Available online at www.sciencedirect.com

Catalysis Today 118 (2006) 385–391

www.elsevier.com/locate/cattod

Activity and acidity of Nb_2O_5-MoO_3 and Nb_2O_5-WO_3 in the Friedel-Crafts alkylation

Katsuhiko Yamashita, Miho Hirano, Kazu Okumura, Miki Niwa *

Department of Materials Science, Faculty of Engineering, Tottori University, Koyama, Tottori 680-8552, Japan

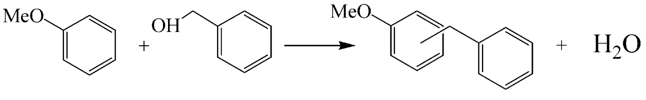
Abstract

Nb_2O_5 loaded on the supports and mixed with oxides was studied to investigate the activity and acidity for Friedel-Crafts benzylation of anisole. From the study on the loaded catalysts, a preliminary conclusion for the selection of metal oxide was obtained; namely, such an acidic oxide as silica was suitable for the support of Nb_2O_5. Then, MoO_3 and WO_3 were mixed with Nb_2O_5, and prominent high catalytic activity and acidities were observed. Both oxides of Nb_2O_5-MoO_3 and Nb_2O_5-WO_3 showed almost similar behavior with respect to characterization and catalytic activity. Surface area increased, X-ray diffraction (XRD) and Raman bands were lost, acid sites, both Brønsted and Lewis characters generated, and surface acid site density was as high as 2–4 nm^{-2}. The acid sites were generated on the amorphous metal oxides consisting of Nb and Mo or W oxides, different in nature from those of Nb_2O_5 calcined and un-calcined, and active for Friedel-Crafts benzylation.

Keywords: Friedel-Crafts benzylation; Nb_2O_5-MoO_3; Nb_2O_5-WO_3

1. Introduction

Niobium oxide has been known as an oxide with the solid acidity which depends on the degree of hydration [1,2]. Hydrated niobium oxide, i.e., so-called niobic acid has the Brønsted acidity, and therefore the solid acid-catalyzed reaction in the presence of water as reactant or product is studied. However, its application to acid-catalyzed reactions has not yet been studied sufficiently. In previous papers, much effort has been devoted to the development of the niobium oxide based catalysts for oxidation and acid-catalyzed reactions. In particular, various modifications of niobium oxide with other elements added or mixed [3–5], or by loading on supports [6] has been studied. Based on these investigations, various profiles have been clarified recently.



In the study of metal oxide supported catalysts, spreading of the loaded metal oxide on supports, or the dispersion of added elements is a fundamental aspect to be studied, and based on the exposed element or active site, catalytic activity is quantitatively analyzed. Although much information is available with respect to the spreading of niobium oxide, overall feature is not sufficiently provided. The purpose of the present study is, therefore, to reveal the spreading or dispersion behavior of niobium oxide. In line with the investigation, we will study the development of niobium oxide based catalysts for benzylation of anisole. We studied, in this paper, mixed oxide catalysts consisting of Nb_2O_5 in order to reveal the catalyst active for Friedel-Crafts alkylation. Among catalysts studied in this paper, Nb_2O_5-MoO_3 and Nb_2O_5-WO_3 were found to be the most active. Benzylation of anisole as shown below is studied as a facile Friedel-Crafts alkylation. A previous study reported the activity of niobic acid for the reaction [7].

2. Experimental

2.1. Preparation of catalysts

Hydrated niobium oxide $Nb_2O_5 \cdot nH_2O$ ($n = 3.8$, measured by TG) kindly supplied by CBMM Co. was dissolved into an oxalic acid solution heated at 353 K. Likewise, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was thoroughly dissolved into deionized water at 353 K. Both the solutions were mixed and stirred vigorously at

---

* Corresponding author. Fax: +81 857 31 5256.
E-mail address: mikiniwa@chem.tottori-u.ac.jp (M. Niwa).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.07.025

Table 1
Activity of Nb_2O_5-containing metal oxides for the benzylation of anisole

Catalyst	Nb surface concentration (nm^{-2})	Conversion (%) benzyl-alcohol	Yield (%)				Carbon material balance
			o-Benzylanisole	*m*-Benzylanisole	*p*-Benzylanisole	Dibenzylether	
Nb_2O_5-WO_3	–	>99	42.6	0.3	46.3	0.6	91
Nb_2O_5/SiO_2[a]	6.2	46.5	8.8	0	12.9	7.6	91
Nb_2O_5/TiO_2[a]	24	24.6	3.9	0	6.4	5.0	96
Nb_2O_5/Al_2O_3[a]	7.6	6.3	0.2	0.1	0.4	3.7	102
Nb_2O_5/MgO[a]	17	0.2	0	0	0	0	100
Nb_2O_5[b]	–	10.7	–	–	1.0	3.2	94

[a] Loading of Nb_2O_5 on supports, 20 wt%, and 0.2 g of the catalyst was used at 413 K for 3 h.
[b] 0.04 g of Nb_2O_5 was used for the reaction, because the supported catalysts contained 0.04 g of Nb_2O_5.

