Catalytic activity of FSM-16 for photometathesis of propene

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Mesoporous silica (FSM-16) catalyses metathesis of propene under photoirradiation at a higher activity than amorphous silica whereas microporous silica crystals (silicalite-1) do not catalyse the reaction.

Mesoporous silica materials such as MCM-41[1,2] and FSM-16[3,4] attract a great deal of attention as new materials and many applications are expected. Although the application of these materials for catalysis has been widely studied, attention has also been paid to the generation of catalytic activity through the introduction of other metal ions into the silica lattice, but not to the catalytic activity of unmodified mesoporous silica.

Here, we show that unmodified mesoporous silica (FSM-16) has a higher catalytic activity in the photometathesis of propene than does amorphous silica which was recently found to be catalytically active in this reaction.[5] To elucidate structural factors of mesoporous silica in this reaction, we compare the catalytic activities of other forms of SiO_2; amorphous silica, microporous crystalline silica (silicalite-1)[6] and high-silica zeolite (dealuminated mordenite).

Amorphous silica (AMS) was prepared by the sol–gel method[7] by hydrolysis of tetraethylorthosilicate (TEOS) followed by calcination at 773 K for 5 h. FSM-16 was prepared essentially in the same manner as described by Inagaki *et al.*[3,4] except that hexadecyltrimethylammonium bromide was used as a template and the resulting material was calcined at 873 K in an N_2 atmosphere for 1 h and subsequently in air for 5 h. Silicalite-1 was synthesized from TEOS and tetrapropylammonium bromide (TPABr) by hydrothermal synthesis (433 K, 24 h) followed by washing, drying and calcination at 823 K. Dealuminated mordenite (DM, SiO_2/Al_2O_3 = 328) was obtained by extraction (12×) of aluminium using 8 m HCl at 333 K for 24 h[8] from JRC-Z-HM15 (a reference catalyst,[9,10] Catalysis Society of Japan). The structures of the samples were confirmed by XRD and N_2 adsorption–desorption isotherms.

Photocatalytic conversion of propene was carried out under irradiation for 1 h using a 250 W Hg lamp in a closed static system (120 ml; propene 100 μmol) at room temperature. The powdered catalyst (200 mg) was spread on the flat bottom (12 cm^2) of a quartz reactor irradiated from beneath. Pretreatment of catalyst was performed at 873 K (or 1073 K) in air for 2 h and in the presence of 100 Torr oxygen for 1 h, followed by evacuation at the same temperature. After 1 h reaction, products and unreacted propene were collected with a liquid-N_2 trap when the catalyst was under irradiation, and were analysed by GC.

The XRD patterns of the samples pretreated at 873 K and that of silicalite-1 pretreated at 1073 K are shown in Fig. 1. AMS (*a*) showed a very broad diffraction peak at 2θ *ca.* 22°, indicating its amorphous nature. The FSM-16 sample (*b*) exhibited low-angle diffraction peaks at 2θ 2.36, 4.06 and 4.68° and a very broad diffraction peak at 2θ *ca.* 23° as reported,[3,4] indicating that this material has ordered hexagonal mesopores with XRD amorphous walls. Silicalite-1 (*c*) and DM (*d*) were clearly assigned by comparison with their published structures.[6,11] The structures of AMS, FSM-16 and DM were essentially unchanged upon calcination at 1073 K, while silicalite-1 calcined at 1073 K (*e*) gave an XRD pattern resembling that of amorphous silica.

The N_2 adsorption isotherms of AMS and FSM-16 were of type IV indicating the presence of mesopores; isotherms of silicalite-1 and DM were of type I, also suggesting microporous structures.

Table 1 shows the catalytic activities of the samples evacuated at 873 K for propene metathesis under photoirradiation. AMS catalysed the metathesis reaction quite slowly, the activity roughly corresponding to that reported previously.[5] By contrast, FSM-16 showed a much higher metathesis activity than AMS. It should be noted that FSM-16 seemed to exhibit a higher specific activity than AMS. This is because the ratio of catalytic activity of FSM-16 to that of AMS is larger than the ratio of BET surface areas (1170 and 580 m^2 g^{-1} for FSM-16 and AMS, respectively). The C_2/C_4 ratio on FSM-16 was close to unity, indicating the metathesis reaction proceeded selectively. In contrast, silicalite-1 showed no activity, indicating its microporous structure is of no advantage under the reaction conditions. DM also give no gaseous products and judging from

