SYNTHESIS, ADSORPTION ABILITY AND ACTIVITY OF MOF-199 IN THE REACTION OF METHANOL SYNTHESIS FROM CARBON OXIDES

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Abstract

Metal-organic framework (MOF) is a material which can be applied in many fields. In this research MOF-199 was synthesized using solvothermal method. Based on this product, ZnO@MOF-199 and Cu,ZnO@MOF-199 were synthesized and their properties were characterized. The adsorption capacity of CO_2 and CH_4 on MOF-199 were investigated and results show that adsorption capacity of CO_2 is higher than that of CH_4 at 30 bar and 30 $^{\circ}$C, reaching 277.25 cm^3/g and 170.38 cm^3/g, respectively. The catalytic activity of MOF-199, Cu,ZnO@MOF-199 and ZnO@MOF-199 were also tested for methanol production from synthesis gas at atmospheric pressure and 200 $^{\circ}$C. Methanol yield after 1 h for MOF-199 and Cu,ZnO@MOF-199 reached 157.9 and 27.63 $\mu mol.g_{cat}^{-1}.h^{-1}$, respectively. Meanwhile, the methanol yield for catalyst ZnO@MOF-199 is not significant. However, the structure of MOF-199 collapsed after 60 minutes of reaction.

Keywords: Adsorption, Methanol synthesis, MOF-199, Synthesis gas

Introduction

Recently, Metal-organic framework (MOF) materials were studied and many kinds of MOFs were improved to apply into many fields, especially in catalysis application [1-3]. MOFs have very high porosity and special surface up to thousands m^2/g, their particle size is varied in range of submicrometer to micrometer. Another application of MOFs is gas storage, this property can be applied into green energy, separation techniques or environmental engineering [4-5].

Fuel cells are now developing very fast as shown in many researches, and the gas storage capacity is very important property for this application. High adsorption capacity of MOFs for H_2 and CH_4 is applied in green energy, while their large adsorption capacity for CO_2 is applied in environmental protection. Rosi *et al.* measured H_2 adsorption in MOF-5, IRMOF-6 and IRMOF-8, and showed that MOFs have much larger capacity for H_2 storage than traditional zeolites and activated carbon [6]. Besides, CO_2 can be adsorbed on MOFs up to 40 mmol/g at high pressure without changing in its structure [7]. Millward *et al.* has studied the adsorption capacity of CO_2 on 9 different kinds of MOFs and results showed the minimum adsorption capacity is MOF-2 (3.2 mmol/g) and maximum is MOF-177 (33.5 mmol/g) at room temperature and pressure of 42 bar [8]. Other studies on adsorption capacity of CH_4 on CPO-27 showed result of 129 cm^3/g at room temperature and 34 bar [9] and 1.1 mmol/g at 1 bar with UiO-66 as adsorbent [10].

MOFs also can be applied as catalysts for many other reactions such as isomerization of α-pinene oxide [11], Knoevenagel condensation and cyanosilation reaction [12]. Not only using as catalyst, MOFs are also used as a catalyst carrier such as Pd@MOF-5 for

ethylbenzene hydrogenation [13], Cu@MOF-5 and Cu,ZnO@MOF-5 for the methanol synthesis from CO and H_2 [14]. MOF-199 (HKUST-1) has opened and nonsaturated coordination centers of Cu(II) that can be considered as Lewis acid centers [11].

In this study, MOF-199 is synthesized by solvothermal method. The gas (CO_2 and CH_4) storage capacity was investigated and catalyst activities of MOF-199 and its derivative compounds in hydrogenation reaction of carbon oxides to produce methanol were also studied.