353 K, followed by evaporation to dryness. Thus obtained materials were calcined at 773 K for 3 h in a muffle furnace to obtain the mixed oxides consisting of Nb and Mo oxides. For preparation of W-containing mixed oxides, $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ was used as a starting material with other conditions for preparation kept unmodified.

Before the studies, supported catalysts were studied using four kinds of metal oxides as support: SiO_2, S_{BET}, 182 $m^2\ g^{-1}$; TiO_2, S_{BET}, 47 $m^2\ g^{-1}$; Al_2O_3, S_{BET}, 148 $m^2\ g^{-1}$; MgO, S_{BET}, 66 $m^2\ g^{-1}$. Hydrated niobium oxide $Nb_2O_5\cdot nH_2O$ dissolved into an oxalic acid solution was impregnated to support metal oxides, followed by evaporation to dryness, and calcined at 773 K for 3 h.

2.2. Characterization of catalyst

Surface area was measured by a BET method using an adsorption apparatus, Nippon BEL SORP-mini. X-ray diffraction (XRD) was measured by a Rigaku Mini-flex plus X-ray diffractometer with Cu Kα radiation. XPS was measured by an ESCAPROBE2 of Omicron Co. From the intensities of Nb $3d_{5/2}$, Mo $3d_{5/2}$, and W $4f_{7/2}$ (ca. 207, 233, and 36 eV, respectively) and cross-sectional areas, surface composition of Nb and Mo, or W was calculated.

2.3. EXAFS measurements

The data of Mo-K edge EXAFS were collected at BL01B1 station in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2005B0022-NXa-np). A Si(3 1 1) single crystal was used to obtain monochromatic X-ray beam. Two ion chambers filled with N_2 50%, Ar 50% and Ar 75%, Kr 25% were used as detectors for I_0 and I, respectively. The measurement was carried out under ambient conditions. The Fourier transformation of the k^3-weighted EXAFS oscillation from k space to r space was performed over the range of 30–130 nm^{-1} to obtain a radial distribution function.

2.4. Catalytic reaction

Mixed oxide and loaded catalysts were dehydrated at 673 K by flowing oxygen or nitrogen before the reaction. Unless otherwise described, catalytic reactions were performed at 353 K for 3 h in the solution of benzyl alcohol (6.25 mmol) and anisole (92.5 mmol) with 0.1 g of the catalyst in a flask immersed in an oil-bath heater. Products were analyzed by a gas chromatography (Shimadzu GC-2010) equipped with a silicone capillary column MDN-12.

3. Results

3.1. Activity of Nb_2O_5 supported catalysts for the benzylation and characterization

In a preliminary study, Nb_2O_5 supported catalysts were tested for the Friedel-Crafts benzylation. As shown in Table 1, four kinds of supported catalysts had the activities for the reaction in a following sequence:

$$Nb_2O_5/SiO_2 > Nb_2O_5/TiO_2 > Nb_2O_5/Al_2O_3 > Nb_2O_5/MgO$$

o-Benzylanisole and *p*-benzylanisole isomers were formed, and the material balance of carbon-containing molecules was close to 100%. Because the activity of Nb_2O_5/SiO_2 was much higher than the same amount of non-supported Nb_2O_5, a synergetic effect was obviously found on the support SiO_2.

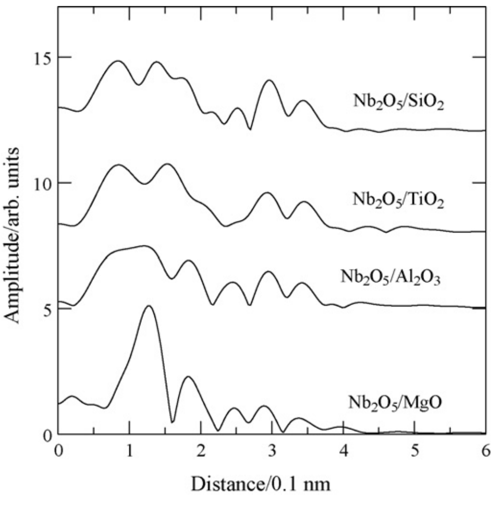


Fig. 1. Nb-K edge EXAFS Fourier transforms of 20 wt% Nb_2O_5 loaded on various supports.

