RESEARCH ARTICLE

A study on the catalytic performance of Pd/γ-Al₂O₃, prepared by microwave calcination, in the direct synthesis of dimethylether

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Abstract   A series of Pd/γ-Al₂O₃ hybrid catalysts were prepared by impregnation and subsequent calcination under microwave irradiation. The catalysts were used for direct synthesis of dimethylether (DME) from syngas. The results show that calcination under microwave irradiation improved both the activity and selectivity of the catalysts for DME synthesis. The optimum power of the microwave was determined to be 420 W. Under such optimum conditions, CO conversion, DME selectivity and time space yield of DME were 60.1%, 67.0%, and 21.5 mmol·mL⁻¹·h⁻¹, respectively. Based on various characterizations such as nitrogen physisorption, X-ray diffraction, CO-temperature-programmed desorption, and Fourier transform infrared spectral analysis, the promotional effect of the microwave irradiation on the catalytic property was mainly attributed to both the higher dispersion of Pd and the significant increase in the adsorption on the CO-bridge of Pd. Microwave irradiation with very high power led to the increase in CO-bridge adsorption and thereby decreased the catalytic activity, whereas the coverage by metallic Pd of the active sites on acidic γ-Al₂O₃ significantly occurred under microwave irradiation with very low power, resulting in a decrease in the selectivity to DME.

Keywords   Pd/γ-Al₂O₃, direct synthesis, dimethyl ether, calcination under microwave irradiation

1   Introduction

Interest in hydrogen production for fuel cell applications is

steadily increasing due to environmental concerns [1]. Among the various feed gases, dimethyl ether (DME) has proven to be a good alternative fuel to minimize the emissions of global warming gases and hazardous components such as SO$_x$, NO$_x$ and particulate matter, because DME is similar in nature to liquefied petroleum gas [2]. In addition, DME is an important chemical intermediate for the production of chemicals such as ethylene, dimethyl sulfate, polishing agents, anti-rust agents, aerosol freezing agents, and alkylation agents [3]. Therefore, the production and utilization of DME has attracted ever-increasing attention.

Recently, direct synthesis of DME from syngas has received ever-increasing attention due to its higher conversion and lower cost in comparison to methanol dehydration [4]. Direct conversion of syngas to DME requires hybrid catalysts with two kinds of active sites - one for methanol formation and the other for methanol dehydration [5–7].

The synthesis of DME from coal via some new processing schemes like the integrated gasification combined cycle (IGCC) is currently attracting great attention. However, syngas from IGCC still contains at least 40 ppm sulfur even after desulfurization by acidic gas-removal technologies, while commonly used Cu/ZnO/Al₂O₃ catalysts for methanol synthesis cannot tolerate more than 0.1 ppm H₂S [8]. Pd catalysts retain up to 40% of their activity in the presence of sulfur [9,10], because Pd sulfides are catalytically active in the selective hydrogenation of CO to alcohols. Therefore, using Pd catalysts in methanol synthesis has become an important research topic.

The performance of a catalyst in terms of its activity, selectivity, and stability is significantly affected by the content and distribution of active species (e.g., metallic species), particle size, dispersion and surface structure [4–

7]; these properties are in turn related more or less to the roasting method and conditions for the catalyst preparation.

In this investigation, we focus on the effect of microwave-irradiated calcination on the performance of Pd/γ-Al$_2$O$_3$ hybrid catalysts for direct synthesis of DME from syngas.

2 Experiment

2.1 Catalyst preparation

PdCl$_2$ (18.8 mL, 0.02 mol·L^{-1} aqueous solution) was impregnated into 4 g of γ-Al$_2$O$_3$ in a 150 mL flask at 50°C for 2 h. The suspension was heated to 80°C and vigorously stirred at this temperature until most of the water was removed by evaporation, followed by calcination in a muffle at 300°C or 500°C for 5 h, or in a microwave oven with a pre-set power between 280 W and 700 W for 1 h. MWI$_p$ (MWI and p denote microwave irradiation and calcination power, respectively) and M_T (M and T denote muffle and calcination temperature, respectively) are used to indicate calcination conditions.

2.2 Catalyst characterizations

The surface area was measured with the BET method by N$_2$ physisorption in an AS1V150 adsorption apparatus. Powder X-ray diffraction (XRD) patterns were determined at room temperature in air with a Bruker D8 Advance X-ray diffractometer using CuKα radiation (0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA. The CO desorption tests were conducted with the method of CO-temperature-programmed desorption (CO-TPD). Before the tests, the samples were treated at 500°C for 30 min under nitrogen flow. Desorbed gases were analyzed with a GC 508 gas chromatography. Surface acidities of the catalysts were detected with a Nicolet IR-380 Fourier transform infrared (FTIR) spectrometer. Before the detection, each catalyst was placed in a disk and pressurized in the disk, followed by heating in vacuum at 300°C for 2 h then cooling to room temperature. During the detection, pyridine gas was charged into the disk at 150°C for 0.5 h and then vacuumed for 0.5 h.

