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Generation of Brønsted Acid Sites on Alumina-supported Tantalum(V) Oxide Calcined at 1223 K

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An alumina-supported tantalum(V) oxide (Ta_2O_5/Al_2O_3) calcined at 1223 K promoted the Friedel–Crafts alkylation of anisole with benzyl alcohol, and exhibited Brønsted acidity despite the high-temperature calcination. Among the Ta_2O_5/Al_2O_3 catalysts tested, 33 wt % Ta_2O_5/Al_2O_3 calcined at 1223 K showed the highest activity.

Niobic acid ($Nb_2O_5 \cdot nH_2O$, hydrated niobium oxide) is a water-tolerant solid acid catalyst that exhibits strong Brønsted acidity and is effective for reactions in aqueous media such as esterification, olefin hydration, and alcohol dehydration.[1,2] However, when heated at >773 K, dehydration of niobic acid leads to loss of its acidity.[3] Hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$) is another well-known solid acid catalyst.[4] Hydrated tantalum oxide shows mainly Lewis acid properties in the absence of water, but Brønsted acid sites are generated by treatment with steam at 373 K. Compared to $Nb_2O_5 \cdot nH_2O$, $Ta_2O_5 \cdot nH_2O$ retains its strong acidity after calcination at higher temperatures. However, when heated at temperatures >1073 K, dehydration and crystallization occur and $Ta_2O_5 \cdot nH_2O$ loses its acidic properties. Metal oxide solid acids such as aluminosilicate, zeolite, and binary oxides are usually prepared by calcination at or below 873 K, and pretreatment at >873 K reduces or eliminates the acid sites.[5–7] If a solid acid could be prepared by calcination at high temperatures required for the formation of ceramics (>1173 K), it would be a useful acid-catalyst even under strict conditions because of its high stability. However, there are very few reports aside from a couple of exceptions, like SiO_2/Al_2O_3 prepared by CVD,[8] highly siliceous zeolites, and layered mixed oxide.[9]

Recently, we found that a solid acid prepared with high loading of Nb_2O_5 on an Al_2O_3 support and calcined at 1173 K exhibited Brønsted acidity despite the high-temperature calcination. This strongly suggests that the alumina support stabilizes the Brønsted acid sites during calcination at high temperature,[10] which suggests that Ta_2O_5/Al_2O_3 could also act as a stable Brønsted acid catalyst. Here, we prepared a series of Ta_2O_5/Al_2O_3 solid acids and investigated their unique acidic properties in a Brønsted acid-promoted Friedel–Crafts alkylation of anisole with benzyl alcohol.

A series of Ta_2O_5/Al_2O_3 solid acids were prepared by impregnation of γ-alumina (JRC-ALO-8, Catalysis Society of Japan, 148 $m^2\,g^{-1}$) with an ethanol solution of tantalum ethoxide ($Ta(OC_2H_5)_5$), followed by calcination at various temperatures for 3 h in dry air. Aluminum tantalate, $AlTaO_4$, was synthesized from tantalum ethoxide and aluminum propoxide ($Al(OC_3H_7)_3$) according to an established procedure.[11] Hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$) was prepared from tantalum ethoxide.[4] Crystalline T-phase Ta_2O_5 was prepared from $Ta_2O_5 \cdot nH_2O$ by calcination at 1223 K. Friedel–Crafts alkylation was carried out as a test reaction to investigate the acidic properties of Ta_2O_5/Al_2O_3. The Friedel–Crafts alkylation between anisole and benzyl alcohol was examined in the liquid phase. The catalyst (0.15 g) was 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 433 K. Products were analyzed by FID-GC (Shimadzu GC-14B, Kyoto, Japan) and GC-MS (Shimadzu QP-5050).

