Synthesis of solid acid by supporting WO_3 or SO_3 on TiO_2–SnO_2 mixed oxide prepared by a novel method of solid–liquid interface reaction

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Abstract: We synthesized solid acid of SO_3/TiO_2-SnO_2 and WO_3/TiO_2-SnO_2 by introducing sulfate or tungstate on the surface of TiO_2-SnO_2 mixed oxide. The mixed oxide was prepared by a reaction of $SnCl_4$•$5H_2O$ with $Ti(OCH(CH_3)_2)_4$ dissolved in ethyl acetate at solid-liquid interface. Result of XRD analysis indicated that TiO_2 and SnO_2 were well mixed. Sulfated TiO_2-SnO_2 showed catalytic activity for skeletal isomerization of pentane at room temperature. A higher temperature tolerance of sulfated and tungstated TiO_2-SnO_2 than those of TiO_2 or SnO_2 was confirmed. Tungstated TiO_2-SnO_2 showed excellent heat tolerance of activity even after heat treatment at 1223 K.

Keywords: mixed oxide, solid acid, interface reaction.

1. Introduction

It is well known that a solid acid having high acid strength can be obtained by introducing an oxoanion such as SO_4^{2-} or WO_4^{2-} on a surface of metal oxide or hydroxide, and following heat-treatment at higher temperatures. As the metal oxide of support, simple oxide such as TiO_2, ZrO_2, and SnO_2 are desirable[1]. Sulfated zirconia has been well known as a solid superacid.

In the field of solid catalysts, mixing of different oxides provides a new characteristics. Formation of acid sites and increase of surface area are frequently observed. Although some examples of sulfated and tungstated mixed metal oxides, such as WO_3/TiO_2-Al_2O_3 [2] and SO_4^{2-}/SiO_2-TiO_2 [3], have been studied, there was no report that a desirable new property was developed [4]. The acidity was in the middle of each sulfated and tungstated oxide. The surface sulfate and tungstate give larger effect on the surface area increasing than mixing of oxides. However, a suppression of crystallization at higher temperature range and resulting higher surface area can be expected. As a result, it becomes possible to synthesize a chemically stable and easy-to-use solid acid.

Titanium oxide has higher water tolerance and sulfates SnO_2 has the highest acidity among the sulfated metal oxides. Additionally, the both TiO_2 and SnO_2 have the same crystal structure of rutile. It was expected that sulfated and tungstated TiO_2-SnO_2 would show a high water tolerance and higher acidity. In this study, we synthesized a mixed oxide of TiO_2-SnO_2 in which WO_4^{2-} and SO_4^{2-} are supported on the surface.

Generally, coprecipitation method is used for preparing mixed oxide. However, the pH ranges, where chemical species of Ti and Sn are dissolved in water, are quite different. Therefore, we applied a novel preparation method of solid-liquid interface reaction using Ti alkoxide and Sn chloride with crystallization water. In this method, Ti alkoxide would be converted into hydroxide by a reaction of alkoxide with crystallization water in the interface of Sn chloride and non-polar solvent dissolving alkoxide. It was expected that a highly mixed oxide would be obtained.

2. Experimental

Mixed oxide of TiO_2-SnO_2 with a molar ratio of 1:1 was prepared by adding $SnCl_4$•$5H_2O$ to ethyl acetate solution of $Ti(OCH(CH_3)_2)_4$ and heating at 343 K. Ethyl acetate was removed by distillation and the solid was dried at 373 K. Before introducing SO_3, dried sample was pre-heated at 523 K for 2 h. Then the mixed oxide was immersed in 0.5-3 mol/L sulfuric acid for 1 h, and dried at 373 K overnight. After that, it was calcined in the air at 673-923 K for 3 h.