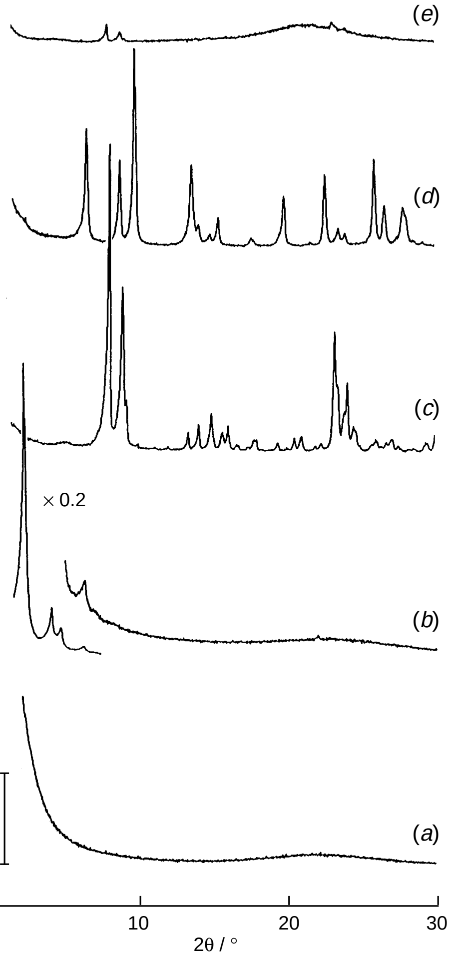

Fig. 1 XRD patterns of porous silica materials: (*a*) amorphous silica (AMS), (*b*) FSM-16, (*c*) and (*e*) silicalite-1 and (*d*) dealuminated mordenite (DM). Samples (*a*)–(*d*) were calcined at 873 K and (*e*) at 1073 K. The intensity of the low-angle region of (*b*) is reduced to 1/5.

Table 1 Results of tests for propene photometathesis on silica materials

		Yield (%)					Conv. (%)	
Pretreatment temperature/K	Sample	C_2[a]	*trans*-C_4	*cis*-C_4	1-C_4	Adsorbed	to metathesis	C_2/C_4 ratio
873	AMS	1.4	1.0	0.7	0.0	1.0	3.1	0.82
	FSM-16	8.2	5.7	2.8	0.3	5.8	16.9	0.94
	Silicalite-1	0.0	0.0	0.0	0.0	2.3	0.0	—
	DM	0.0	0.0	0.0	0.0	100.0	0.0	—
1073	AMS	16.8	11.8	4.4	0.0	2.0	33.0[b]	1.04
	FSM-16	16.2	12.0	4.7	0.4	5.6	33.3[b]	0.95
	Silicalite-1	0.0	0.0	0.0	0.0	1.3	0.0	—
	DM	0.0	0.0	0.0	0.0	98.7	0.0	—

[a] C_2 = ethene, C_4 = butene. [b] Conversions on amorphous silica and FSM-16 reached equilibrium under the reaction conditions.[5]

the colour of DM after reaction, propene appears to have been adsorbed and polymerized on acid sites of DM.

Upon evacuation at higher temperature (1073 K), the activities of AMS and FSM-16 greatly increased, while DM produced no gaseous products, as shown in Table 1. Activation of amorphous silica upon evacuation at high temperature is in agreement with a previous report.[5]

Upon evacuation at 1073 K the zeolite structure of silicalite-1 was destroyed and became XRD amorphous (BET surface area $7.5\ m^2\ g^{-1}$). This amorphous sample gave no metathesis products even after 30 h reaction.

It is suggested from the results on the catalyst samples evacuated at 873 K that an amorphous phase of silica might be necessary for photometathesis on silica since reaction did not proceed on microporous crystalline silica, but only on amorphous silica (AMS) and on FSM-16 whose walls are amorphous.[2,12] The results on the catalysts evacuated at 1073 K, however, indicated that catalytic activity is governed by the other factors, since amorphous samples produced by evacuation of silicalite-1 showed no activity.

Another distinguishable factor between these samples is the concentration of surface hydroxy groups: microporous crystals have few hydroxy groups, while amorphous silica surfaces such as AMS and FSM-16 would possess a large amount of hydroxy groups, The increase of activity of AMS and FSM-16 evacuated at higher temperature indicates that this process produces active sites on the samples. Therefore it is suggested that sites produced by desorption of hydroxy groups would regulate the activity. For silicalite-1, there are only a small number of hydroxy groups prior to evacuation. Therefore, silicalite-1 evacuated at high temperature possesses few active sites, despite its amorphous surface.

There are two possibilities why FSM-16 exhibits higher activity than AMS. One is that FSM-16 has a larger number of surface hydroxy groups than AMS. The second is that the nature of the active sites differs from that of AMS as a consequence of the characteristic walls of FSM-16 which consist of double SiO_4 tetrahedral layers.[13]

In conclusion, the catalytic activity of unmodified mesoporous silica (FSM-16) has been investigated. FSM-16 exhibits higher photocatalytic activity for propene metathesis than amorphous silica. The key point is that FSM-16 has many hydroxy groups on the amorphous walls which constitute the hexagonal mesopore structure. The active sites are proposed to be produced by desorption by hydroxy groups from the amorphous surface of silica.

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