A Rigaku (Tokyo, Japan) MultiFlex DR Powder X-ray diffractometer (XRD) was used to identify the compounds formed on the catalyst samples. The specific surface area was evaluated by the BET method using liquid nitrogen with a BEL Japan (Osaka, Japan) BELSORP28 28A. Infrared spectra of adsorbed lutidine (2,6-dimethylpyridine) were recorded with a Perkin-Elmer (Waltham, MA) Spectrum One Fourier transform infrared spectrometer, and used to elucidate the generation of Brønsted acid sites over Ta_2O_5/Al_2O_3. The sample (13 mg) was pressed into a self-supporting disk (ϕ 13 mm) and pretreated under 13.3 kPa of O_2 for 1 h at 773 K, and then evacuated for 1 h at 773 K. Then the sample was exposed to 0.533 kPa of lutidine vapor at 298 K for 10 min followed by evacuation at 423 K for 10 min.

Figure 1A shows the effect of the calcination temperature of 33 wt % Ta_2O_5/Al_2O_3 on the product yields in the Friedel–Crafts alkylation of anisole with benzyl alcohol. The main products were *ortho*- and *para*-benzylanisole isomers, which were presumably formed on the Brønsted acid sites, and the by-product was dibenzyl ether produced mostly on the Lewis acid sites.[12–15] The ratio of *ortho*- to *para*-benzylanisole was approximately 48:52 throughout the reaction. The yield of benzylanisole increased as the calcination temperature was increased to 1223 K. Calcination at higher temperatures (>1223 K) resulted in a reduced yield of benzylanisole. The yield of dibenzyl ether did not vary largely with the calcination temperature. These results strongly suggest that Brønsted acid sites are generated on Ta_2O_5/Al_2O_3 by calcination at high temperatures such as 1223 K. Figure 2 shows the XRD patterns of 33 wt % Ta_2O_5/Al_2O_3 calcined at various temperatures. Calcination at up to 1223 K did not cause crystallization of tantalum oxide (T-Ta_2O_5) or aluminum tantalate ($AlTaO_4$). In contrast, the XRD patterns of Ta_2O_5/Al_2O_3 calcined at 1273 K or above exhibited peaks for T-Ta_2O_5 and $AlTaO_4$. Ushikubo et al. reported that amorphous $Ta_2O_5 \cdot nH_2O$ crystallized to T-Ta_2O_5 after calcination at 1073 K.[4] Therefore, it appears that Al_2O_3 support stabilizes amorphous Ta_2O_5 and prevents it from crystallizing during calcination even at 1223 K.

Corresponding to the crystallization results, the specific surface area of Ta_2O_5/Al_2O_3 very gradually decreased from 150 to 100 $m^2\,g^{-1}$ with an increase in calcination temperature up to 1223 K, and drastically decreased to 50 $m^2\,g^{-1}$ with calcination at higher temperatures (1273–1423 K) (Figure 3). In this temperature region, the formation of $AlTaO_4$ proceeded and the yield of

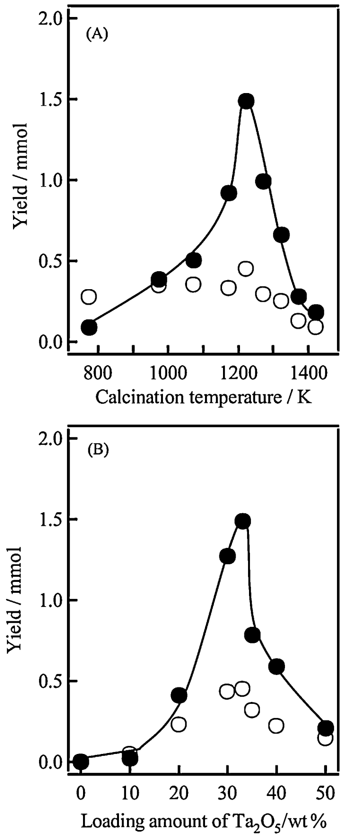

Figure 1. The product yields in the Friedel–Crafts alkylation of anisole with benzyl alcohol. (A) Effect of the calcination temperature of 33 wt% Ta_2O_5/Al_2O_3, (B) effect of Ta_2O_5 loading of the Ta_2O_5/Al_2O_3 calcined at 1223 K, reaction temperature: 433 K, reaction time: 1 h. Symbols are for (●) benzylanisole and (○) dibenzyl ether.

