

Alkene Metathesis on Photoirradiated Silica Surface

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Silica, activated by evacuation at high temperatures, catalyses metathesis reactions of ethene and propene under photoirradiation.

Metathesis reactions are known to be extremely useful for the synthesis of various alkenes. Therefore, many catalysts for such reactions have been extensively developed since the discovery of a molybdenum catalyst by Banks and Bailey¹ in a heterogeneous system and of a tungsten catalyst by Calderon *et al.*² in a homogeneous system. Most of the catalysts contain transition metals such as Mo,¹ W,^{2,3} Re⁴ *etc.*, which can form metal carbene and metallacyclobutane intermediates.⁵ Therefore, it was believed that these transition metals are necessary elements in catalysts for metathesis reactions.

Silica is a common material often used as a catalyst support, an adsorbent and so on, and generally it is inactive itself. However, silica can function as a catalyst for some reactions,⁶ in particular when it is activated by photoirradiation.⁷ So far, there has been no report on catalysis by silica for metathesis. We report here the first discovery that silica can catalyse metathesis reactions of ethene and propene under photoirradiation.

The silica sample employed was mainly Cab-osil M5, which was impregnated with water and dried, followed by calcination in flowing air at 773 K for 5 h. Before each reaction, it was heated in the presence of 50 Torr (1 Torr = 133.3 Pa) oxygen at the given temperature (Table 1) for 1 h and evacuated at the same temperature for 1 h.

Fig. 1 shows the time course of the reaction of propene over silica. Products were ethene (C₂), *trans*-but-2-ene (*trans*-C₄), *cis*-but-2-ene (*cis*-C₄) and a very small amount of but-1-ene (1-C₄). The selectivity (ratio of the total moles of products to the moles of propene consumed) was 100% within experimental error. Furthermore, the amount of ethene and butenes were approximately equimolar; the molar ratio of ethene to butenes (C₂:C₄) at each sampling of products in the gas phase was between 1.03 and 1.08, these values were comparable to the theoretical value of 1.0, suggesting that a metathesis reaction of propene occurred in this system:



These results show that this system is as good as some of the best systems reported in the literature.⁸ The high selectivity presents the potential for a photocatalytic system to promote a selective reaction. The conversion and product yields increased with time, and they seemed to achieve a specific composition, which is lower than the equilibrium conversion (42.3% at 298 K to 47.8% at 811 K).⁸ The cause of saturation of conversion in this closed system might be photoadsorption of butenes onto the active sites of the silica surface. However, the following experiment proved that the cause of the saturated conversion in Fig. 1 was not catalyst deactivation. After the increase in conversion had apparently stopped, the reactor and circulating

part were evacuated at room temperature and propene was reintroduced to the system. The reaction proceeded again under irradiation with virtually the same rate as the first run.

The reaction of ethene was also examined. In the case of ethene, if the only reaction was metathesis, then no new products should be observed. After the reaction under irradiation for 1 h on silica, nothing other than ethene was observed. When a mixture of CH₂=CH₂ and CD₂=CD₂ was introduced as reactant, the production of [2H₂]ethene was observed. Neither [2H₁]- nor [2H₃]-ethene was found in the system, confirming

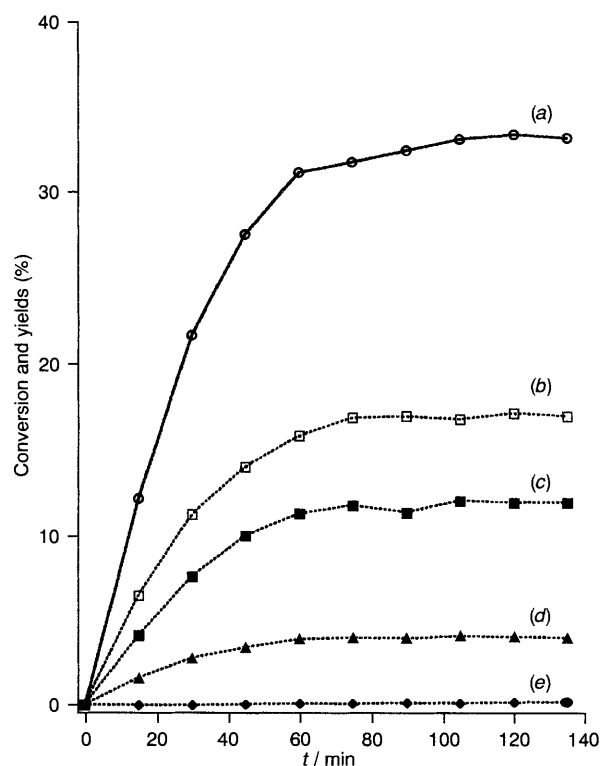


Fig. 1 Time course of the reaction: (a) conversion of propene and yields of (b) ethene, (c) *trans*-but-2-ene, (d) *cis*-but-2-ene and (e) but-1-ene. The reaction was carried out in a closed circulation system (250 ml; propene 200 μmol). The powder catalyst (400 mg) was spread on the flat bottom (12 cm²) of the quartz reactor irradiated from beneath by a 250 W Hg lamp. The pretreatment temperature was 1073 K. Products were analysed by GC.

