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Methanol synthesis over Pd/SiO_2 with narrow Pd size distribution prepared by using MCM-41 as a support precursor

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Abstract

All silicious MCM-41 was investigated as a support or a support precursor for Pd/SiO_2 and prepared catalysts were tested for methanol synthesis from CO and H_2. The methods of Pd loading on the MCM-41 were impregnation, seed impregnation and chemical vapor deposition (CVD). For both impregnations, most Pd existed outside of the pore as large particles, and only a small part of Pd was inserted into the pore of MCM-41 retaining the initial structure. On the contrary, in the catalyst prepared by CVD method, the MCM-41 structure was completely destroyed to become amorphous SiO_2. Yet the average Pd particle size in this catalyst was smaller and its distribution was narrower than those of the catalysts prepared by impregnation methods. In the methanol synthesis from CO hydrogenation the catalyst prepared by CVD showed higher methanol selectivity than other MCM-41-derived catalysts. This result was considered to be due to the more uniform distribution of the Pd particle size.

Keywords: Support precursor; MCM-41; Chemical vapor deposition; Pd/SiO_2; Methanol synthesis

1. Introduction

Catalysis in the 20th century focused primarily on activity to maximize the rate of the formation of product molecules. In the 21st century, catalysis science and technology are concerned more about achieving high selectivity of the desired product because waste disposal has become expensive and often involves negative ecological impacts [1]. The reactivity of heterogeneous catalysts depends sensitively on their structure in many catalytic reactions [2] and the metal structure could be systematically varied by changing particle size of the metal [3]. Hence, preparation of a supported metal catalyst with uniform particle size could be an effective method to increase the overall reaction selectivity. Recent rapid development in nanoscience could guide us to the eventual goal of synthesizing monodispersed metal particles on usual support materials [1,4].

In the preparation of the supported metal catalyst, the great concern has been to produce metal particles that are well dispersed with sizes as small as possible in order to maximize the surface-to-volume ratio. Now the narrow particle size distribution should become an important concern as well for the selectivity purpose. Various techniques to prepare nano-sized materials have been investigated. Among these techniques, the chemical techniques relating to colloidal metal particles have become of considerable interest in recent years, because it can produce monodispersed nanoparticles and their sizes are controllable according to the preparation conditions of the microemulsions [5,6]. However, in the preparation of real metal catalysts with oxide supports, the method based on microemulsions could not avoid formation of large aggregates during subsequent heat treatment and metal particle size distribution of the final form of the catalyst becomes still broad [7].

In 1992, researchers at Mobil Corporation synthesized a new family of mesoporous material known as the M41S family [8]. Silica MCM-41 is a member of the M41S family with a hexagonal array of one-dimensional pores. The diameter of the pores can be varied from 1.6 to 10 nm by using surfactants of different chain lengths or organic molecules for expanding the surfactant micelles. These MCM-41 molecular sieves have attracted considerable and growing attention because of their remarkable properties. The spaces of the mesoporous materials can be used as containers or templates for the synthesis of other

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new materials. Recently, numerous studies have been reported on the synthesis of MCM-41 and its application to prepare nanomaterials [9].

In industrial methanol synthesis processes, Cu-based catalysts (especially Cu/ZnO) are used universally, but they suffer from a disadvantage, i.e. sintering occurs at temperatures greater than about 600 K [10]. Poutsma et al. [11] were the first to recognize that supported Pd could also catalyze the synthesis of methanol. Berlowitz and Goodman [12] found that the metal was an active catalyst but that performance was improved in the presence of a support. Promoters such as MgO, CeO_2 or ZnO were also found to favor the production of methanol [13–15]. We have also studied effects of preparation methods and Pd particle sizes of Pd-ZnO catalysts for methanol synthesis from CO hydrogenation [16–18].

The present study is concerned with preparation of palladium catalysts supported on MCM-41 as a support itself or a precursor to SiO_2 support. We attempted to utilize the uniform pore structure of MCM-41 as a hard template in order to prepare Pd particles of a narrow size distribution. Their catalytic behavior was evaluated for the methanol synthesis from hydrogenation of carbon monoxide at 533 K and 3.0 MPa.

