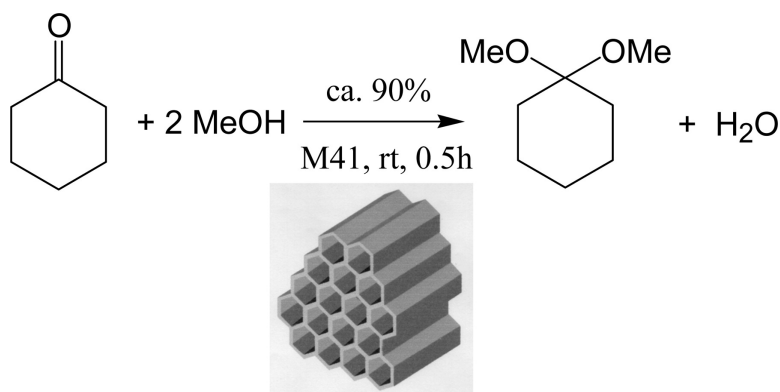## Communication

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Remarkable Effect of Pore Size on the Catalytic Activity of Mesoporous Silica for the Acetalization of Cyclohexanone with Methanol

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Mesoporous materials have attracted a great deal of attention among researchers in the fields of inorganic synthesis, functional materials, and heterogeneous catalysis, due to their regular pore structure, uniform pore diameter, and high surface area.[1] In catalysis, research groups have recently found that mesoporous silica (MCM-41) itself acts as a typical acid catalyst for several reactions, including acetalization,[2] isomerization,[3] and debenzylation.[4] It should be noted, for example, that acetalization is widely reported to be catalyzed by strong/intermediate acids such as HCl or proton-zeolites,[5] while the wall of mesoporous silica is made of amorphous silica and is generally believed to be neutral or slightly acidic. Findings regarding the acidity of mesoporous silica[1−3] raise the important question of how the acidity is created on the surface. Therefore, we focused our efforts on resolving this problem and found that pore size has a remarkable effect on catalytic activity.

MCM-41 (M41) has typically been prepared by using colloidal silica and dodecyltrimethylammonium bromide as the starting materials.[6] The as-synthesized M41 was washed with deionized water and calcined at 873 K for 6 h in air to remove organic components. The obtained M41 was stored in air at room temperature. The hexagonal structure of the resulting M41 was confirmed by the appearance of $2\theta = 2.580°$, 4.476°, and 5.124° peaks in the X-ray diffraction pattern (Cu Kα, Ni filter), which correspond to (100), (110), and (200), respectively. The N_2 adsorption−desorption isotherms and the BET measurements at 77 K indicate a pore diameter of 2.24 nm (the BJH method) and a surface area of 1050 $m^2 g^{-1}$. The pore diameter was controlled by changing the carbon number of the surfactant molecules.[7] The M41 was used in the catalytic reaction after dehydration treatment, as described in the next section. Methanol was the commercially available, nonanhydrous grade and was used without further dehydration treatment. Cyclohexanone of 2.0 mmol was added to 5.0 mL of methanol containing 30 mg of M41 in air at ambient temperature. Yields of dimethoxycyclohexane were determined by GC-MS using *n*-decane as an internal standard.

Acetalization of cyclohexanone was first measured as a function of the evacuation temperature of the catalyst (shown in the Supporting Information figure), where M41 with a pore diameter of 2.2 nm was employed as the catalyst. The increase in the evacuation temperature from 298 to 333 K resulted in a large jump in the catalytic activity. TG-DTA measurement indicated that this increase was caused by the desorption of water molecules physically adsorbed in the pores of M41. Evacuation of M41 at temperatures of 353 K or higher drastically reduced the catalytic activity, although there was no distinct loss of weight in the TG-DTA curves. Changes in the surface structure of the wall or low-level desorption of surface hydroxyl groups may be the reason for such a large decrease; the

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Table 1. Comparison of the Catalytic Activity of Various Silica Catalysts for Acetalization of Cyclohexanone with Methanol[a]

entry	cat.	surface area /$m^2 g^{-1}$	react time /h	yield /%	recv. /%	acid strength H_0[h]
1	M41[b]	1050	5	89	10	−5.6 to −3.0
2	M41[b]	1050	1	87	11	−5.6 to −3.0
3	M41-aw[c]	1035	1	88	12	−5.6 to −3.0
4	M41-Al[d]	995	1	87	12	−5.6 to −3.0
5	JRC-SiO-4[e]	347	24	0	quant.	+3.3 to +4.8
6	silica gel[f]	172	24	0	quant.	+3.3 to +4.8
7	none		24	0	quant.	
8	filtrate[g]		24	0	quant.	

a Experimental conditions: cyclohexanone 2.0 mmol, methanol 5.0 mL, catalyst 30 mg, reaction temp 298 K. *b* The Si/Al ratio of the parent M41 sample was 400. *c* The parent M41 sample was acid-washed with a HCl solution, and the Si/Al ratio of the resulting M41-aw was 2400. *d* Aluminum ions were added into the parent M41 sample by using the template ion exchange (TIE) method.[7] The Si/Al ratio of the obtained M41-Al sample was 48. *e* The reference catalyst is distributed as the standard silica gel by the Catalysis Society of Japan. *f* This type of silica gel was prepared by using the same starting materials as those for the synthesis of the present M41 sample. The solution containing silica source, surfactants, and so on was vigorously stirred to avoid the formation of surfactants' micelles. The surface area was 172 $m^2 g^{-1}$, and therefore 186 mg of silica gel was used for the catalytic run. *g* After the reaction of entry 1, the solid catalyst was removed by the filtration. The filtrate obtained was used in entry 8 to examine the catalytic activity of the possible dissolved materials. *h* The acid strength of silica was measured by using Hammett's indicators.

exact reason is a topic for future study. We found that overdrying or high temperature treatment of M41 resulted in reduction of catalytic activity and that M41 evacuated at 333 K is the best for acetalization. The catalyst was subsequently evacuated at 333 K before use.

