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Photopreparation of Heterogeneous Metathesis Catalysts from Metal Carbonyls Adsorbed on Solids

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It was demonstrated that $Mo(CO)_6$ and $W(CO)_6$ adsorbed on solid supports, such as porous Vycor glass and NaY zeolite, were photoactivated to be catalytically active for propene metathesis.

Many researches have been reported on thermoactivation of metal carbonyls adsorbed on solids as catalysts.1) The knowledge accumulated in this kind of activation provides us with a certain direction to design catalytically active sites on solid surfaces. On the other hand, only a few attempts have been made for photoactivation of metal carbonyls adsorbed on solid surfaces,2) although the carbonyls in homogeneous systems are known to become catalytically active by photoactivation.3-5)

We have found that $Mo(CO)_6$ and $W(CO)_6$ adsorbed on solids became catalytically active for metathesis of propene by photoirradiation.

Porous Vycor glass(PVG), NaY zeolite, HY zeolite, TiO_2, and Al_2O_3 were used as the supports of metal carbonyls. These solids except for HY were calcined in pure oxygen gas at 778 K for 1 h and degassed for 1 h in a vacuum system before use. HY was prepared by decomposition of NH_4Y at 678 K. The vapor of metal carbonyls were brought into contact with the solids at 333 K for 0.5 h. Weakly adsorbed metal carbonyls were collected to a cold trap of 77 K. The solids adsorbing metal carbonyls are denoted by $M(CO)_6$/name of solid support hereafter. A reaction system used was a conventional gas-circulating one. The catalysts were irradiated at room temperature by the light of a medium pressure mercury lamp through the glass filter which attenuated the light of wavelength below 290 nm.

Figure 1 shows a time course of the formation of butene by metathesis on $Mo(CO)_6$ adsorbed on various supports. The catalysts except for $Mo(CO)_6$/alumina were inactive for metathesis of propene under dark. The photoinduced catalytic activity was observed for the supports of NaY and PVG. The products were ethene, and cis- and trans-2-butenes($C'_2/C'_4=1$, trans/cis=1.8). The catalysts which were once activated remained active after the light irradiation was ceased, indicating that the catalytically active species was prepared by a photoreaction of metal carbonyl on the surface. $Mo(CO)_6/Al_2O_3$ was catalytically active without the irradiation and its activity was enhanced by the irradiation.

Figure 2 shows the photoinduced catalytic activity of three kinds of metal carbonyls adsorbed on PVG. All the three catalysts were inactive under dark.

$Mo(CO)_6$ and $W(CO)_6$ showed the catalytic activity for propene metathesis under the irradiation, while $Cr(CO)_6$ was inactive.

The appearance of CO from $Mo(CO)_6$/PVG under the irradiation was observed by mass spectroscopy. For the homogeneous photoinduced catalysis by $W(CO)_6$, a cocatalyst, such as $TiCl_4$, WCl_4,[4] or CCl_4[5] is necessary. These cocatalysts are considered to substitute CO of metal carbonyl and to form an adduct like $W(CO)_5TiCl_4$.[4] Darsillo et al. have reported the formation of an adduct of $Fe(CO)_5$ with the PVG surface after UV irradiation.[6] Since the formation of a subcarbonyl of molybdenum was observed on PVG after the irradiation by UV spectroscopy in the present work, it is plausible that the subcarbonyl stabilized by the interaction with the surface of the solids acts as the active site or its precursor for the metathesis. The catalyst with HY or TiO_2 support changed its color as that with PVG after the UV irradiation, but no catalytic activity was observed, suggesting that the stability of the subcarbonyl depends on the chemical property of the solid surface.

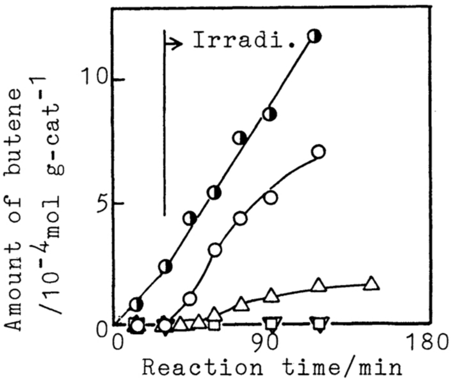

Fig.1. Photoinduced metathesis on $Mo(CO)_6$/various supports. (◑)Al_2O_3, (○)NaY, (△)PVG, (□)HY, (▽)TiO_2.

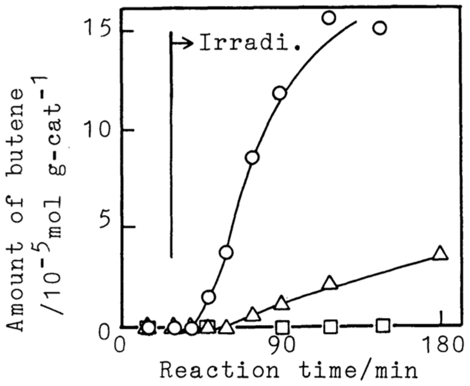

Fig.2. Photoinduced metathesis on Mo, W, $Cr(CO)_6$/PVG. (○)Mo, (△)W, (□)Cr.

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