2. Experimental

2.1. Preparation of catalysts

MCM-41 was synthesized following a procedure similar to those described in the literature [19,20], which was optimized to improve the structural regularity of the product. Thus, an aqueous solution of sodium silicate and fumed silica was used as the silica source and was added drop by drop to an aqueous solution of cetyltrimethylammonium bromide (CTAB, $C_{16}H_{33}(CH_3)_3NBr$, Aldrich) surfactant at room temperature while the solution was stirred vigorously. After the mixture had been continuously stirred for 1 h, the resultant gel mixture was heated for 24 h at 100 °C. The molar composition of the gel mixture was $0.25CTAB:1.0SiO_2:0.25Na_2O:50H_2O$. The mixture was cooled to room temperature, and the pH was adjusted to 10.2 with acetic acid. The mixture was heated again for 72 h at 100 °C. The pH adjustment and subsequent heating were repeated, and the precipitated MCM-41 product was collected by filtration. The product was washed with ethanol and dried for 6 h at 110 °C. Finally, the product was calcined in air for 6 h at 550 °C.

For impregnation, the calcined MCM-41 sample was slurried in a 5.0 wt% aqueous solution of palladium nitrate (Aldrich) for 3 h at room temperature. The solution-to-silica ratio was 100 ml/g. After the solvent was completely evaporated in a rotary evaporator, the sample was dried in oven for 12 h at 110 °C. The product was finally calcined for 6 h at 500 °C to obtain the sample denoted as IMP-Pd/MCM-41. For seed impregnation (SEED-Pd/MCM-41), the calcined MCM-41 sample was slurried in a 0.5 wt% aqueous solution of palladium nitrate (Aldrich) for 3 h at room temperature to incorporate Pd ions into the channels of MCM-41 by exploiting the weak ion-exchange capability of the silica material. The solution to silica ratio was 100 ml/g. After this treatment, the sample was collected by filtration and subsequently dried in oven for 12 h at 110 °C. The ion-exchanged Pd precursor was activated by heating slowly to 350 °C in a stream of O_2 and then reduction with a stream of H_2 at 300 °C. This sample was immersed in aqueous solution of Pd nitrate which corresponded to 5.0 wt% Pd/MCM-41. After the solvent was completely evaporated in a rotary evaporator, the sample was dried in oven for 12 h at 110 °C. The impregnated Pd-metal precursor was finally reduced in a stream of H_2 while the temperature was increased from room temperature to 300 °C over 4 h and maintained at 300 °C for 2 h.

To prepare chemical vapor deposition (CVD-Pd/MCM-41), an aqueous solution of sodium hydroxide and hexafluoroacetylacetone (hfac) were mixed with an aqueous solution of Na_2PdCl_4. The mixture was stirred for 1 h at room temperature, filtered with water, and dried. The precipitate was dissolved with hot hexane, and then quenched to −78 °C. After the cooled sample was purified in vacuum, Pd metal organic precursor, $Pd(hfac)_2$, was obtained. The calcined MCM-41 was pretreated at 400 °C in a vacuum for 4 h. After cooling the MCM-41, prepared $Pd(hfac)_2$ was connected to the MCM-41 at 55 °C in a vacuum. As Pd organic precursor was deposited on MCM-41, its color changed from white to yellow. Finally, the sample was reduced in a stream of H_2 at 150 °C for 2 h. The CVD-Pd/SiO_2 catalyst was also prepared with the same procedure except that the support was SiO_2 instead of MCM-41. The targeted Pd loading of both catalysts was 5.0 wt%.

2.2. Characterization of catalysts

All the materials were examined by TEM for observation of their shape and morphology. From the X-ray diffraction (XRD) pattern at small angles, the lattice structure of MCM-41 was examined. From XRD pattern at wide angles, Pd particle size was estimated by applying Debye–Sherrer equation to broadening of XRD peaks. From N_2 adsorption–desorption isotherms obtained at 77 K in a constant-volume adsorption apparatus (Micromeritics, ASAP 2010), BET surface areas and pore size distributions were obtained.

2.3. Methanol synthesis by CO hydrogenation

The catalytic hydrogenation of carbon monoxide was carried out using a fixed bed flow reactor (SUS-316, inside diameter = 11 mm). The standard reaction conditions were: $T = 523$ K, $P = 3.0$ MPa with H_2/CO (3/1 vol.%), and space velocity = 12,000/h. Before each run, the catalyst was reduced in situ at 573 K for 2 h in a stream of H_2. The gaseous products were analyzed by a gas chromatograph (HP 5890II) with Porapak T packed column and a thermal conductivity detector.