Experimental

MOF-199 was synthesized with the same method that was reported in our previous study [15]. Product was used for synthesis of ZnO@MOF-199 and Cu,ZnO@MOF-199 catalysts. ZnO@MOF-199 was synthesized by metal organic chemical vapor deposition (CVD) method which described by Müller *et al.* [14] as follows: 100 mg MOF-199 powder was placed into a chamber of 1 mL of precursors $Zn(C_2H_5)_2$ under vacuum condition at 25 ^oC for 1 h. $Zn(C_2H_5)_2$@MOF-199 then was treated with oxygen (6 vol.%, 1 cm^3/s) at 25 ^oC for 2 h. The product after that was activated in vacuum at 200 ^oC for 4 h to produce ZnO@MOF-199. The Cu,ZnO@MOF-199 catalyst has been prepared by the metal organic chemical vapour deposition method with the volatile precursors $CpCu(PMe_3)$ (cyclopentadienyl trimethylphosphine copper) and $Zn(C_2H_5)_2$ (diethylzinc) in a two step process. In the first step, ZnO@MOF-199 was prepared according to the above procedure. In the second step, 100 mg of ZnO@MOF-199 powder was placed into a chamber of 100 mg of precursors $CpCu(PMe_3)$ in vacuum at 73 ^oC for 5 h. Alternatively, sample of $CpCu(PMe_3)$,ZnO@MOF-199 was treated with hydrogen (100 vol.%, 1 cm^3/s) at 220 ^oC for 5 h. After hydrogenolysis, the product was activated under vacuum condition at 200 ^oC for 4 h to obtain Cu,ZnO@MOF-199 catalyst.

To investigate the morphologies of the materials, scanning electron microscope (SEM, JEOL 7401), X-ray diffraction (XRD, Bruker D8), Elemental analysis (Shimadzu AAS – 6800) were used. Characteristics of the reduction of catalysts were investigated by the method of temperature-programmed reduction (TPR) on the apparatus Altamira Instruments – AMI 200 where firstly the samples were passed a preliminary treatment in nitrogen stream 2 h at 200 ^oC. The TPR process was carried out in a stream of nitrogen, containing 5 vol.% of hydrogen and the speed of linear temperature was rised from room temperature to 700 ^oC with the ratio of 10 ^oC/min.

CO_2 and CH_4 were used to test the adsorption capacity of MOF-199 at pressure from 1 to 30 bar and 30 ^oC using a high pressure volumetric analyzer (Micromeritics HPVA –100). Activity of the catalysts in the methanol synthesis reaction from the hydrogenation of CO were investigated in a microflow reactor at atmospheric pressure, at 200 ^oC and the flow rate of 4 L/h, where the mass of catalyst is 0.5 g and the concentration of CO was 6 vol.%. The mole ratio H_2 : CO is 50. The reactants and products mixture were analyzed using the Gas-chromatograph Agilent 6890 Plus GC, with flame ionization detector (FID) and capillary column DB-624 (30 m of length, 0.32 mm of outer diameter, 0.25 μm of thickness) and a thermal conductivity detector (TCD), capillary column HP-PLOT MoleSieve 5A (30 m of length, 0.32 mm of outer diameter and 12 μm of thickness).

Results and Discussion

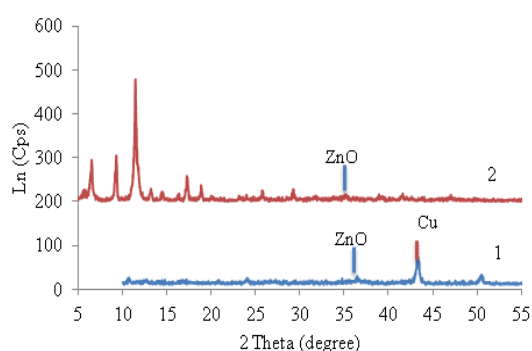### Characteristics of ZnO@MOF-199 and Cu, ZnO@MOF-199 Catalysts

In our previous study [15], MOF-199 was synthesized and investigated. The octahedral shape and 3D structure of crystalline of MOF-199 was obtained. The synthesized MOF-

199 has the following characteristics: high value of specific surface area (1448 m^2/g by BET method and 2028 m^2/g by Langmuir method) with the pore size of crystal 11.8 Å, the specific volume 0.693 cm^3/g. It has been mentioned in the experimental.