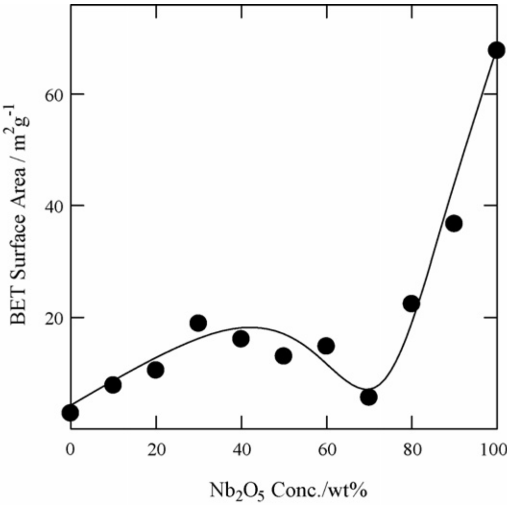


Fig. 2. BET surface area of Nb_2O_5-MoO_3 plotted as a function of Nb_2O_5 loading.

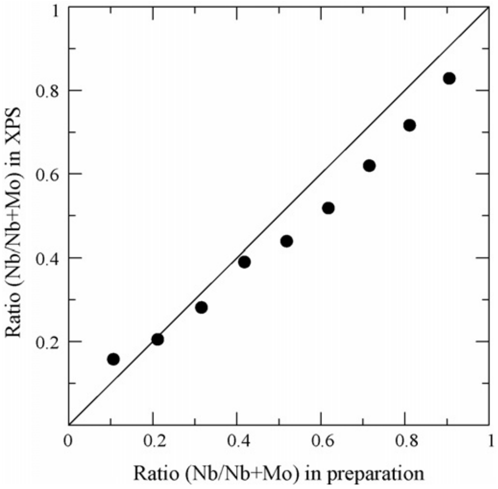


Fig. 4. Surface composition of Nb_2O_5-MoO_3 measured by XPS.

Studies on dispersion and acidity on Nb_2O_5/SiO_2 have already been reported in the literature [8]. Therefore, it seemed that such an acidic oxide as silica was appropriate for loading of Nb_2O_5 with the solid acidity. On the other hand, niobic oxide loaded on basic metal oxides did not provide high catalytic activity.

Nb-K edge EXAFS Fourier transforms of Nb on these supports were measured, as shown in Fig. 1. From the intensity at the distance ca. 0.3–0.35 nm due to Nb-Nb bonds, the loading conditions of Nb could be estimated. Namely, because of the weak intensity, Nb or niobia was spread mostly on MgO, while on SiO_2 niobia was agglomerated into a large particle. These different profiles on MgO and SiO_2 are in agreement with usual findings of V_2O_5 [9] and MoO_3 [10] supported catalysts. Due to different surface areas of supports, surface concentrations of Nb were different, 6–24 Nb nm^{-2} (Table 1); however, the difference is not so large as to affect the conclusion on the spreading behavior.

Based on the preliminary studies, such acidic metal oxides as WO_3 and MoO_3 were studied as a component for mixing with Nb_2O_5. As shown in Table 1, a mixed oxide of Nb_2O_5 with WO_3 was found to have a superior activity to arrive at 100% of the conversion at 413 K. For a comparison of catalytic activities, the reaction temperature was thus lowered to 353 K, and these catalyst systems were studied in detail.

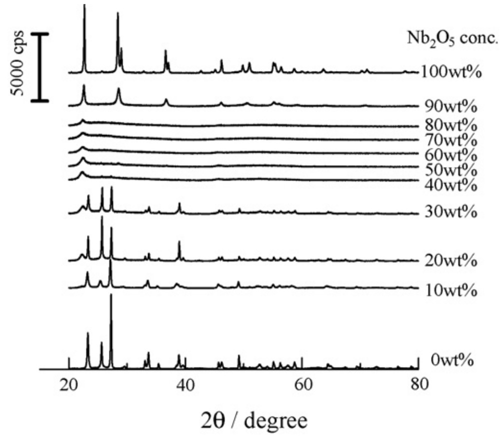


Fig. 3. XRD patterns of Nb_2O_5-MoO_3 having different concentration of Nb_2O_5.

