Catalytic Methanol Decomposition at Low Temperature over Pd Catalyst Derived from Mesoporous Silica Carried Pd-Hydrotalcite

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Pd-Hydrotalcite (denoted by Pd(HT)) was uniformly dispersed on HMS (hexagonal mesoporous silica) by synthesizing Pd(HT) in the HMS suspension and the composite was used as a catalyst precursor for methanol decomposition. The novel catalyst showed high activity and selectivity to synthesis gas at low temperature due to the large surface area and high Pd dispersion.

The decomposition of methanol to synthesis gas is not only one of the ways to produce hydrogen, but also possesses applied possibilities for fuel cell and on-board reforming for vehicles.[1] We are focusing on this reaction since it is endothermic and is applicable for chemical storage of the waste heat from factories.[2] The Pd-based catalysts seem to be preferred for recovery of the waste heat from factories by methanol decomposition due to their high activity, selectivity and stability. ZrO_2 and CeO_2 have been reported to be effective supports for Pd in the reaction.[2]

Hydrotalcite ($Mg_3Al(OH)_{16}CO_3 \cdot 4H_2O$, denoted by HT) has brucite-like positively charged layers of magnesium and aluminium hydroxide octahedra sharing edges and has interstitial carbonate anions to compensate for the charges.[3] Calcined hydrotalcite (Mg(Al)O) is a peculiar support of noble metal catalysts for several reactions.[4,5] We have reported that Pd(Mg(Al)O) showed a higher activity than those over Pd/ZrO_2 and Pd/CeO_2 for methanol decomposition.[6] On the other hand, the synthesis of silica-based mesoporous materials, such as M41S[7] and HMS,[8] has attracted great interest recently. High thermal stability (up to 1073 K), large surface area (above 1000 $m^2\ g^{-1}$) and uniform-sized pores render these materials very interesting for catalysis and support.[9] In the present study, in order to maximize the surface area and increase the Pd dispersion of the catalyst, we dispersed Pd(HT) on HMS by synthesizing Pd(HT) in the suspension of HMS. The novel catalyst which was derived from HMS carried Pd(HT) showed high activity and selectivity to synthesis gas for methanol decomposition.

Pd(HT) was prepared by adding an aqueous solution containing $Pd(NO_3)_2$, $Mg(NO_3)_2$ and $Al(NO_3)_3$ (molar ratio of Mg to Al is 3 to 1) to a solution containing a slight excess Na_2CO_3 at 333 K. A 2 mol dm^{-3} NaOH aqueous solution was added during the operation to maintain the pH at 10. The resultant precipitate was washed and dried at 373 K. The Pd(Mg(Al)O) (denoted by PMA) catalyst was obtained by the calcination of Pd(HT) at 698 K for 3 h. HMS was prepared by adding a solution of $Si(OC_2H_5)_4$ in ethanol to a stirred solution of dodecylamine and HCl in water.[8] The resulting gel was aged for 18 h at ambient temperature, and then dried at 373 K and calcined in air at 923 K for 4 h. Pd/HMS was prepared by an impregnation method. Pd(HT)/HMS was prepared as follows. HMS powder (< 100 mesh) was added to an aqueous solution containing $Pd(NO_3)_2$, $Mg(NO_3)_2$ and $Al(NO_3)_3$, and then vigorously stirred for 30 min at 333 K to form a suspension. A solution of Na_2CO_3 was acidified by adding dilute HNO_3 till pH 10. The suspension was slowly added to the Na_2CO_3 solution at 333 K under vigorous stirring. The operation was completed in about one hour while keeping the pH at 10 by adding 2 mol dm^{-3} NaOH. After aging at 363 K for one hour, the precipitate was filtered off, washed with distilled water, and finally dried at 373 K for 24 h. The molar ratio of Mg to Al was 3 and the mass ratio of Pd(HT) to HMS was 1 to 2 or 2 to 1 in the Pd(HT)/HMS precursor. The Pd(Mg(Al)O)/HMS catalyst (denoted by PMAH) was obtained by the calcination of the Pd(HT)/HMS precursor at 698 K for 3 h. A mixed catalyst, Pd(Mg(Al)O)+HMS (denoted by PMAH-M), was prepared as a reference for the PMAH catalyst by stirring the Pd(HT) suspension and HMS suspension together for 30 min, and then filtered off and calcined at 698 K for 3 h. The designed Pd loadings were 3.6 wt%, 15 wt% and 30 wt% for the catalysts and the actual amounts of Pd loadings in the catalysts were measured by ICP analysis. The abbreviations of the catalysts are listed in Table 1.