Table 1. The Content of Cu and Zn in Catalyst according to AAS Analysis

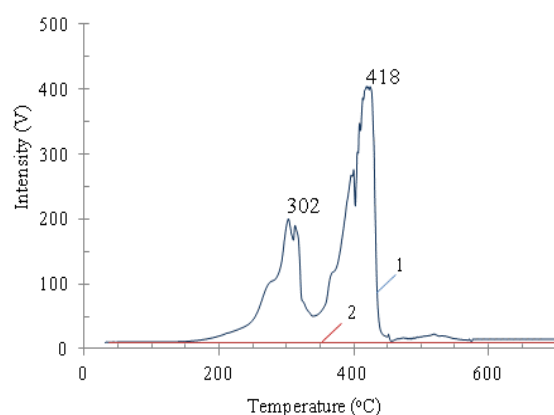| Sample	MOF-199	ZnO@MOF-199	Cu,ZnO@MOF-199
Cu content (wt%)	20.7	20.7	29.8
Zn content (wt%)	-	5.31	5.31

Atomic absorption spectrophotometry (AAS) was used to analyze the elemental content of copper and zinc in ZnO@MOF-199 and Cu,ZnO@MOF-199 samples. As it follows from Table 1, the content of Cu and Zn determined by AAS method approximate to loaded amount.
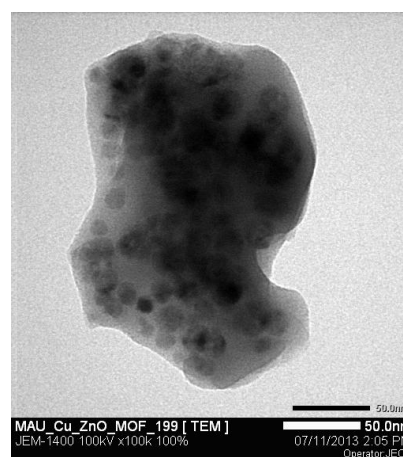

a) XRD pattern of Cu,ZnO@MOF-199 (1) and ZnO@MOF-199 (2) catalysts
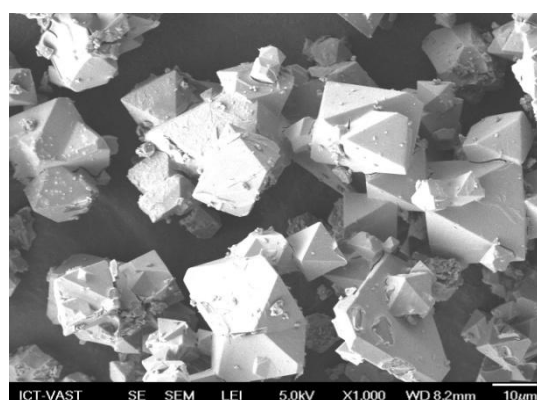
b) SEM imagine of ZnO@MOF-199 catalyst

c) TPR spectra of MOF-199 (1) and ZnO@MOF-199 (2) catalysts

d) TEM images of Cu,ZnO@MOF-199 catalyst

Figure 1. Characteristics of catalysts

The XRD pattern of sample ZnO@MOF-199 (Figure 1a, line 2) comprises the characteristic peak of MOF-199 at 2θ = 11.6°. The results show that observed peak is very sharp, that indicates the loading MOF-199 with ZnO does not affect the MOF-199

structure. In addition, SEM images (Figure 1b) show that the crystal particles of ZnO@MOF-199 still remain in octahedral shape indicating an intact host matrix after loading the sample with zinc oxide. Additionally, new reflections appear at $2\theta = 36.15^{o}$, corresponding to the incorporated ZnO. The similar results were found in the other researches [16, 17]. In the XRD spectra of Cu,ZnO@MOF-199 (Figure 1a, line 1) there are some peaks at $2\theta = 36.15^{o}$ and $2\theta = 43.34^{o}$, corresponding to the incorporated ZnO and the incorporated copper, respectively [18], but characteristic peaks of MOF-199 are not shown. This can be explained that the surface of MOF-199 was collapsed by Cu and ZnO addition. Besides, the appearance of characteristic peaks of crystalline ZnO on XRD spectra of two samples (ZnO@MOF-199 and Cu,ZnO@MOF-199) and Cu in the XRD spectrum of Cu,ZnO@ MOF-199 demonstrated that doped ZnO and Cu exist in the crystalline phase on the surface of the carrier. This is proved by the TEM image of sample Cu,ZnO@MOF-199 (Figure 1d). TEM images clearly showed copper nanoparticles in a size range of 8 – 9 nm as darker spots and ZnO nanoparticles in a size of 5 – 6 nm as grey spots. This is similar to the TEM images of binary Cu/ZnO catalyst that was obtained by Malte Behren [19].