3.2. Characterization of catalysts prepared by mixing of Nb and Mo oxides

BET surface area increased by mixing of Nb_2O_5 to show the high value at ca. 40 wt% of Nb_2O_5 concentration, and finally increased up to the maximum of 60 m^2 g^{-1} of the pure Nb_2O_5 (Fig. 2). XRD showed the diffraction patterns which were identified as MoO_3 and Nb_2O_5 at respective pure oxides, but in mixed oxides only broad and weak diffractions were revealed (Fig. 3). Surface composition measured by XPS almost agreed with that estimated from the preparation conditions (Fig. 4). Surface enrichment of neither Nb nor Mo was therefore observed. Strong Raman intensity of MoO_3 was observed in less than 30 wt% of Nb_2O_5 concentration, but on mixing with a concentration larger than 30 wt%, Raman spectrum intensity

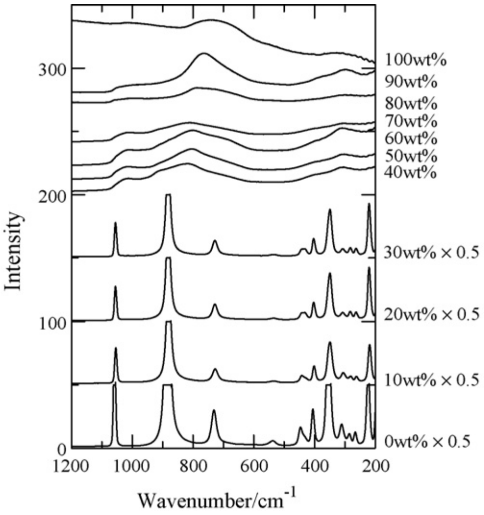


Fig. 5. Raman spectra of Nb_2O_5-MoO_3 having different concentration of Nb_2O_5.

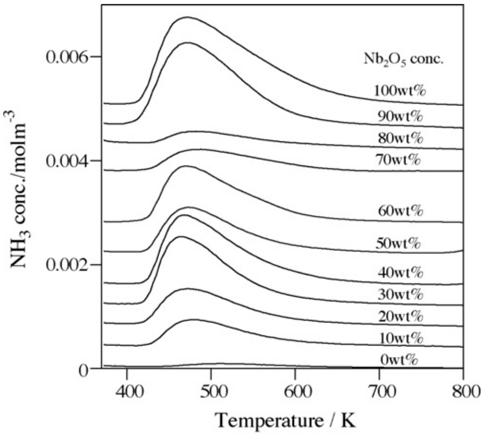


Fig. 6. Ammonia TPD of Nb_2O_5-MoO_3 having different concentration of Nb_2O_5.

disappeared completely (Fig. 5). Therefore, distinct bonds due to crystalline MoO_3 were lost in the region above 40 wt% of Nb_2O_5 concentration. These characterization data showed that MoO_3 and Nb_2O_5 mixed thoroughly to be stabilized as an amorphous species with high surface area. Mixing of Nb_2O_5 with MoO_3 resulted in such a synergy effect to form the unidentified amorphous mixed oxide consisting of Mo, Nb, and O atoms.

3.3. Solid acidity of Nb_2O_5-MoO_3

The profile of ammonia TPD showed ammonia desorption at less than 500 K and it was almost independent of the composition of Nb_2O_5 (Fig. 6). Number of the acid sites measured from the desorbed ammonia increased by mixing with Nb_2O_5 to show the high value at ca. 40 wt% of Nb_2O_5, and finally increased up to the highest value at the pure Nb_2O_5. The profile of the change therefore resembled that of BET surface area. Surface acid site density, i.e., number of acid site divided by surface area, showed about 2 nm^{-2} between 0 and 70 wt% of Nb_2O_5 concentration (Fig. 7). A common profile of the acid site formed was therefore suggested in these regions of Nb_2O_5 concentration. On the other hand, pure Nb_2O_5 showed a different value of surface acid density such as 1 nm^{-2}. Therefore, Nb_2O_5 pure crystal had the acidity different from on the mixed oxides. Pyridine adsorption revealed the formation of Brønsted acid sites on the mixed oxides, though only Lewis acid site was observed on pure oxide of MoO_3 and Nb_2O_5 (Fig. 8).

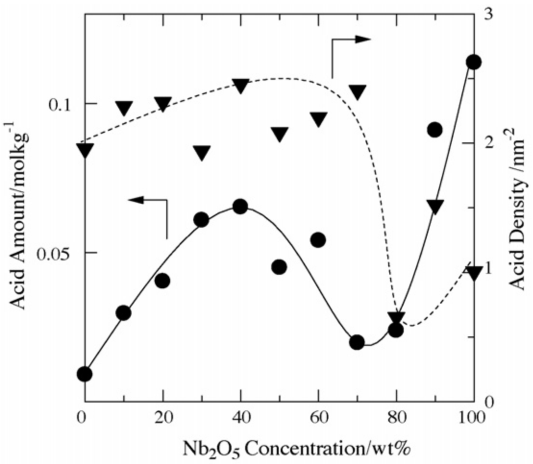


Fig. 7. Acid amount and acid density of Nb_2O_5-MoO_3 plotted as a function of Nb_2O_5 concentration.