2.3 Catalytic test

The synthesis of DME from syngas was carried out under gas phase in a WSFM-3060 pressurized fixed-bed microreactor, using a reaction tube with 5 mm inner diameter. About 0.5 g of a catalyst was loaded into the tube and placed between two quartz wool plugs. The catalyst was heated to 220°C under hydrogen flow at 1°C·min^{-1} and the temperature was maintained for 2 h. Then H$_2$ and CO, with a volume ratio of 2 : 1 and airspeed 1600 L·kg^{-1}·h^{-1} were introduced through a mass flow controller by slowly raising pressure to 3 MPa and temperature to 300°C to initiate the reaction. The reaction mixture was introduced to the gas chromatography for analysis through a pressure release valve.

3 Results and discussion

3.1 Surface properties of the catalysts

As Table 1 lists, in comparison with corresponding surface parameters of the catalysts prepared under MWI, the specific surface area and mesopore volume ratio of the catalyst prepared by calcination in the muffle are significantly lower, whereas mean pore size and total pore volume are obviously higher. The much higher uniformity in thermal conduction during calicination under MWI compared to that in the muffle could be the main reason for the result. As for the catalysts prepared under MWI, the mean pore diameter monotonously decreased with an increase in calcination power, but at 420 W both specific surface area and total pore volume reached a minimum, whereas mesopore volume ratio reached maximum.

3.2 State of Pd particles in the catalysts

Metal dispersion on the carrier is an important surface property of a catalyst. Such a property significantly depends on the method of catalyst preparation and may have a significant impact on catalyst performance. As listed in Table 2, in comparison with the catalysts prepared by calcination in the muffle, calcination under MWI remarkably improved Pd dispersity and reduced the mean

Table 1 Specific surface area, pore volume, and mean pore diameter of the catalysts

calcination conditions	specific surface area/(m^2·g^{-1})	mean pore diameter/nm	total pore volume/(cm^3·g^{-1})	mesopore volume ratio/%
M$_{500}$	285.5	5.401	0.3855	27.3
MWI$_{700}$	305.9	4.507	0.3548	34.3
MWI$_{560}$	304.7	4.589	0.3522	35.6
MWI$_{420}$	301.2	4.595	0.3515	37.2
MWI$_{280}$	303.8	4.769	0.3532	35.3

Table 2 Dispersion and mean diameter of Pd particles in the catalysts

calcination conditions	Pd dispersity/%	mean diameter of Pd particles/nm
M_{300}	14.65	7.31
M_{500}	14.25	7.55
MWI_{700}	17.86	6.16
MWI_{560}	17.59	6.25
MWI_{420}	18.41	5.98
MWI_{280}	18.77	5.49

diameter of Pd particles, which is also related to the much higher uniformity in thermal conduction during calicination under MWI than that in the muffle. It is noteworthy that reducing both calcination temperature (from 500°C to 300°C) and power (from 560 W and 700 W to 280 W and 420 W) substantially increased Pd dispersity and reduced the mean diameter of Pd particles in the catalysts, indicating that mild conditions are favorable for making Pd highly disperse in the catalysts.

3.3   XRD patterns of the catalysts

Almost similar intensities of 5 typical diffraction peaks at 27.6°, 37.7°, 48.2°, 65.8° and 72.2°, which resulted from the γ-Al_2O_3 phase [11], can be seen for all the catalysts in Fig. 1, implying that the calcinations both in the muffle and under MWI did not destroy the crystal structure of γ-Al_2O_3. The 2 diffraction peaks at 39.5° and 46.4° correspond to the typical diffraction 111 and 200 crystal planes in the PdO phase [12]. Both those from the catalyst prepared by calcination in the muffle are much higher and sharper than those from the catalyst prepared by calcination under MWI, and the intensities of both peaks tend to decrease at lower calcination temperatures under MWI. More severe Pd oxidation and, subsequently, more severe PdO sintering at higher temperatures could be responsible for the result. In other words, catalyst preparation under

mild conditions can reduce Pd oxidation and PdO sintering and thereby increase Pd dispersity in the catalysts.

3.4   CO adsorption of the catalysts

In Fig. 2 the peaks around 180°C and 490°C account for the linear and bridge adsorptions, respectively, of CO on Pd [13]. The peaks around 490°C attributed to CO desorption from bridge adsorption on Pd in the catalysts prepared by calcination under MWI are significantly higher than that in the catalyst prepared by calcination in the muffle, suggesting that a much larger amount of CO was adsorbed on the catalysts prepared by calcination under MWI than on the catalyst prepared by calcination in the muffle. In addition, the peaks attributed to CO desorption from the catalysts prepared by calcination under MWI at lower power appeared at higher temperatures, which are ascribed to higher desorption energy [14,15]. This result implies that milder conditions are favorable for preparing Pd-containing catalysts in which CO more strongly adsorbs on Pd in the form of bridge adsorption.