3. Results and discussion

As shown in the XRD pattern in Fig. 1, the prepared MCM-41 shows the strong peaks at $2\theta = 2.2$, 3.8 and 4.4 and at least two more peaks could be identifiable in the higher angles. First

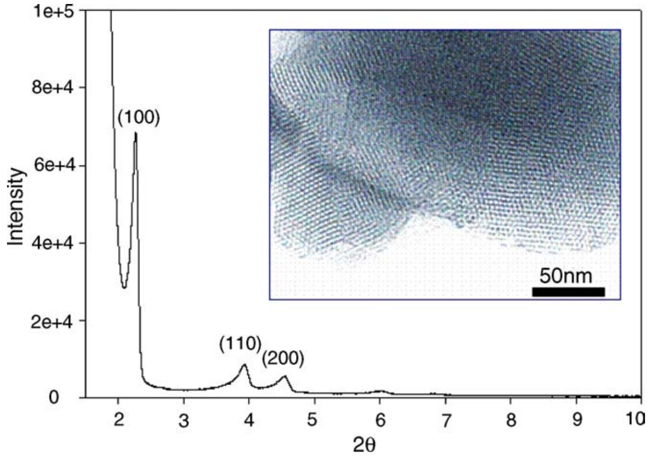

Fig. 1. The small angle XRD pattern and TEM image (inset) of MCM-41.

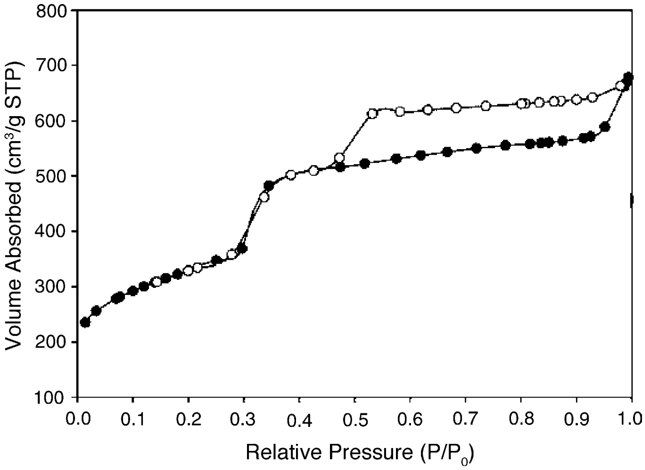

Fig. 2. The N_2 adsorption (filled circles) and desorption (open circles) isotherms for MCM-41 at 77 K.

strong peak at $2\theta = 2.2$ ($d_{100} = 4.016$ nm) represents the periodicity of the pore structures of mesoporous MCM-41. The obtained d_{100} value agrees well with the reported values for MCM-41 prepared with C_{16} surfactant template [21–23]. The presence of higher angle peaks indicates that the material has been prepared with an excellent regularity of the pore structure. The TEM image also indicates that this material has a well ordered structure made of regular hexagonal array of uniform channels. The N_2 adsorption–desorption isotherms in Fig. 2 showed a typical type IV adsorption isotherm characterized by a well defined step in the desorption branch of the isotherm curve at P/P_0 of ca. 0.5 [24]. This is characteristic of capillary condensation within uniform pores of MCM-41. From the Brunauer–Joyner–Halenda (BJH) analysis of the pore size distribution, the pore diameter was determined to be 2.6 nm. This gives a wall thickness of 1.40 nm from the difference between d_{100} and the pore size. The BET surface area was 823 m^2/g. Based on these results, we can conclude that high quality MCM-41 has been prepared.

Fig. 3 shows the TEM images of IMP-Pd/MCM-41 and SEED-Pd/MCM-41, in which palladium were loaded by conventional impregnation and seed impregnation methods, relatively. Most of palladium particles in IMP-Pd/MCM-41 existed outside of the pore as large particles. The particle size distribution obtained from this TEM image (see inset) was very broad. In the case of SEED-Pd/MCM-41, the palladium particles are more uniformly dispersed and their sizes were smaller compared with IMP-Pd/MCM-41. The distribution was also more uniform. The small angle XRD patterns in Fig. 4a show that the structure of MCM-41 was retained for both impregnated samples. However, the (1 0 0) peak intensity was reduced and two peaks of MCM-41 at $2\theta = 3.8$ and 4.4 were not observed for IMP-Pd/MCM-41. This indicates that the structure was partially disrupted and disordered. The average Pd particle size obtained by line broadening of wide angle XRD pattern of Pd in Fig. 4b was 16.9 nm. For SEED-Pd/MCM-41, all the XRD peaks were retained although their intensities were