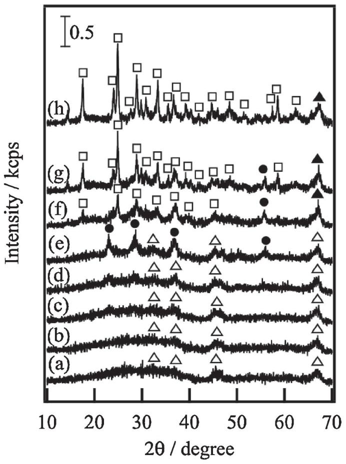

Figure 2. XRD patterns of 33 wt% Ta_2O_5/Al_2O_3 calcined at (a) 773, (b) 973, (c) 1173, (d) 1223, (e) 1273, (f) 1323, (g) 1373, and (h) 1423 K. Peaks are for (△) γ-Al_2O_3, (▲) θ-Al_2O_3, (●) T-Ta_2O_5, and (□) $AlTaO_4$.

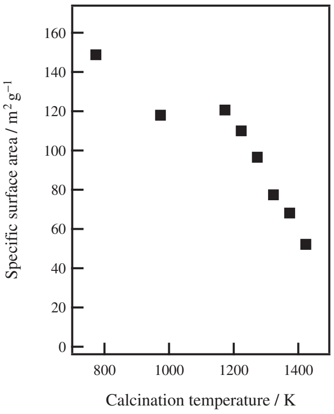

Figure 3. Reduction of the specific surface area of 33 wt% Ta_2O_5/Al_2O_3 with the calcination temperature.

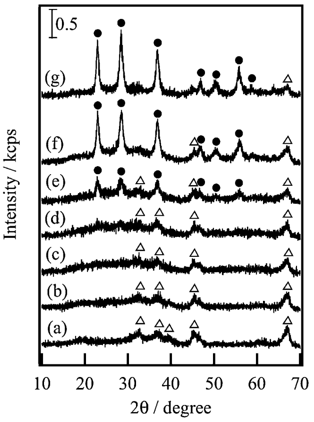

Figure 4. XRD patterns of Ta_2O_5/Al_2O_3 solid acids with various Ta_2O_5 loadings and calcined at 1223 K. Ta_2O_5 mass fraction: (a) 10, (b) 20, (c) 30, (d) 33, (e) 35, (f) 40, and (g) 50 wt%. Peaks are for (△) γ-Al_2O_3 and (●) T-Ta_2O_5.

benzylanisole drastically decreased. Moreover, $AlTaO_4$ was completely inert for the Friedel–Crafts alkylation. These results strongly suggest that the formation of inert $AlTaO_4$ phase reduces the catalytic activity.

The results of Friedel–Crafts alkylation over Ta_2O_5/Al_2O_3 solid acids with various Ta_2O_5 loadings and calcined at 1223 K are shown in Figure 1B. The catalyst with a Ta_2O_5 mass fraction of 33% exhibited the highest activity. The XRD patterns of Ta_2O_5/Al_2O_3 (Figure 4) showed that T-Ta_2O_5 was not present in the catalysts with Ta_2O_5 mass fraction of less than 33%. With Ta_2O_5 mass fractions >35%, the intensity of the diffraction lines for T-Ta_2O_5 increased and the full width at half maximum of these diffraction lines decreased with increasing Ta_2O_5 loading. These results indicate that the amorphous Ta_2O_5 supported on γ-Al_2O_3 crystallized to T-Ta_2O_5 and the crystallite size increased. When the Ta_2O_5 mass fraction was >35%, the yield of benzylanisole was greatly reduced, suggesting that formation of the inert T-Ta_2O_5 phase reduced the catalytic activity. Indeed, the Friedel–Crafts alkylation did not proceed over T-Ta_2O_5.