3.5   Surface acidity of the catalysts

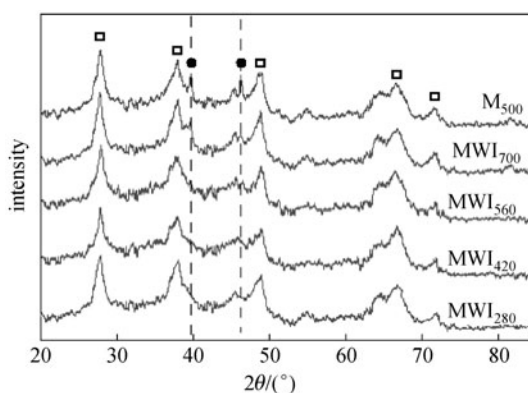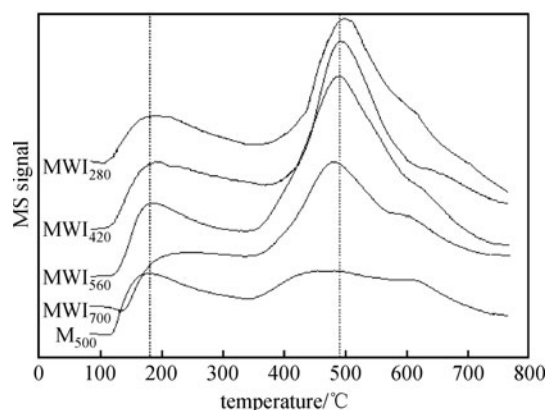Pyridine is a typical probe molecule for determining

Fig. 1 XRD patterns of the catalysts prepared under different conditions

Fig. 2 CO-TPD curves of the catalysts prepared under different conditions

Table 3 Catalytic performance of the catalysts[a)]

calcination conditions	CO conversion/%	selectivity/%			time space yield of DME/ $(mmol \cdot mL^{-1} \cdot h^{-1})$
		CO$_2$	CH$_3$OH	DME	
M$_{300}$	23.6	30.3	13.3	56.4	7.13
M$_{500}$	27.5	28.8	10.9	60.3	8.88
MWI$_{700}$	54.8	18.9	18.7	62.4	18.3
MWI$_{560}$	58.4	13.9	19.5	66.6	20.8
MWI$_{420}$	60.1	16.5	18.6	67.0	21.5
MWI$_{280}$	59.4	16.8	19.4	63.8	19.3

a) 300°C, 3 MPa, GHSV = 1600 L·kg^{-1}·h^{-1}, V_{H_2}/V_{CO} = 2.0

Lewis and Brönsted acid sites on a catalyst surface. Its ring-stretching vibrations can be classified into a coordinative bond to Lewis acid sites on the P-L bands at 1440 – 1460 cm^{-1} and pyridinium ion on Brönsted acid sites (PH$^+$-B band at 1540 cm^{-1}). The amount of Lewis and Brönsted acid sites can be compared by the intensities of the peak area in the P-L and PH$^+$-B bands [16]. As Fig. 3 demonstrates, no absorbance band at 1540 cm^{-1} was observed for any catalyst and the intensity in the absorbance band at 1450 cm^{-1} for the catalysts prepared under different conditions increases in the order: MWI$_{280}$ < MWI$_{420}$ = MWI$_{560}$ < MWI$_{700}$ < M$_{500}$, indicating that only Lewis acid sites are present in the catalysts and the catalysts prepared under more severe calcination conditions have larger amounts of Lewis acid sites.

3.6 Catalytic performance

As summarized in Table 3, the catalysts prepared by calcination under MWI have much higher activity for CO conversion, much higher selectivity to methanol, much higher time space yield of DME and appreciably higher selectivity to DME. Taking CO conversion, DME selectivity and time space yield of DME into account, MWI$_{420}$ should be optimum conditions for calcination during the catalyst preparation. According to data from the catalyst characterizations mentioned above, the good catalytic performance of the catalyst prepared by calcination under MWI$_{420}$ should be closely related to higher mesopore volume ratio and Pd dispersity, stronger CO adsorption and moderate surface acidity of the catalyst.

4 Conclusions

The physicochemical properties and catalytic performance of a series of Pd/γ-Al$_2$O$_3$ catalysts prepared under different conditions were investigated. The catalysts prepared by calcination under MWI showed much better catalytic performance than those prepared by calcination in a muffle in terms of CO conversion, methanol and DME selectivities, and time space yield of DME, which are closely
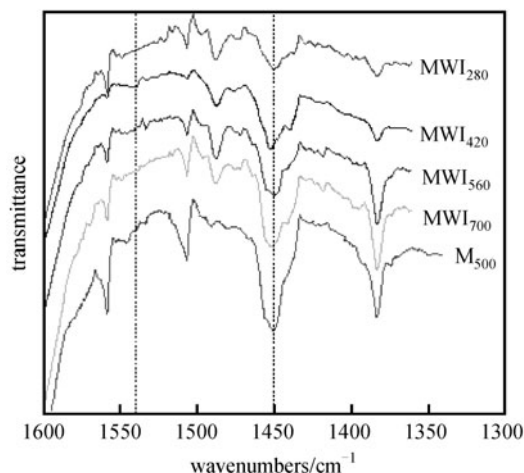

Fig. 3 FIIR spectra of the catalysts prepared under different conditions

related to mesopore volume ratio, Pd dispersity, and CO adsorption strength on the catalysts. MWI$_{420}$ proves to be optimum calcination conditions for the catalyst preparation.

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