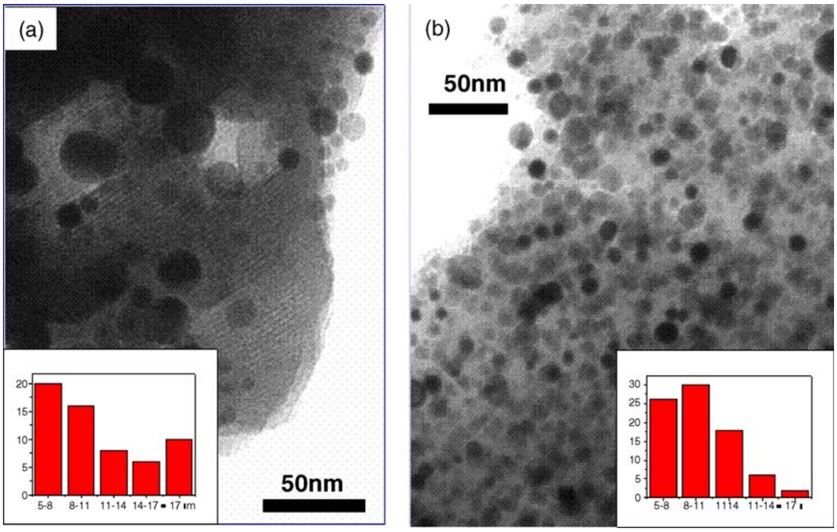

Fig. 3. TEM images of Pd/MCM-41 prepared by (a) impregnation and (b) seed impregnation. The insets show size distributions of Pd particles obtained from these images.

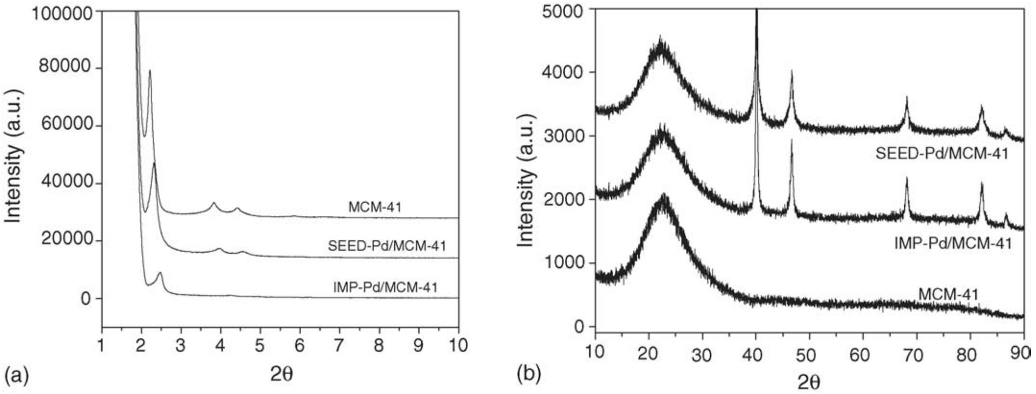

Fig. 4. XRD patterns of IMP-Pd/MCM-41 and SEED-Pd/MCM-4. (a) Small angle XRD and (b) large angle XRD.

reduced. This means that the original structure was better preserved for this sample. For SEED-Pd/MCM-41, the BET surface area was reduced from 823 to 668 m^2/g and the wall thickness of MCM-41 was slightly increased from 1.40 to 1.46 nm upon Pd loading. These could mean that Pd is inserted into the pore of MCM-41. However, the average Pd particle size calculated from XRD line broadening was 13.3 nm (greater than the pore size of MCM-41), indicating that the majority of Pd particles still existed outside of the pore as large particles.

To obtain better dispersion of Pd particles, CVD method was tried, which was widely used for inserting metal particles into the pore of mesoporous material [20]. First, organic Pd metal precursor, $Pd(hfac)_2$, was prepared. To deposit Pd particle on the MCM-41, the Pd precursor was evaporated in vacuum and the vapor was directed to the MCM-41. After reduction in a stream of hydrogen, CVD-Pd/MCM-41 was obtained. Fig. 5 shows TEM images of CVD-Pd/MCM-41. Now, the size of Pd particles was much smaller and the particle size distribution was much narrower than those of conventional and seed impregnation methods. The analysis of TEM image showed almost monodispersed particle size distribution. Surprisingly, however, TEM image did not show the lattice structure of MCM-41. The small angle XRD pattern did not show any characteristic peaks of MCM-41 as shown in Fig. 6 (inset). Thus, the structure of MCM-41 in CVD-Pd/MCM-41 has been completely destroyed and it turned into amorphous SiO_2. The average Pd particle size obtained by XRD line broadening was 8.1 nm (Fig. 6).

