Active and Reusable Catalyst in the Friedel–Crafts Alkylation Derived from a Heteropoly Acid

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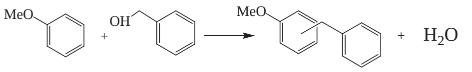
The H_3PO_4–WO_3–Nb_2O_5 derived catalyst exhibited excellent activity and reusability in the benzylation of anisole at low temperature. On the basis of the XRD and IR data, the oxide derived from heteropoly acid was ascribed to the active and insoluble species in the reaction. It was found that the calcination temperature was the key factor in the generation of active species.

In organic synthesis using solid acid catalysts, not only high activity but the reusability of the active species is desired in view of the separation of the products and the recycle use of the catalysts. Heteropoly acids (HPA) have been employed as catalysts for the various kinds of organic reactions using their strong Brønsted acidity.[1] However, the high solubility of HPA in the solvent hampered the application of HPA to the liquid phase reaction. The difficulty was overcome by inclusion of HPA in the silica matrix.[1,2] Herein, we report that intermediate in the decomposition of heteropoly acid derived from the mixed oxides (H_3PO_4–WO_3–Nb_2O_5) exhibited excellent catalytic performance in that it showed facile reusability as well as high activity in the Friedel–Crafts alkylation. Recently, much attention has been paid to the Friedel–Crafts alkylation in which alkyl group could be readily introduced on an aromatic ring. The scheme of the reaction conducted here was given in eq 1. A side reaction occurs to form dibenzylether.



(1)

Niobium oxalate was prepared by the dissolution of 1.27 g of niobic acid (supplied by CBMM Co.) in a oxalic acid (4.77 g) solution in 100 mL on a hot plate. $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ (1.69 g) was dissolved in deionized water (100 mL). The solutions of niobium oxalate and $(NH_4)_{10}W_{12}O_{41}$ were mixed, followed by addition of 85% phosphoric acid (0.22 g). The admixture solution was evaporated on a hot plate with continuous stirring. The obtained solid was calcined in air at 573 K to 773 K for 3 h. The K-10 modified with sulfuric acid was prepared according to the lieterature.[3] A 0.1 g of catalyst was used for benzylation of anisole. The pretreatment was carried out in an N_2 flow at 673 K for 1 h. For the sample calcined at 573 K in the synthesis, the pretreatment was conducted at 573 K (Figure 1). The reaction was performed using 10 g of anisole and 0.675 g (6.25 mmol) of benzyl alcohol in an oil bath at 333–353 K under an N_2 atmosphere for 3 h. In the recycled catalytic reaction, the catalyst was separated with filtration and washed with anisole. Then the catalyst was repeatedly used for further reaction without pretreatment. The products were analyzed by GC equipped with capillary column. In the analysis, tridecane was used as an internal standard.

The data of catalytic performance over H_3PO_4–WO_3–Nb_2O_5 as well as several combinations of oxides were listed in Table 1. Nb_2O_5, WO_3, H_3PO_4–Nb_2O_5, and H_3PO_4–WO_3 prepared in a similar manner as H_3PO_4–WO_3–Nb_2O_5 were substantially inactive in the reaction at 353 K. On the other hand, 35% of conversion of benzyl alcohol was obtained on WO_3–Nb_2O_5. The H_3PO_4–WO_3–Nb_2O_5 exhibited the highest activity among these oxides, where 98% conversion of benzyl alcohol was reached at 343 K. The ortho- and para-substituted benzylanisole were obtained as products, where the distribution of *p*-benzylanisole was 54% at 353 K. The conversion of H_3PO_4–WO_3–Nb_2O_5 was 4 times higher than that of K-10 treated with sulfuric acid when comparison was made at 343 K, which was reported to be active for this class of reaction.[3] The activity of H_3PO_4–WO_3–Nb_2O_5 was higher than H-β zeolite (Si/Al_2 = 25, PQ co.) as well. The recycle use of H_3PO_4–WO_3–Nb_2O_5 was attempted simply by separating the catalyst by filtration and washing with anisole. The deactivation was not observed after the recycle use at least three times at 353 K as given in Table 1. By contrast, no further reaction took place over the filtrated solution under the presence of remained benzyl alcohol, indicating the catalytic reaction truly took place over the solid catalyst. The H_3PO_4–WO_3–Nb_2O_5 catalysts having different amount of H_3PO_4 were subjected to the reaction at 333 K in order to optimize the composition of the catalyst. The highest activity was reached when the concentration of H_3PO_4 was 8.6 wt % (54.8 wt %, WO_3; 36.6 wt %, Nb_2O_5) as analyzed by ICP method. As a comparable experiment, HPW (60 wt %) were impregnated on Nb_2O_5, followed by calcination at 773 K in air. Although the catalyst exhibited high conversion (42%) of benzyl alcohol in the first run at 333 K, the conversion decreased to 8.9% in the second run, meaning the recycle use was not possible over the impregnated catalyst.