To examine the generation of Brønsted acid sites on Ta_2O_5/Al_2O_3 calcined at 1223 K, the acid sites were characterized based on FT-IR spectra of lutidine adsorbed on the catalysts. Figure 5

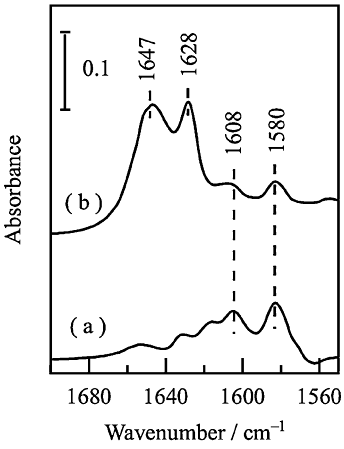

Figure 5. IR spectra of lutidine adsorbed on (a) alumina, and on (b) 33 wt % Ta_2O_5/Al_2O_3 calcined at 1223 K.

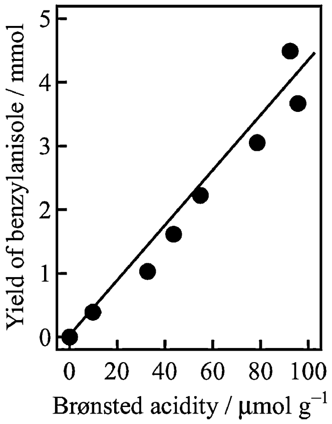

Figure 6. Yield of alkylated products over Ta_2O_5/Al_2O_3 solid acids with various Ta_2O_5 loadings and calcined at 1223 K, plotted against the Brønsted acidity of the catalyst.

shows the IR spectra of lutidine adsorbed on 33 wt % Ta_2O_5/Al_2O_3 calcined at 1223 K and bare γ-Al_2O_3. The bands at 1580 and 1608 cm^{-1} can be assigned to lutidine adsorbed on Lewis acid sites, and the bands at 1628 and 1647 cm^{-1} can be assigned to lutidine adsorbed on Brønsted acid sites.[16,17] The IR spectrum of lutidine adsorbed on 33 wt % Ta_2O_5/Al_2O_3 calcined at 1223 K showed intense bands at 1628 and 1647 cm^{-1}. In the spectrum of bare γ-Al_2O_3, the bands were observed at 1580 and 1608 cm^{-1} for lutidine adsorbed on Lewis acid sites. These results clearly indicate that Brønsted acid sites are generated on Ta_2O_5/Al_2O_3 calcined at high temperature. When T-Ta_2O_5 and $AlTaO_4$ were exposed to lutidine, no band for adsorbed lutidine was observed in the IR spectra of these samples. This result indicates that both Brønsted and Lewis acid sites are absent on T-Ta_2O_5 and $AlTaO_4$.

Figure 6 shows the correlation between the yield of benzylanisole and the Brønsted acidity, which was evaluated from FT-IR spectra of adsorbed lutidine (see Supporting Information[18]), of Ta_2O_5/Al_2O_3 calcined at 1223 K with various Ta_2O_5 loading. The yield of benzylanisole correlated well with the Brønsted acidity, indicating that the Friedel–Crafts reaction is promoted on the Brønsted acid sites. Interestingly, Brønsted acid sites were still detected for the Ta_2O_5/Al_2O_3 catalysts calcined at 1223 K. In contrast, pure Ta_2O_5 calcined at higher temperatures (>1073 K, T-Ta_2O_5) exhibits neither Brønsted nor Lewis acidity at all as mentioned above. Both calcination temperature and the amount of Ta_2O_5 loaded on the Al_2O_3 affected the Brønsted acidity. This suggests that structural changes around the tantalum have a major impact on the Brønsted acidic property. The detailed local structure of tantalum species of Ta_2O_5/Al_2O_3 is currently under investigation.

From these results, we conclude that a Ta_2O_5/Al_2O_3 solid acid with a high Ta_2O_5 mass fraction and calcined at 1223 K can exhibit Brønsted acidity. This is a new type of stable solid acid. Among the Ta_2O_5/Al_2O_3 catalysts tested, 33 wt % Ta_2O_5/Al_2O_3 calcined at 1223 K showed the highest activity.

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18 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.