined at 773 K and the fraction of Brønsted acid sites. Dibenzyl ether was selectively formed on alumina but with an increase of the loading amount of Nb_2O_5, the selectivity to benzyl anisole was increased and attained constant, 60% at around 10 wt% of Nb_2O_5. Evidently, the change in selectivity is in good accordance with the Brønsted acid site fractions although the amount of Brønsted acid sites could not be evaluated for the catalyst sample with lower Nb_2O_5 loading than 10 wt% because the molar absorption coefficient of the IR band due to pyridinium ion was so small that the band intensity was hidden within an error. The result strongly indicates that the Friedel–Crafts reaction is promoted on Brønsted acid sites in the present case and we can confirm the presence of Brønsted acid sites on highly loaded Nb_2O_5/Al_2O_3.

The subsequent interest is whether or not Brønsted acidity is retained on the catalyst sample calcined at higher temperatures. The reactions were carried out over 11 wt% Nb_2O_5/Al_2O_3 calcined at 673–1423 K and the product yields were shown in Fig. 2. In case of the ordinary metal oxide solid acid, pretreatment temperature of higher than 773 K brings about the disappearance of acid sites, while in the present case, catalytic activity for benzyl anisole yield is enhanced by raising the calcination temperature up to 1173 K. The calcination at higher temperature than 1273 K results in the reduction of activity of the catalyst. In addition, the yield of dibenzyl ether does not vary significantly. The conversion of benzyl alcohol attained 92% over the catalyst calcined at 1173 K for 3 h. The calcination up to 1173 K does not cause the formation of niobium oxide crystallite nor aluminium niobate crystallite clarified by powder X-ray diffraction and Raman spectroscopy. Both the XRD pattern and the Raman spectrum of the sample calcined at 1273 K exhibits the presence of aluminium niobate. This suggests that alumina support stabilizes amorphous niobia and prevents it from crystallization against calcination even at 1173 K. With the connection of the crystallization, specific surface area of Nb_2O_5/Al_2O_3 is very gradually decreased with an increase in calcination temperature up to 1173 K (155–115 $m^2\ g^{-1}$) and drastically dropping down to 40 $m^2\ g^{-1}$ by calcination at higher temperatures than 1173 K up to 1423 K as shown in Fig. 3.

We optimized the loading amount of Nb_2O_5 over alumina for the catalysts calcined at 1173 K as shown in Fig. 4. At around 16 wt% loading, the catalyst exhibits the highest activity; the conversion of benzyl alcohol attained 100%, and 5.45 mmol of benzyl anisole was produced for 1 h. This is an outstanding catalytic result. In case of niobic acid calcined at 473 K, conversion was found to be 31% and 0.34 mmol of benzyl alcohol and 0.27 mmol of dibenzyl ether were produced for 1 h. The yield curve of benzyl anisole varies similarly with the conversion curve, while that of benzyl ether does not vary significantly. To

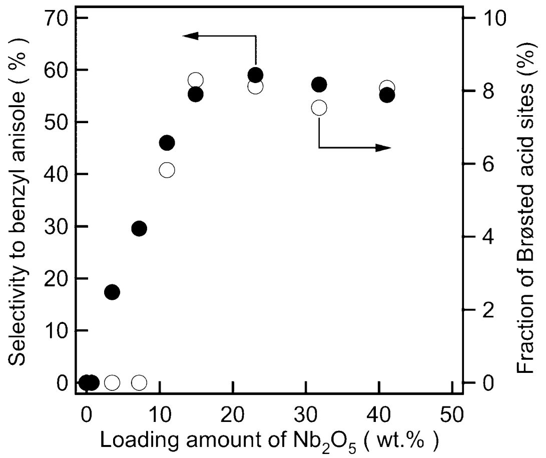


Fig. 1 Selectivity to benzyl anisole and fraction of Brønsted acid sites over Nb_2O_5/Al_2O_3 with various loadings calcined at 773 K. Reaction time 3 h. (○) Fraction of Brønsted acid sites, (●) selectivity to benzyl anisole

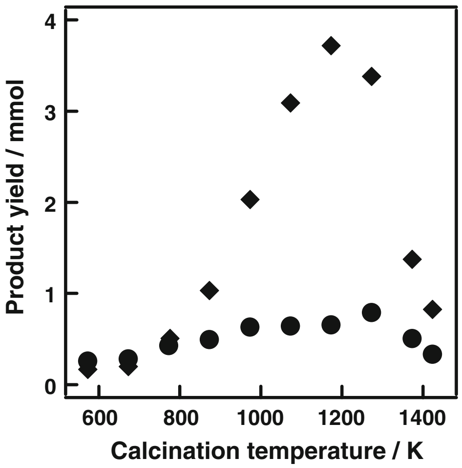


Fig. 2 Yield of products over 11 wt% Nb_2O_5/Al_2O_3 calcined at various temperatures. Reaction time 3 h. (◆) Benzyl anisole, (●) dibenzyl ether