Table 1 Effects of pretreatment temperature and irradiation wavelength^a

Entry	T/K	Filter	Conv. (%)	C ₂ :C ₄	Yields (%)			
					C ₂	<i>trans</i> -C ₄	<i>cis</i> -C ₄	1-C ₄
1	1073	Y-43 ^b	0.27	1.25	0.15	0.07	0.05	0.00
2	1073	UV-29 ^c	4.75	1.05	2.43	1.59	0.73	0.01
3	1073	None	11.4	1.02	5.74	4.08	1.56	0.05
4	873	None	6.95	1.00	3.47	2.50	0.95	0.01
5	673	None	5.86	0.78	1.37	0.92	0.70	0.13

^a The measurement was carried out under irradiation for 1 h using a 250 W Hg lamp after pretreatment in a closed static system (39.5 ml; sample 100 mg; propene 30 μmol ; irradiated area of catalyst bed 12 cm²). ^b Y-43 filter admits light with $\lambda > 430$ nm. ^c UV-29 filter admits light with $\lambda > 290$ nm.

that the only reaction occurring over the silica was metathesis:

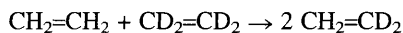


Fig. 2 indicates the response of the reaction to photoirradiation. It reveals that the reaction proceeded only under irradiation. The good response indicates clearly that the metathesis reaction was induced by irradiation. The dependence of the reaction upon the excitation wavelength was examined by using a UV filter, as shown in Table 1 (entries 1–3). Irradiation with visible light only (entry 1), the reaction was limited to low conversion levels with a high ratio of $\text{C}_2:\text{C}_4$. On the other hand, irradiation with UV light (entries 2, 3), caused the metathesis reaction to accelerate, indicating that UV light is required for the metathesis reaction on silica surface.

The effect of the pretreatment temperature is shown in Table 1 (entries 3–5). The silica is more activated by pretreatment at the higher temperature, suggesting that the desorption of the hydroxy groups on the silica surface might relate to active sites.

We also examined other kinds of silica as catalysts; JRC-SIO-4 (supplied by the Catalysis Society of Japan) and some silica samples prepared by the sol-gel method⁹ from $\text{Si}(\text{OEt})_4$. The metathesis reaction was observed on each silica, except for

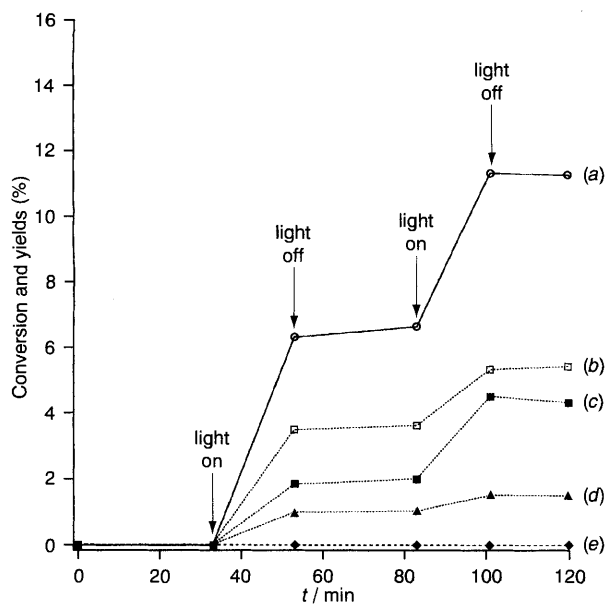


Fig. 2 Response of the reaction to the irradiation: (a)–(e) as in caption to Fig. 1

an aged silica prepared by the sol-gel method thirty months ago. Among the silica samples prepared by the sol-gel method in the last three years, the newer samples exhibited higher metathesis activity. This means that the number of active sites decreased with time. In order to reactivate a silica prepared twenty months ago, the sample was impregnated in water and dried, calcined in flowing air at 773 K before pretreatment at 1073 K. The refreshed silica exhibited higher activity, suggesting that this treatment restored the active site.

We tested other typical metal oxides such as MgO , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$. On these oxides, although other reactions occurred to a small extent, the distribution of products was quite different from that for the metathesis reaction. The metathesis reaction under irradiation seems to be characteristic of silica surface among such typical metal oxides.

From the results mentioned above, we conclude that silica catalysed metathesis reactions of propene and ethene under photoirradiation, and it was activated by the treatment of impregnation in water and calcination in flowing air followed by evacuation at high temperatures.

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