In the case of WO_3/TiO_2-SnO_2, mixed oxide was treated as follows. A desired amount of WO_3 was dissolved in NH_3 solution by heating to form ammonium tungstate solution, and further heating was continued to remove excess ammonia. The pH of resulting solution was 8. The mixed oxide pre-heated at 523 K for 2 h was put into the prepared ammonium tungstate solution, and water was removed by evaporation on a hot plate. Finally, it was calcined in the air at 773–1273 K. The amount of tungstic acid supported was set to 5–25 wt%.

The catalytic activity was evaluated by activity of ethanol dehydration in a flow reaction system. Prepared catalyst (50 mg) was placed on a glass wool packed in a reaction tube, and heated in a He stream at 773 K for 2 h before reaction. The reaction was carried out at a reaction temperature of 443 K. Ethanol partial pressure of 1.5 kPa, and a He flow rate of 20 ml/min. The product was analyzed using a gas chromatograph.

3. Results and discussion

X–ray diffraction of SO_3/TiO_2-SnO_2 calcined at 773-873 K was measured. XRD peaks assigned to rutile structure were appeared between peak positions of TiO_2 and SnO_2. This result indicated that well–mixed TiO_2-SnO_2 was prepared by the novel preparation method applied in this study. No significant change in the peak position was not observed until SO_4^{2-} decomposition temperature.

The activity of the catalyst increased with increasing concentration of sulfuric acid. The maximum of the activity was obtained by heating at 773 K. The sample using 3 mol/L of sulfuric acid, and heated at 873 K also showed activity, and it was decreased greatly at 923 K. This temperature was higher than those of sulfated TiO_2 and SnO_2. The sulfate ions were more stabilyzed on the mixed oxide surface.

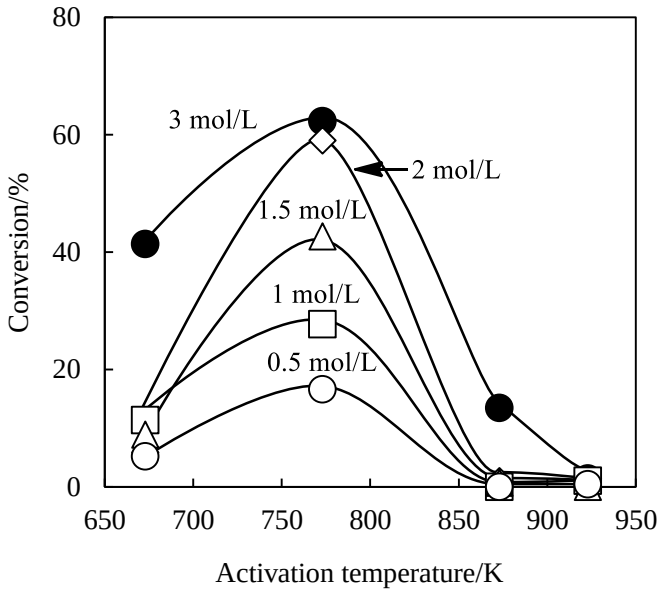

Figure 1. Effects of H_2SO_4 concentration and activation temperature on ethanol decomposition activity of SO_3/TiO_2-SnO_2. Diethyl ether and small amount of ethylene were obtained in all catalysts.

WO_3/TiO_2-SnO_2 showed activity even after heating at 1223 K. This catalyst was excellent in tolerance against heating at higher temperature. This temperature of preparation was the same as that of WO_3/SnO_2. However, a large amount of WO_3 could be loaded on the mixed oxide.

4. Conclusions

We synthesized solid superacid of SO_3/TiO_2-SnO_2 and strong acid of WO_3/TiO_2-SnO_2 using mixed oxide of TiO_2-SnO_2. A higher temperature tolerance than sulfated TiO_2 was confirmed. WO_3/TiO_2-SnO_2 showed activity even after firing at 1223 K and was excellent in heat resistance. It was revealed that well-mixed oxide of TiO_2-SnO_2 could be synthesized by the novel method of solid–liquid interface reaction of Ti alkoxide with $SnCl_4$ including crystallization water.

References

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