The catalytic test was conducted using a fixed-bed flow reactor at 523 K under atmospheric pressure. A 300 mg sample of the catalyst was sandwiched between quartz wool and packed in a 10 mmϕ U-shaped quartz tubular reactor. After reduction in flowing of 10% H_2 at 673 K for 1 h, the reaction was started under flowing 40% methanol diluted with N_2 gas at the total flow rate of 10000 mL h^{-1} $(g\text{-}cat)^{-1}$. The products were analyzed by three on-line TCD-gas chromatographs. The selectivity of each product was calculated based on the converted methanol.

FT-IR spectra were recorded on a JASCO FT/IR-7000 spectrometer. Thermogravimetric and differential thermal analyses (TG-DTA) were carried out using a Shimadzu TGA-50 instrument. X-Ray diffraction (XRD) patterns were recorded with a MAC Science MXP-18 diffractometer. BET surface areas were measured at 77 K using a Belsorp 28SA automatic adsorption instrument. ICP analyses were done with a Thermo Jarrell Ash IRIS/AP. The dispersion of Pd was measured by the CO pulse method at room temperature.[10] Transmission electron micrograph (TEM) analyses were carried out using a JEOL JEM-2010/EDS system.

The FT-IR spectrum of the calcined HMS showed Si-O vibrations of SiO_4 tetrahedra at about 1090, 810 and 470 cm^{-1}, and showed a hydrogen-bonded silanol groups vibration at 3400 cm^{-1}.[9] As for Pd(HT), the bands at 1380 cm^{-1}, 820 cm^{-1} and 630 cm^{-1} are associated with CO_3^{2-} vibrations between the layers, and the bands at 410 and 430 cm^{-1} are related to the cation-oxygen vibrations in the brucite-like layer.[3] The synthesized Pd(HT)/HMS precursors showed all the bands of HMS and Pd(HT) with little shift, which indicated that Pd(HT) had been synthesized in the Pd(HT)/HMS precursors.

Since HMS had been calcined at 923 K for 4 h, there is

Table 1. Catalytic activity and physical properties of catalysts containing palladium[a]

Catalyst	Abbreviation	Pd loading /wt%[b]	CH_3OH Conv./%	Select./%[c]		BET surface area /m^2 (g-cat)$^{-1}$	Particle size of Pd/nm[d]
				CO	H_2		
Pd/HMS	3PH	3.5	13.7	99.9	98.4	818	3.3
	15PH	15.2	25.6	99.4	99.1	684	6.4
	30PH	29.1	20.8	99.0	98.6	513	12.7
Pd(Mg(Al)O)	3PMA	3.3	34.7	99.6	99.3	143	3.7
	15PMA	14.6	47.1	99.2	99.2	112	5.4
	30PMA	27.3	43.2	98.7	98.8	87	9.6
Pd(Mg(Al)O)/HMS	3PMAH-1[e]	3.4	52.5	99.8	98.2	361	3.0
	3PMAH-2[f]	3.3	45.1	99.7	99.1	332	3.1
	15PMAH[f]	14.1	78.4	99.8	99.7	296	3.6
	30PMAH[f]	26.4	91.7	98.5	97.8	234	5.8
Pd(Mg(Al)O)+HMS	3PMAH-M[e]	3.4	33.6	99.7	99.2	736	4.9