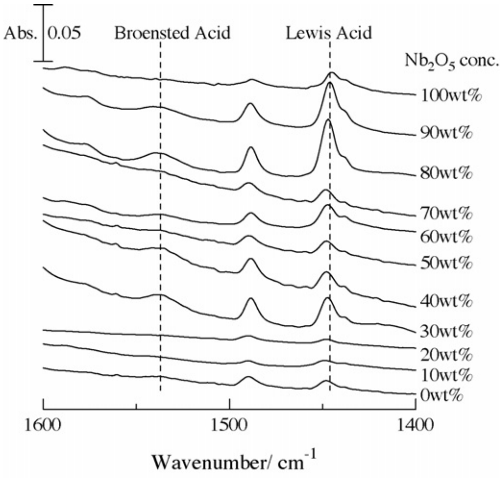


Fig. 8. IR of adsorbed pyridine over Nb_2O_5-MoO_3 having different concentration of Nb_2O_5.

3.4. Catalytic activity of mixed oxide with the different composition

Catalytic activity in the benzylation showed the maximum value at about 50 wt% of Nb_2O_5 mixed with MoO_3 (Fig. 9). *o*-Benzylanisoles and *p*-benzylanisoles were formed, and the ratio was about 44:55; however, *m*-benzylanisole was not observed. A side reaction, i.e., formation of dibenzylether, also showed the similar dependence upon the Nb_2O_5 composition, and therefore the selectivity in the formation of benzylanisole was kept a similar value between 65 and 85%.

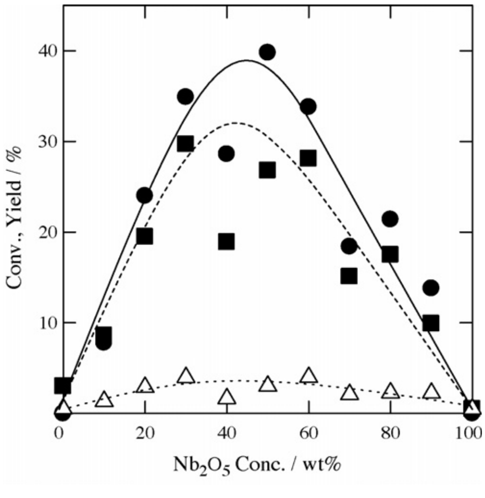


Fig. 9. Conversion of benzyl alcohol (●), yield of benzylanisole (■) and dibenzylether (△) plotted as a function of Nb_2O_5 concentration of Nb_2O_5-MoO_3. Temperature, 353 K; time, 3 h; benzyl alcohol, 6.25 mmol; anisole, 92.5 mmol, catalyst, 0.1 g.

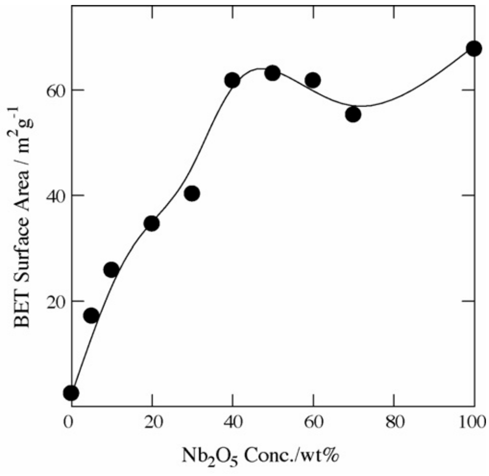


Fig. 10. BET surface area of Nb_2O_5-WO_3 plotted as a function of Nb_2O_5 loading.

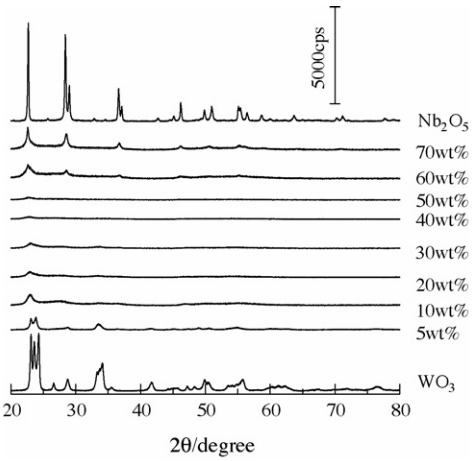


Fig. 11. XRD patterns of Nb_2O_5-WO_3 having different concentration of Nb_2O_5.