Figure 1 shows the relationship between calcination temperature and the catalytic performance of H_3PO_4–WO_3–Nb_2O_5. The reaction was performed at 333 K. The conversion and yield of products increased with increasing the calcination temperature, and the optimum activity was attained when the catalyst was cal-

Table 1. Data of the reaction between benzyl alcohol and anisole over various catalysts

Catalyst	Benzyl alcohol conv. /%	Benzyl anisole yield /%	Dibenzyl ether yield /%	Material balance /%
Nb_2O_5[a]	0	0.2	0.1	102
WO_3[a]	1.2	0.3	0.1	99
H_3PO_4–Nb_2O_5[a]	0	3.4	1.5	105
H_3PO_4–WO_3[a]	0	0.5	0.1	105
WO_3–Nb_2O_5[a]	35.0	26.8	3.5	99
H_3PO_4–WO_3–Nb_2O_5[a]	100	93.4	0.3	93
H_3PO_4–WO_3–Nb_2O_5[b]	100	94.0	0.3	94
H_3PO_4–WO_3–Nb_2O_5[c]	98.0	93.5	11.5	102
modified K-10 [c]	25.4	19.5	3.5	96
H-β (Si/Al_2 = 25) [a]	40.6	23.2	6.6	96

[a]353 K, [b]3rd run in the repeated reaction at 353 K, [c]343 K, the oxides were calcined at 773 K in the preparation.

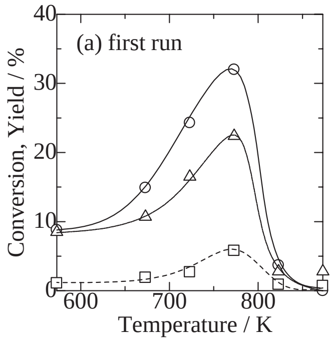


Figure 1. Dependence of the (○) conversion of benzyl alcohol, (△) yield of benzyl anisole, (□) yield of dibenzyl ether on the calcination temperature of H_3PO_4–WO_3–Nb_2O_5. (a) 1st run, (b) 2nd run. Reaction temperature, 333 K; time, 3 h.

cined at 773 K. On further raising the calcination temperature (above 823 K), the activity attenuated drastically. In agreement with the dropping of the activity between 773 and 823 K, the color of catalysts changed from white to green. The repeated reaction was conducted after the separation of the catalysts used in the first run by filtration and the data was given in Figure 1b. The activity of the catalysts calcined at 573–673 K significantly dropped owing to the dissolution of HPA as will be noted afterwards. In marked contrast, the catalyst calcined at 773 K kept almost the same activity as the first run. As a result, the dependence of the calcination temperature on the activity became sharp. Therefore, it could be noted that catalytic activity and the degree of solubility were significantly sensitive to the calcination temperature.