[a] Reaction temperature: 523 K, F/W: 10000 ml h^{-1} (g-cal^{-1}), CH_3OH: 0.4 atm, N_2: 0.6 atm. [b] Pd loadings were measured by ICP analyses.
[c] By-products were methane, carbon dioxide, methyl formate, dimethyl ether and water. [d] Pd particle size was measured by CO pulse method.
[e] Mass ratio: Pd(HT) : HMS = 1 : 2. [f] Mass ratio: Pd(HT) : HMS = 2 : 1.

almost no weight loss and energy change in the TG and DTA curves of HMS. For Pd(HT), the weight loss below 473 K was ascribed to the loss of physically absorbed and interlayer water, and the second weight loss in the temperature range from 573 to 698 K could be attributed to the removal of CO_2 from the interlayer carbonate anions and hydroxy groups from the brucite-like layers.[3] Pd(HT)/HMS also shows two weight losses in the TG due to the loss of absorbed and interlayer water during the first stage, and the loss of carbonate anions and hydroxy groups during the second stage. The two peaks in the DTA curve of Pd(HT)/HMS shifted to low temperature coinciding with the weight loss in the TG curve. This indicated that the Pd(HT) particles formed in Pd(HT)/HMS were very small and collapse at low temperature.

The X-ray diffraction pattern of calcined HMS exhibited a strong reflection (100) at about 2.3 degrees. Pd(HT) showed the pattern of a layered structure from 10 to 70 degrees. However, the peaks of Pd(HT) were not observed and there no peak appeared from 10 to 70 degrees in the XRD pattern of Pd(HT)/HMS. We think that the Pd(HT) particles, which were synthesized on the surface and/or in the pores of HMS in the Pd(HT)/HMS, are too small to exhibit an XRD pattern.

The all Pd-containing catalysts prepared in this work showed high selectivities to CO and H_2 (Table 1). Very small amounts of methane, carbon dioxide, methyl formate, dimethyl ether and water were formed as by-products. The 3PH catalyst, which has the highest surface area, showed a low conversion of 13.7% at 523 K. This result indicated that HMS is not a suitable support for methanol decomposition although Pd/SiO_2 is one of the most active catalysts for methanol synthesis from CO and H_2.[11] The 3PMA catalyst[6] showed a conversion of 34.7% at 523 K. The 3PMAH-1 catalyst showed a 52.5% conversion which was much higher than that over the 3PMA catalyst at 523 K. This proved that the dispersion of PMA on HMS increased the catalytic activity for methanol decomposition. On the contrary, the mixed 3PMAH-M catalyst showed a 33.6% conversion which was much less than that over the 3PMAH-1 catalyst at 523 K. These results strongly indicated that the uniform dispersion of Pd(HT) on HMS was very important for improving the catalytic activity for methanol decomposition.

The catalytic activity of the PMAH catalyst with 3.6 wt% designed Pd loading showed the maximum conversion when the mass ratio of Pd(HT) to HMS is 1 to 2 in the Pd(HT)/HMS precursor. However, the mass ratio of 2 to 1 between Pd(HT) and HMS in the Pd(HT)/HMS precursor was used for 15PMAH and 30 PMAH to ensure a sufficient amount of Mg(Al)O in the catalysts. The methanol conversion over PMA increased from 3PMA to 15PMA and decreased from 15PMA to 30PMA, but the conversion over PMAH increased from 3PMAH-2 to 30PMAH. 30PMAH showed a 91.7% conversion at 523 K which was about two times greater than the conversion of 15PMA (47.1%). This result is important for the availability of recovery the waste heat from factories by methanol decomposition.

A TEM image confirmed that Pd particles located on the Mg(Al)O crystallites were dispersed on the surface of HMS in the 3PMAH-1 catalyst. The average Pd particle size measured from TEM images were in agreement with the results of the CO absorption measurement. The PMAH catalysts showed a larger BET surface area and smaller Pd particles than those of the PMA catalysts, which caused the high activity over the PMAH catalyst. Moreover, the relatively small Pd particles were obtained in the PMAH catalyst even with high Pd loading due to the high surface area. This is the reason why the conversion of methanol decomposition increased with the increase in the Pd amount even for the designed Pd loading of up to 30 wt% for the PMAH catalyst.

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