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Annihilation of the Catalytic Activity in Butene Isomerization of Porous Vycor Glass by Washing with EDTA Aqueous Solution

Shoji HIRAI,* Akira MORIKAWA, Yoshio ISHINAGA, Kiyoshi OTSUKA, and Yuji WADA

Department of Chemical Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152

* *Atomic Energy Research Laboratory, Musashi Institute of Technology, 971 Ozenji, Tama-ku, Kawasaki 215*

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Synopsis. The catalytic activity of porous Vycor glass in the isomerization of butenes was eliminated by washing the glass with EDTA aqueous solution, though the contents of Al and Zr in the glass remained unchanged. Destruction by decationation of active sites of silica-alumina character has been suggested.

Porous Vycor glass is one of the most favourable materials for examining molecules bound to the surface by means of spectroscopy. The mechanism of the photoisomerization of butenes was investigated by sensitization of molecules adsorbed on the glass or of the Vycor glass itself.[1-3] However, the glass shows an appreciable thermal catalytic activity in the isomerization,[1,4] occasionally making the experimental results vague.

The minor components of the Vycor glass (96% SiO_2) are mainly alumina, boria, and zirconia. Aluminium forms acid surface sites of a silica-alumina character, with which butene molecules interact to isomerize.[5] Silica-zirconia is also a solid acid.[6] Thus, removal of aluminium or zirconium from the glass might cause annihilation of the thermal catalytic activity of the glass for isomerization. It has been reported that aluminium in zeolites is successfully removed by EDTA treatment.[7] We have applied this technique to porous Vycor glass and suppressed the activity. This paper deals with the results with respect to the change in the isomerization activity and the contents of aluminium and zirconium.

Experimental

A porous Vycor glass plate $30\times8\times0.9$ mm was calcined at 750 °C in the air for 3 h, washed with 0.01 M neutral aqueous solution of EDTA for an appropriate duration, washed twice with distilled water for 15 min each and dried for 2 h at 400 °C in the air. The glass plate was then placed in a coaxial tubular, quartz-made reactor, calcined at 500 °C for 2 h in a stream of oxygen gas with a pressure of 20 kPa, and degassed for 2 h under a pressure of 7×10^{-3} Pa at the same temperature. At 60 °C a reacting gas, *cis*-2-butene, of pressure 20 kPa was introduced into the reactor, the reaction then proceeding in a closed gas-circulation apparatus with a volume of 190 ml. The products were analyzed by gas chromatography at appropriate intervals. Elements other than Si, B, and O contained in the glass plate were analyzed by means of neutron activation analysis with the GAMA system at Atomic Energy Research Laboratory, Musashi Institute of Technology.

Results and Discussions

The elements present in appreciable amounts were Al, Zr, As, Ti, V, Mn, Fe, Na, and Mg among a large number of elements detected. The amounts of aluminium and zirconium were considerably greater than those of the others.

TABLE 1. *cis*-2-BUTENE ISOMERIZATION ACTIVITY AND CONTENTS OF ALUMINIUM AND ZIRCONIUM

Duration of EDTA washing (h)	0	0.5	1	2	3
Amount of Al (ppm)	2670	3070	2940	2550	3050
Amount of Zr (ppm)	962	960	978	938	852
Catalytic activity (mol s^{-1} g-cat^{-1})	5.1×10^{-9}	trace	none	a)	none

a) Transparency was measured.

The amounts of both aluminium and zirconium in the glass with various durations of EDTA washing are summarized in Table 1. The unwashed glass is denoted by zero duration. No effect of EDTA washing was detected on the contents of the two elements. On the other hand, the catalytic activity was drastically eliminated by only 30 min washing. For the unwashed glass the activities at 60 °C for the isomerization of *cis*-2-butene to 1-butene and *trans*-2-butene are 3.3×10^{-9} and 1.8×10^{-9} mol s^{-1} g-cat^{-1}, respectively, the corresponding apparent activation energies for the isomerization being *ca.* 71 and 83 kJ mol^{-1}, which may be reasonable values for isomerization on the acid sites of a silica-alumina character. For the washed glass, however, even at 80 °C, no activity could be measured.

The results lead us to the following conclusions. (1) Aluminium and zirconium atoms on the surface of the glass, contributing to formation of acid sites, can be removed by EDTA, resulting in annihilation of the catalytic activity for the butene isomerization. (2) Most of the aluminium and zirconium atoms probably entrapped in the silica network of the bulk of glass are resistant to the EDTA washing and inert for the reaction. (3) Such entrapped aluminium or zirconium atoms are immobile under heating at 500 °C for 4 h during the course of pretreatment. If mobile, they may diffuse from the bulk to the surface of the glass, forming acid sites during the course of pretreatment.

The transparency of the washed glass hardly decreased. Only 0.02 increase of absorbance to the light of wavelength 700—400 nm and 0.02—0.15 to 400—250 nm were observed for the 2 h washed glass.

Thus EDTA washing can be utilized for preparing catalytically inert supports of catalysts.

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