As mentioned, the uniform pores of MCM-41 have been used as a hard template to prepare metal rods of uniform diameter [20]. However, in the present case, metal does not remain in the pore structure of MCM-41, but destroy the structure and form a Pd catalyst supported on amorphous silica. Fortunately, the Pd particles in CVD-Pd/MCM-41 are small and highly uniform in size. Thus, the MCM-41 pores should have played the role of a hard template before they were destroyed. Further, Pd particles over this kind of open support structure are more easily accessible by reactant molecules and more useful in catalysis than Pd particles entrapped in the one-dimensional pores of MCM-41. Since the obtained Pd particles are considerably larger (8.1 nm by XRD) than the pore diameter of MCM-41 (2.6 nm), the templating effect of the MCM-41 appears to be limited only to the early stage of Pd particle growth. Yet the behavior at this stage should be important for the size and its distribution of the obtained Pd particles. In order to verify that the particle size and distribution of Pd in CVD-Pd/MCM-41 are indeed due to the effects of MCM-41 pore structure, the Pd/SiO_2 catalyst was prepared with the same CVD method on silica gel. As shown in Fig. 7, although the average Pd particle size was smaller, its

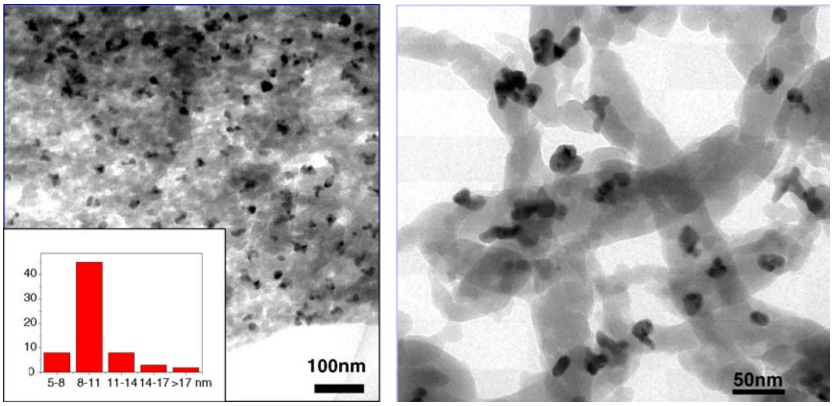

Fig. 5. TEM images of CVD-Pd/MCM-41. The inset shows the particle size distribution obtained from this TEM image.

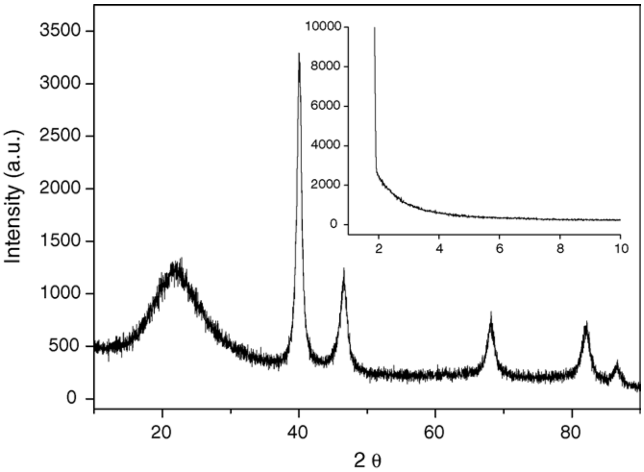

Fig. 6. XRD patterns of CVD-Pd/MCM-41. The inset is the small angle XRD pattern. Note that MCM-41 structure has completely disappeared.