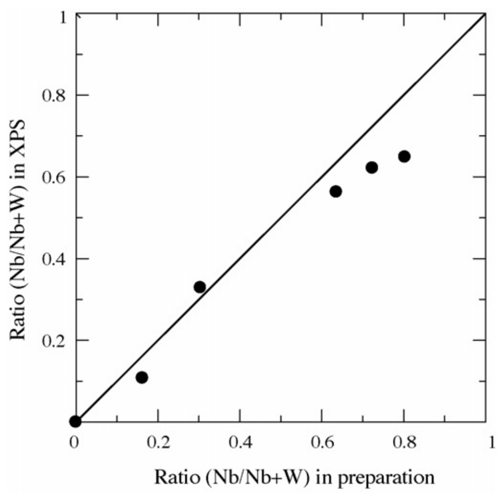


Fig. 12. Surface composition of Nb_2O_5-WO_3 measured by XPS.

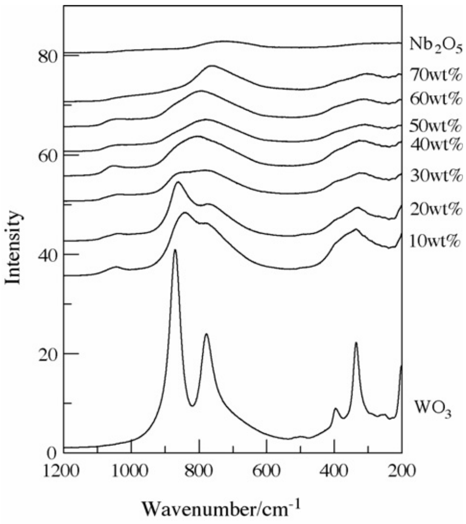


Fig. 13. Raman spectra of Nb_2O_5-WO_3 having different concentration of Nb_2O_5.

3.5. Characterization and activity of catalysts prepared by mixing of Nb and W oxides

Then, we studied W-containing Nb_2O_5 mixed catalysts. By mixing Nb_2O_5, the BET surface area increased, and showed the maximum value at 50 wt% of Nb_2O_5 concentration (Fig. 10). X-ray diffraction was observed on pure WO_3 and Nb_2O_5 only, but not distinctively on mixed oxides (Fig. 11). XPS did not show any surface enrichment of Nb or W (Fig. 12). Raman spectroscopy showed the strong intensity due to WO_3 only at the pure oxide end (Fig. 13). The Raman intensity became weak when two oxides mixed over the wide concentration of Nb_2O_5. TPD of ammonia showed the ammonia desorption at nearly 500 K, and the behavior was almost independent of the concentration of Nb_2O_5 (Fig. 14). Number of the acid sites increased by mixing Nb_2O_5, and the maximum value was observed at 50 wt%. The surface acid site density showed the high value, 4 nm^{-2}, in the region of 10–20 wt% of Nb_2O_5, and this was larger than on other concentrations (Fig. 15). IR spectrum of the adsorbed pyridine showed the presence of

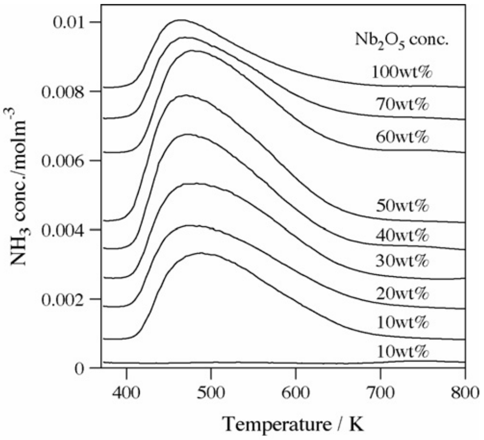


Fig. 14. Ammonia TPD of Nb_2O_5-WO_3 having different concentration of Nb_2O_5.

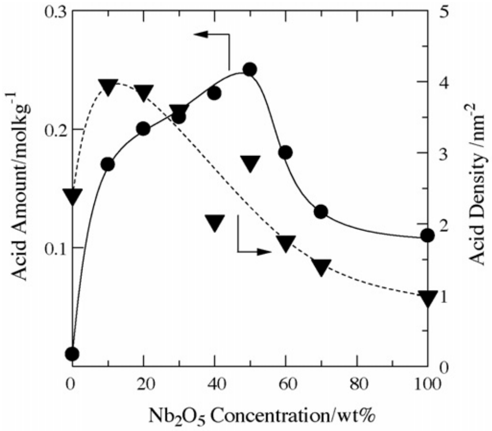


Fig. 15. Acid amount and acid density of Nb_2O_5-WO_3 plotted as a function of Nb_2O_5 concentration.