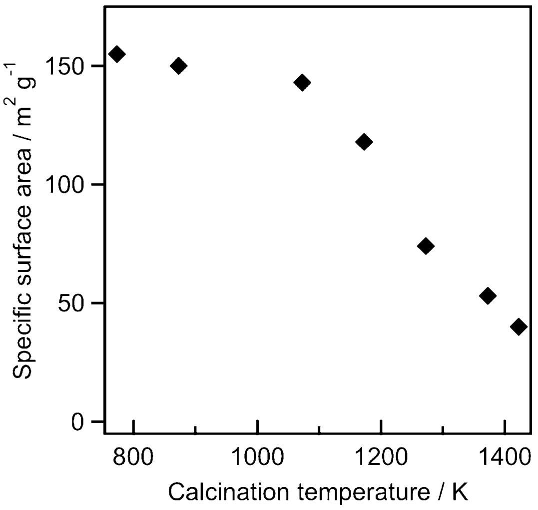


Fig. 3 Reduction of specific surface area of 11 wt% Nb_2O_5/Al_2O_3 with calcination temperature

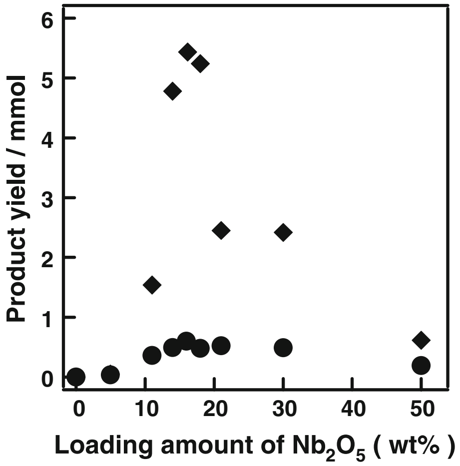


Fig. 4 Yield of products over Nb_2O_5/Al_2O_3 with various loadings calcined at 1173 K. Reaction time 1 h. (◆) Benzyl anisole, (●) dibenzyl ether

examine whether or not Brønsted acidity controls the benzyl anisole production still in case of the catalyst sample calcined at 1173 K, we evaluate the specific amount of the adsorbed pyridinium ions for Brønsted acid sites and pyridine coordinated to Lewis acid sites over each Nb_2O_5/Al_2O_3. The yield of benzyl anisole correlates with the Brønsted acidity very well. As shown in Fig. 5, it correlates with the Brønsted acidity evaluated from the amount of pyridinium ions remaining on the surface in vacuo at 473 K, indicating that Friedel–Crafts reaction is promoted on strong Brønsted acid sites. It is very interesting that Brønsted acid sites are still remaining on the Nb_2O_5/Al_2O_3 calcined at 1173 K. This is in a marked difference from the evidence that niobium oxide itself calcined at higher temperatures than 773 K does not exhibit Brønsted acidity at all.

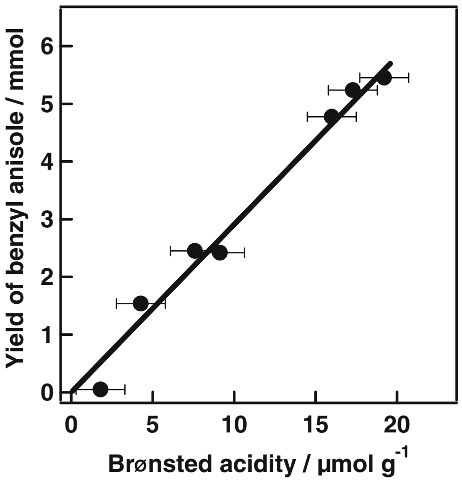


Fig. 5 Yield of alkylated products over Nb_2O_5/Al_2O_3 with various loadings calcined at 1173 K plotted against specific amount of Brønsted acid sites over each catalyst. Reaction time 1 h

Because the catalyst sample undergoes the structural change around niobium cations on the surface, XRD pattern and Raman spectrum gives the same information that a trace of $AlNbO_4$ is appearing on the Nb_2O_5/Al_2O_3 with loading higher than 16 wt%. Although $AlNbO_4$ was not detected for the catalyst containing Nb_2O_5 less than 11 wt%, undetectable tiny amount of crystallites would appear also on these catalyst samples. To investigate the catalytic activity of $AlNbO_4$, $AlNbO_4$ was prepared by sol–gel method, and added to the reaction mixture. We found that $AlNbO_4$ is completely inert.

From the results mentioned above, we conclude that highly loaded Nb_2O_5/Al_2O_3 calcined at 1173 K can act as a strong solid acid with Brønsted acidity and expect it as a water-tolerant solid acid. As for the active species, stabilized niobic acid-like compound was expected but the present result strongly suggests that the precursor of $AlNbO_4$ is relating to the active species. We speculate that the highly positive hydrogen atom is located at Al–O-Nb bond in $AlNbO_4$ precursor.

The more detailed structural analysis and application to the other reaction system is now in progress.

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