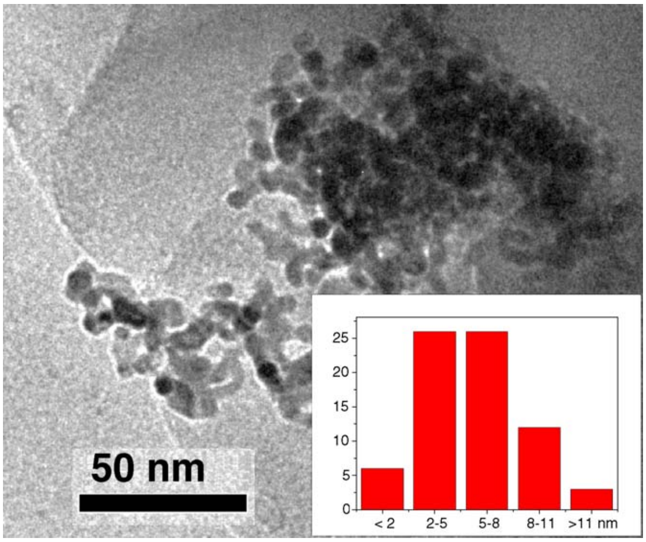

Fig. 7. TEM image of CVD-Pd/SiO_2. The inset shows the particle size distribution obtained from this TEM image.

particle size distribution was broader in comparison with CVD-Pd/MCM-41. Thus, it was considered that the growth of Pd particles on MCM-41 had been regulated by the MCM-41 pore structure.

All the Pd catalysts prepared in this study were tested for the reaction of CO hydrogenation to methanol at $T = 533$ K, $P = 3.0$ MPa with H_2/CO (3/1 vol.%) and space velocity = 12,000/h. The results are summarized in Table 1. All the Pd/MCM-41 catalysts showed similar CO conversions, although that for CVD-Pd/MCM-41 was a little lower. However, the selectivity of methanol was increased in following order: conventional impregnation < seed impregnation < CVD method. The main by-products were CH_4 and CO_2 formed by reactions (2) and (3).

$$CO + 2H_2 \rightarrow CH_3OH \tag{1}$$

Table 1
Methanol synthesis by CO hydrogenation over various Pd catalysts[a] and their average particle sizes

Catalysts	Pd particle size (nm)		CO conversion (%)	MeOH selectivity (%)	MeOH yield (%)
	XRD[b]	TEM			
IMP-Pd/MCM-41	16.9	11.6	5.90	8.9	0.53
SEED-Pd/MCM-41	13.3	10.2	4.98	15.8	0.78
CVD-Pd/MCM-41	8.1	10.1	3.75	40.7	1.53
CVD-Pd/SiO_2	6.5	5.7	15.1	17.8	2.68
Cu/ZnO/Al_2O_3[c]			2.01	87.5	1.76

[a] $T = 523$ K, $P = 3.0$ MPa, $H_2/CO = 3/1$ vol.% and space velocity = 12,000/h.
[b] Average Pd particle size measured by XRD peak broadening with Scherrer equation.
[c] Lee et al. [25].

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

The particularly high methanol selectivity for CVD-Pd/MCM-41 is interesting. In the catalytic CO hydrogenation to methanol on Pd/SiO_2, the active site is known to be Pd metal [11,12]. Because MCM-41 is basically similar to SiO_2, the catalytic performance may not be affected whether the structure is retained or not. In order to show the high selectivity may originate from the uniform Pd particle size distribution of CVD-Pd/MCM-41, not from the CVD method itself, the activity of CVD-Pd/SiO_2 was tested. As shown in Table 1, the methanol selectivity of CVD-Pd/SiO_2 was much lower than that of CVD-Pd/MCM-41 although its CO conversion was higher. Thus, the excellent methanol selectivity observed over CVD-Pd/MCM-41 is considered to be due to the uniform Pd metal particle size distribution that we achieved with the special preparation method using MCM-41 as a hard template although its structure is destroyed during the catalyst synthesis. For reference, the activity of Cu/ZnO/Al_2O_3, the commercial catalyst, is also shown under the same condition. Its high selectivity to methanol is impressive. The thermal stability is considered to be the limitation of this catalyst.

4. Conclusion

The palladium loaded on MCM-41 prepared by various methods were investigated and tested for methanol synthesis from CO and H_2. The catalyst prepared by CVD method showed the smallest metal particle size and the narrowest size distribution. During the early stage of Pd particle growth, the MCM-41 structure seemed to play the role of a hard template to form small and uniform Pd particles. This catalyst showed the highest methanol selectivity in CO hydrogenation, which was considered to be due to the more uniform distribution of the Pd particle size. Thus, CVD onto MCM-41 is a promising method to prepare small Pd particles with highly uniform size distribution.

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