The catalytic activity of various silica samples is summarized in Table 1. It is clear that M41 catalyzed acetalization with high yield and selectivity. In contrast, silica gel prepared from the same raw materials as those used for preparation of the M41 showed no catalytic activity (entry 6). Note that the amount of silica gel used in the catalytic run was about 6 times greater than that of M41 (entry 1) to adjust the application surface area. The standard silica gel sample distributed by the Catalysis Society of Japan also showed no activity (entry 5). This great difference between the catalytic activities of M41 and silica gel is very strange considering that the walls of M41 and silica gel are all made of amorphous silica. What is the cause of this great difference? First, we compared the H_0 values obtained by using Hammett's reagents. As shown in Table 1, the values for the silica gels were +3.3 to +4.8, which indicates the presence of neutral or slightly acidic surface sites. On the other hand, the values for M41 were −5.6 to −3.0. These values are similar to those reported previously.[3] The presence of acidic sites in the mesopores is obvious, but the strength is not as great as that of HCl and proton-zeolites.
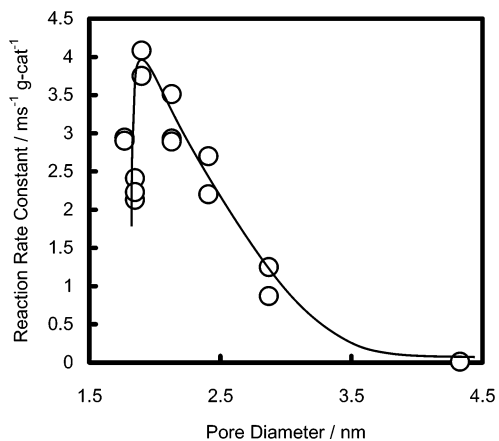
Figure 1. Dependence of catalytic activity for the acetalization of cyclohexanone on the pore diameter of silica MCM-41. The catalyst was evacuated at 333 K for 1 h before use in the catalytic run. Experimental conditions: cyclohexanone 2.0 mmol, methanol 5.0 mL, catalyst 30 mg, reaction temp 298 K.

Next, we studied the effect of aluminum ion concentration in the samples, which derives from impurities in the colloidal silica. The Si/Al ratios of the M41 samples were all 380−670. The Si/Al ratio of silica gel prepared from the colloidal silica was 400, which was the same as that of the M41 samples. This shows the importance of the pore structure of M41 samples in producing catalytic activity. In addition, the aluminum ion concentration was varied widely from Si/Al = 400 to 2400 or to 48 by acid washing or template ion exchange treatment,[8] and we investigated the catalytic activity of the resulting M41 samples (Table 1, entries 3 and 4). As can be seen, the catalytic activity of these M41 samples is almost the same as that of the parent M41, which clearly demonstrates that aluminum content is not a significant factor determining catalytic activity.

We studied the dependence of catalytic activity on the pore size of the M41 samples, as shown in Figure 1. Surprisingly, catalytic activity was strongly dependent on the pore diameter of the catalyst and was maximized at around 1.9 nm. Smaller or larger pores were not suitable for the catalytic acetalization of cyclohexanone. The catalytic activity of M41 with a pore diameter of 4.0 nm was almost zero. The M41 samples were repeatedly prepared and used in the catalytic reaction, and the catalytic activity values all fell on one correlation line within experimental error, as shown in Figure 1.

Three kinds of shape selective catalysis are widely known:[9] reactant, product, or intermediate selectivity. The underlying concept is that one of the compounds cannot pass through or be produced in the narrow pores and therefore the catalytic selectivity is controlled by the pore diameter. In the present reaction, the diameter of cyclohexanone is 0.75 nm (the distance between oxygen and most distant hydrogen is 0.51 nm; the van der Waals radius of oxygen is 0.14, and that of hydrogen is 0.10), and that of the product should be 0.96 nm, while the most appropriate pore diameter for the catalysis is approximately 1.9 nm. The phenomenon cannot be accounted for by existing concepts. Why does such a correlation exist between pore diameter and catalytic activity? We first checked the aluminum content of the different samples, but there was no evidence of correlation between catalytic activity and aluminum content, as was already discussed in the previous section.

At present, we can suggest a few possible explanations. First, some synergistic effect may be involved at larger pores, but for pores less than 1.9 nm, diffusion effects may determine the rate. Second, the local concentration or orientation of methanol may play a role, although we have not as yet clarified the state of methanol on the M41 surface. Previous work has described the importance of the radius of curvature in determining the adsorption properties of molecular sieves.[10] The third possible explanation is that an assembly of weak acid sites may act as an effective/strong acid site. A reasonable hypothesis is that all of the surface hydroxyl groups on the pore wall point to the center of each pore, and thus they could work as a group. Such an assembly might induce very active acid catalysis despite the low acidity of each OH.

In a separate experiment, we employed pentanal as a substrate for acetalization on the M41 samples and confirmed again that the best pore diameter for catalysis was 1.9 nm. This indicates that the catalytic activity is not dependent on the molecular size of the substrate but on the pore diameter of catalyst.

Many previous studies have reported on the preparation and the use of mesoporous materials, but few studies have found characteristic phenomena deriving from regular mesopores. Our discovery in this research sheds light on a new effect of nanometer-sized spaces on the activation of the substrates in pores, although it is clear that this work raises many questions. The specific effects of nanospaces have also been reported in the fields of molecular recognition[11] and organic zeolites.[12]

Supporting Information Available: Temperature dependence of the catalytic activity (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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