The TPR diagram of MOF-199 (Figure 1c, line 1) comprises two main reduction peaks at $T_{max} = 302$ ^{o}C and $T_{max} = 418$ ^{o}C. According to Lenarda et al [20], CuO buck shows one reduction peak at 400 ^{o}C due to complete reduction of Cu^{2+} to Cu^{o}. Wei-Ping Dow [21] reported that for the CuO/Al_2O_3 catalyst, a peak with a maximum at 210 ^{o}C is created due to the reduction of the highly dispersed copper oxide species and the reduction peak with $T_{max} > 250$ ^{o}C has been ascribed to the reduction of bulk-like CuO phases. Therefore, it can be suggested that the peak at $T_{max} = 302$ ^{o}C on TPR diagram of the MOF-199 sample characterizes the reduction of Cu^{2+} on the surface of Cu-BTC sites, while the second one characterizes the reduction of Cu^{2+} inside of the octahedral sites. On TPR diagram of the ZnO@MOF-199 sample (Figure 1c), the reduction peaks of Cu^{2+} in both regions 180 ^{o}C ÷ 342 ^{o}C and 342 ^{o}C ÷ 450 ^{o}C are not observed. The sample was destroyed at 700 ^{o}C without the reduction. The reason no reduction peak appeared for copper ions could be explained by the fact that, although the addition of ZnO did not lead to any changes in the structure of MOF-199, it covered all Cu^{2+} nodes of MOF-199, so Cu^{2+} could not contact with hydrogen to be reduced.

The Storage Capacity CO₂ and CH₄ on MOF-199

Our previous results [15] show the pore size of MOF-199 is 11.8 Å, which is much larger than that of the kinetic diameter of CO_2 (3.3 Å) and CH_4 (3.8 Å) [22], hence the adsorption of these gases into the pores of the MOF-199 will not be hampered. The adsorption isotherms of CH_4 and CO_2 on MOF-199 at 30 ^{o}C and pressure from 0 to 30 bar are shown in Figure 2.
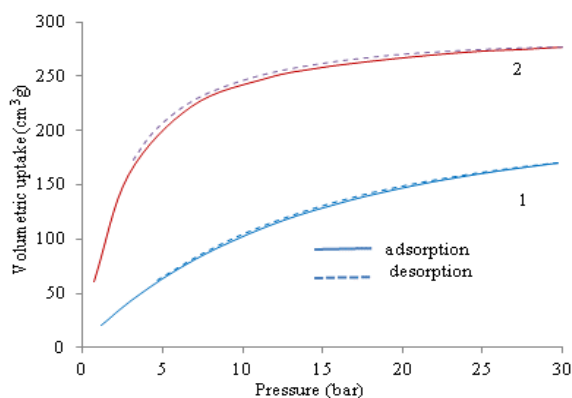

Figure 2. Adsorption and desorption isotherms of CH4 (1), CO2 (2)
on MOF-199 at 30 oC

Results show that the adsorption capacity of gas on MOF-199 is increased with the increasing of pressure. At 30 bar and 30 °C, the volume of CO_2 adsorption is higher than that of CH_4, reaching 277.25 cm^3 (STP)/g and 170.38 cm^3 (STP)/g, respectively. Higher adsorption of CO_2 compared to CH_4 could be explained by a high quadrupole moment of CO_2 (13.4 x 10^{-40} $C.m^2$), whereas CH_4 is a nonpolar molecule [23]. Consequently, CO_2 interacts stronger with the framework.

The reusability of MOF-199 in adsorption process was also tested and showed in Table 2. From the data of Table 2, it follows that the adsorption capacity of CO_2 and CH_4 on MOF-199 are nearly unchanged after 10 cycles of adsorption. At the pressure of 30 bar, the average adsorbed amount of CO_2 and CH_4 after 10 cycles on MOF-199 are 272.6 cm^3/g and 168.53 cm^3/g (decreased about 1.67 % and 1.1% compare to the 1st adsorption, respectively), indicating that the crystal structure of MOF-199 was not changed. Besides, the coincidences of the adsorption and desorption isotherms of CO_2, CH_4 indicatēs that the adsorption of CO_2 and CH_4 on MOF-199 are reversible.