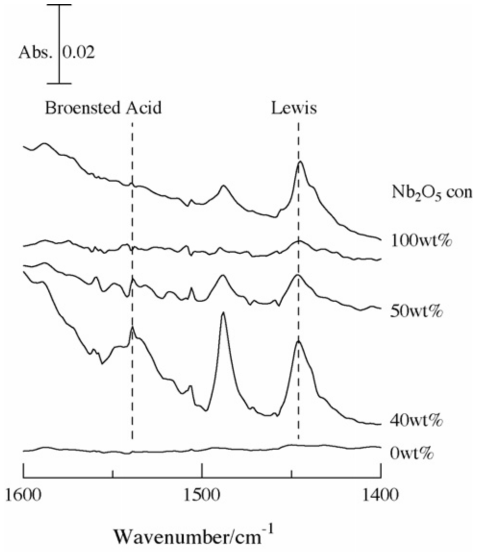


Fig. 16. IR of adsorbed pyridine over Nb_2O_5-WO_3 having different concentration of Nb_2O_5.

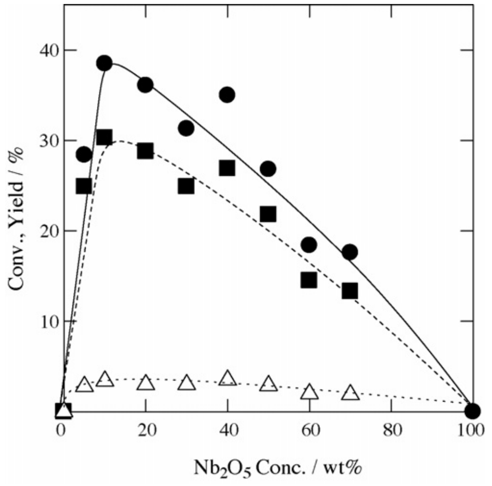


Fig. 17. Conversion of benzyl alcohol (●), yield of benzylanisole (■) and dibenzylether (△) plotted as a function of Nb_2O_5 concentration. Temperature, 353 K; time, 3 h; benzyl alcohol, 6.25 mmol; anisole, 92.5 mmol, catalyst, 0.1 g.

Brønsted acid site at 1545 cm^{-1} on the mixed oxide catalysts (Fig. 16). Catalytic activity of the mixed oxides was the high in the 10–20 wt% of Nb_2O_5 concentration (Fig. 17). When these findings were summarized, therefore, the Nb_2O_5-WO_3 mixed oxide showed the acid property, amorphous structure and the catalytic activity similar to on the Nb_2O_5-MoO_3 mixed oxide.

4. Discussion

4.1. Activity and acidity of Nb_2O_5 mixed with MoO_3 and WO_3

In the present study, Nb_2O_5-based catalysts were studied with a purpose of investigation of the solid acidity available for Friedel-Crafts benzylation of anisole. Nb_2O_5 mixing with MoO_3 and WO_3 created the prominent high activity, and these were much higher than on the supported catalysts. Nb_2O_5 mixing had similar effects on MoO_3 and WO_3, because on both oxides amorphous compounds consisting of Nb and Mo or W were formed. These unidentified amorphous mixed oxides had the relatively high surface area and the Brønsted acidity, and characterized to have a large surface density of acid sites of not only Brønsted but also Lewis acidity character. Previous studies reported the solid acidity and catalytic activity of the catalyst comprising of Nb_2O_5 and WO_3 [3,11]. In particular, a study by Hino et al. [11] revealed the high catalytic activity of cumene cracking on Nb_2O_5-WO_3, in consistent with the present investigation. On the other hand, for the MoO_3 loaded on Nb_2O_5 catalyst, characterization and oxidation activity have been reported [12].

Because the catalysts were calcined at 773 K before the reaction, the inherent Brønsted acidity of niobic acid, most probably, seems to be lost almost completely. Niobic oxide shows the acidity even after the calcination, though it is the nature of Lewis type acidity. Therefore, the acidity created by mixing is different from that of niobic oxide un-calcined and calcined.

4.2. Nb_2O_5 as an oxide for the loaded and mixed catalysts

We have previously studied the solid acidity observed on the monolayer on supports [13]. Loading acidic oxides on the weak basic metal oxides (supports) generate the strong acid sites exposed on the surface. Former acidic oxides are WO_3, MoO_3, V_2O_5, and SO_4^{2-}, and supports are such metal oxides as SnO_2, ZrO_2, TiO_2 and Al_2O_3. Among these combinations consisting of metal oxide and support, many kinds of important catalytic system are observed. Formation of the monolayer of metal oxide, and thus created solid acidity, is caused by the acid and base interaction between those oxides to form M_1–O–M_2 chemical bond (M_1, element of metal oxide, and M_2, element of support).

On the other hand, Nb_2O_5 is not included in this kind of acidic metal oxides loaded. In the present study, Nb_2O_5 loaded on TiO_2 was not selected as the catalyst with the strong acidity, and the highest activity was observed on SiO_2 among the loaded catalysts. Creation of Brønsted acid sites on Nb_2O_5 loaded on SiO_2 was also reported by Burke and Ko [14] and Datka et al.

