

## Hydrated Tantalum Oxide as a Solid Acid Catalyst

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The hydrated tantalum oxide in an amorphous form, is strongly acidic and shows high catalytic activity in the gas-phase esterification of methacrylic acid with methanol.

Tantalum oxide has been seldom studied as a catalyst. We wish to report that the hydrated tantalum oxide showed the strong acid property and a high catalytic activity in the gas-phase esterification of methacrylic acid with methanol.

The hydrated tantalum oxide was prepared by the hydrolysis of  $\text{TaCl}_5$  with KOH in ethanol. After aging the precipitate for one day, the precipitate was suspended into boiling 1 M HCl aqueous solution for one hour. Then, the precipitate was suspended into a boiling deionized water for one hour for washing. The washing with boiling water was repeated until chloride ions were not detected. The solid was dried at 120 °C in a vacuum oven for six hours, and calcined in air at various temperatures. For the measurement of acid strength, Hammett indicators were adsorbed on the oxides suspended in benzene, and the color change of the indicators was observed. The thermogravimetry (TG) and differential thermal analysis (DTA) were done in air at the heating program rate of 10 °C/min. The gas-phase esterification of methacrylic acid with methanol was carried out in a flow-type reactor. The catalytic activity of the hydrated tantalum oxide was compared with those of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (Nikki Kagaku N631H,  $\text{SiO}_2/\text{Al}_2\text{O}_3 =$  about 70/30 wt%),  $\text{SiO}_2\text{-TiO}_2$  (followed by the literature,<sup>1)</sup>  $\text{SiO}_2/\text{TiO}_2 = 93.5/6.5$  wt%), and the hydrated niobium oxide (CBMM AD-382).

Figure 1 shows (a) the acid strength, (b) TG-DTA, and (c) the specific surface area of the hydrated tantalum oxide, which was heat-treated at different temperatures. Apparently, the hydrated tantalum oxide, especially, heat-treated below 400 °C, is strongly acidic. On heat-treatment at the higher temperatures, the acid property was weakened, and the surface area drastically decreased. The hydrated tantalum oxide, heat-treated at 120 °C, was represented as  $\text{Ta}_2\text{O}_5 \cdot 2.1\text{H}_2\text{O}$  by the TG analysis. In the DTA analysis, an exothermic peak, due to crystallization, appeared at about 730 °C, which was confirmed by the X-ray diffraction measurement. The loss in the strong acid property of the hydrated tantalum oxide may be due to the crystallization process itself.

The hydrated tantalum oxide was the most active catalyst in the gas-phase esterification of methacrylic acid with methanol among the catalysts examined, as shown in Table 1. The selectivity for methyl methacrylate was virtually 100%.

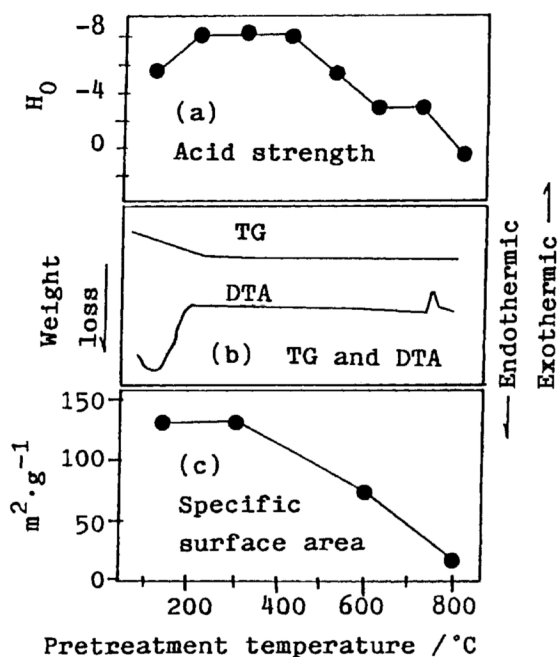


Fig. 1. Acid strength (a), TG-DTA analysis (b), and specific surface area (c) of the hydrated tantalum oxide.

Table 1. Activities of the hydrated tantalum oxide and the other solid acids in the gas-phase esterification of methacrylic acid with methanol<sup>a)</sup>

Catalyst	Pretreatment temperature / °C	Ester Yield / mol%
Hydrated tantalum oxide	300	96.2
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	400	15.4
SiO <sub>2</sub> -TiO <sub>2</sub>	300	22.5
Hydrated niobium oxide	300	84.4

a) Reaction conditions :  
 Temperature : 200 °C, SV : 2500 h<sup>-1</sup>,  
 Catalyst amount : 1 ml,  
 Feed gas ratio :  
 methacrylic acid/methanol/N<sub>2</sub>  
 = 3.7/14.7/81.6 mol%.

With SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-TiO<sub>2</sub>, on the contrary, considerable amounts of dimethyl ether were produced (4.2% and 1.0%, respectively).

The present results with the hydrated tantalum oxide remind us the physico-chemical properties of the hydrated niobium oxide reported earlier.<sup>2)</sup> However, the hydrated tantalum oxide was more active in the gas-phase esterification, and crystallized at higher temperature than that of the hydrated niobium oxide.

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#### References

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