Figure 2 shows IR spectra of H_3PO_4–WO_3–Nb_2O_5 calcined at different temperatures. The samples were diluted with KBr prior to the measurement. Intense peaks appeared at 1080, 985, 889, 595, and 524 cm^{-1} when the catalyst was calcined at 673 K. The peaks were ascribed to the $H_3PW_{12}O_{40}$ from the comparison with the spectrum of authentic $H_3PW_{12}O_{40}$ (HPW).[1] The intensity of the peaks decreased accompanied by raising the calcination temperature, and small peaks remained in the sample calcined at 773 K. The absorption ascribed to the HPW completely diminished on the catalyst calcined above 823 K, where the spectra became similar to that of WO_3. The change suggested that the decomposition of HPW species took place completely between 773 and 823 K. The intensity of the peaks ascribed to the HPW markedly decreased on the catalyst calcined at 673 K after the benzylation reaction. The change indicated that the decrease in the activity of the catalyst calcined at 573–673 K in the second run was caused by the dissolution of HPW into the solution.

Figure 3 shows XRD patterns of H_3PO_4–WO_3–Nb_2O_5 calcined at different temperatures. Intense diffractions appeared on the catalysts calcined at 573 and 673 K. The patterns were similar to that of HPW dehydrated at 373 K, although the angles slightly shifted to the higher angle. Probably the shift may be due to the difference in the dehydration degree of HPW.[4] The intensity of the diffractions decreased at 723 K and completely disappeared at 773 K. On further increasing the calcination temperature (823–873 K), new diffractions emerged. These could be obviously assigned to the WO_3 from the comparison with that of authentic WO_3. The change in the XRD indicated that the initially formed HPW began to decompose at 723 K and the complete transformation took place between 773 and 823 K. The temperature of transformation agreed well with that found in the IR spectra. The acid property of H_3PO_4–WO_3–Nb_2O_5 was measured with NH_3 TPD method. An enhancement of the amount and density of weak acidity was observed on the catalyst calcined at 773 K, accompanied by the transformation of HPW.[5]

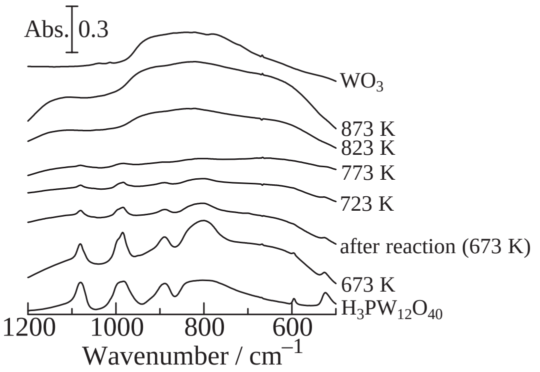


Figure 2. IR spectra of H_3PO_4–WO_3–Nb_2O_5 calcined at different temperatures.

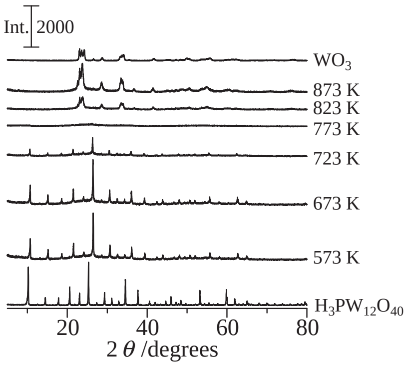


Figure 3. Powder XRD patterns of H_3PO_4–WO_3–Nb_2O_5 calcined at different temperatures.

From the IR and XRD data, we confirmed that the optimum calcination temperature (773 K) for catalytic reaction corresponded to the intermediate in the decomposition of HPW to form crystalline WO_3. The catalyst calcined at 773 K possessed excellent nature in that it exhibited high activity and reusability. Probably, the novel acidity generated in the intermediate species was responsible for the high activity. It has been proposed that the decomposition of heteropoly acids progressed via the formation of fragments.[6] In consideration of the fact, the present active and insoluble species could be ascribed to the fragment of HPW generated in the course of the decomposition of HPW over Nb_2O_5 support. Further investigation is necessary to reveal the structure of the intermediate species generated at 773 K.

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