[15] observed the Brønsted acidity only on the supports of SiO_2 and Al_2O_3, but not on magnesia, titania, and zirconia, consistently in this study. Shirai et al. reported an activity of esterification on Nb-containing compounds attached on silica [16]. This observation of niobia loaded on silica support is therefore different from those previously observed for V_2O_5, WO_3 and MoO_3 supported catalysts. As shown by the present EXAFS study, Nb-O spreads on such a basic oxide as MgO, and not on SiO_2. The behavior is fundamentally in agreement with the observation on the acid metal oxide loaded catalysts. However, the strong acid site was not observed, and interestingly the acid sites available for the reaction were observed on the SiO_2 support. On the support of SiO_2, a small particle of niobic oxide or an Nb-O species dispersed on the surface may show the solid acidity.

On the other hand, Nb or niobia was mixed thoroughly with the MoO_3 and WO_3. Though the metal oxide phase was unidentified, it seems that Nb atom is stabilized to become a solid solution in the metal oxide lattice of MoO_3 and WO_3. Because the size of cations, Nb, Mo, and W are close, these could form solid solutions. The solid acidity seemed to be formed on the materials consisting of two elements. The generation of acid sites on the material is not known yet at the present stage. As pointed out by Hino et al. [11], an isomorphous replacement model, which is known in the zeolite, seems to explain the generation of the acid site. As recently found by us [17,18], the metal oxide consisting of Nb, W, and P, which was formed during the calcination at 773 K, has the structure similar to the heteropoly acid and the prominent high catalytic activity of benzylation of anisole. Therefore, the formation of a heteropoly compound is another plausible idea to explain the solid acidity on the present catalysts.

5. Conclusions

1. Among Nb_2O_5 loaded catalysts, the Nb_2O_5 on SiO_2 showed the high activity. A small particle of Nb_2O_5 or a Nb-O compound dispersed on the surface seems to play the role of active sites.
2. Nb_2O_5 and MoO_3, and Nb_2O_5 and WO_3 are thoroughly mixed to be stabilized as unidentified amorphous phase with the acid sites, which have the Brønsted character and high surface density, different from on pure calcined Nb_2O_5. Thus created acid sites play a role of active site for benzylation of anisole.

References

[1] M. Paulis, M. Martin, D.B. Soria, A. Diaz, J.A. Odriozola, M. Montes, Appl. Catal. A: Gen. 180 (1999) 411.
[2] T. Ushikubo, Catal. Today 57 (2000) 331.
[3] C. Martın, G. Solana, P. Malet, V. Rives, Catal. Today 78 (2003) 365.
[4] F. Barbieri, D. Cauzzi, F. De Smet, M. Devillers, P. Moggic, G. Predieri, P. Ruiz, Catal. Today 61 (2000) 353.
[5] K.V.R. Chary, C.P. Kumar, K.R. Reddy, T. Bhaskar, T. Rajiah, Catal. Commun. 3 (2002) 7.
[6] L.J. Burcham, J. Datka, I.E. Wachs, J. Phys. Chem. B 103 (1999) 6015.
[7] M. Morais, E.F. Torres, L.M.P.M. Carmo, M.M.R. Pastura, W.A. Gonzalez, A.C.B. dos Santos, E.R. Lachter, Catal. Today 28 (1996) 17.
[8] M. Suzana, P. Francisco, R. Landers, Y. Gushikem, J. Solid State Chem. 177 (2004) 2432.
[9] M. Niwa, Y. Matsuoka, Y. Murakami, J. Phys. Chem. 91 (1987) 4519.
[10] Y. Matsuoka, M. Niwa, Y. Murakami, J. Phys. Chem. 94 (1990) 1477.
[11] M. Hino, M. Kurashige, K. Arata, Catal. Commun. 5 (2004) 107.
[12] K.V.R. Chary, T. Bhaskar, G. Kishan, K.R. Reddy, J. Phys. Chem. B 105 (2001) 4392.
[13] M. Niwa, Y. Habuta, K. Okumura, N. Katada, Catal. Today 87 (2003) 213.
[14] P.A. Burke, E.I. Ko, J. Catal. 129 (1991) 38.
[15] J. Datka, A.M. Turek, J.M. Jehng, I.E. Wachs, J. Catal. 135 (1992) 186.
[16] M. Shirai, N. Ichikuni, K. Asakura, Y. Iwasawa, Catal. Today 8 (1990) 57.
[17] K. Okumura, K. Yamashita, M. Hirano, M. Niwa, Chem. Lett. 34 (2005) 716.
[18] K. Okumura, K. Yamashita, M. Hirano, M. Niwa, J. Catal. 234 (2005) 300.