Table 2. Volume Uptake of CO_2 and CH_4 on MOF-199 in 10 Cycles (From 1 to 10) of Adsorption

Gas	Pressure (bar)	Cycles of adsorption (cm^3/g)										Mean error (%)
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	
	1	86	83	82	84	87	86	86	83	89	83	2.2
	14	250	255	248	249	251	256	250	249	246	249	0.9
CO_2	30	272	278									0.9
	1											3.3
	14	129	122	127	125	121	119	122	124	122	121	2.2
	30	172	163	176	172	165	163	166	172	167	165	2.4

The Activity of Catalysts in Hydrogenation Reaction of CO to Produce Methanol

The methanol yield for 60 minutes reaction using MOF-199 catalyst is 157.9 $\mu mol.g_{cat}^{-1}.h^{-1}$. According to the results in previous references [24-28], the copper catalysts without modification by ZnO could not be active for methanol synthesis reaction. While in this study MOF-199 can be used as a catalyst for this reaction because of the presence of open centers of Cu^{2+} in catalyst.

Loading of Cu and ZnO on MOF-199 are supposed to reveal high activity for methanol synthesis reaction. However, the result showed that methanol yield of ZnO@MOF-199 catalyst is not significant. This could be explained that addition of ZnO led to cover of all Cu centres in MOF-199 structure, as shown by TPR (Figure 1c) and XRD spectra (Figure 1a) that decreased the activity of catalyst. However, the addition of both Cu and ZnO led to appearance of activity for methanol synthesis from synthesis gas again, although the methanol's yield of Cu,ZnO@MOF-199 catalyst (27.63 $\mu mol. g_{cat} h^{-1}$) is about 5.7 times lower than that of MOF-199. Thus, from the obtained results it is possible to propose that in this case, well-dispersed Cu and ZnO clusters on the catalyst surface, as seen in TEM images (Figure 1d), are recognized as active centers.

The methanol yield of MOF-199 was shown to be higher than that of Cu@MOF-5 [14] and Cu,ZnO@MCM-48 [25] but lower than that of the Cu,ZnO@MOF-5 [14] and Cu,ZnO/Al_2O_3 samples [24]. These results confirmed that opened centers Cu^{2+} in MOF-199 are mainly active centers in the reaction of synthesis of methanol, which is the special

property of MOF-199. However, the biggest drawback of MOF-199 in this reaction is low thermal stability, resulting in the short lifetime of catalyst and the structure of MOF-199 is totally collapsed after 60 minutes, as shown in XRD pattern of MOF-199 after reaction (Figure 3).
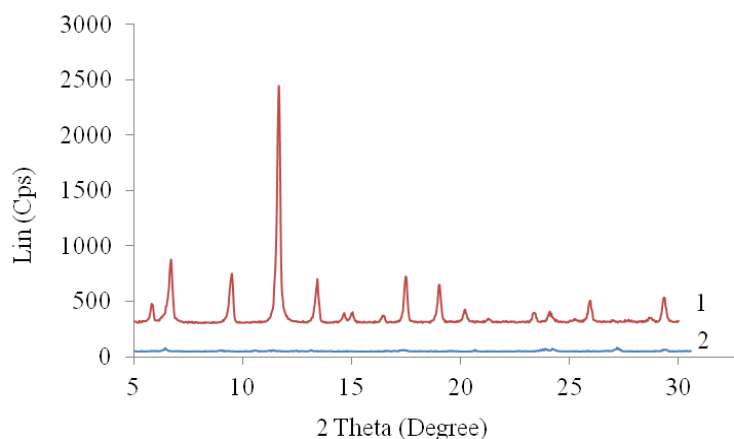

Figure 3. The powder XRD pattern of MOF -199 (1) and MOF-199 after reaction (2)

Conclusions

The synthesized MOF-199 reveals high adsorption capacity of CO_2 and CH_4 at high pressure (up to 30 bar). At 30 bar and 30 ^{o}C, the volume of CO_2 adsorption is higher than that of CH_4, reaching 277.25 cm^3/g and 170.38 cm^3/g, respectively. Unchanged structure of MOF-199 under high-pressure adsorption process and reversible adsorption of CO_2 and CH_4 allow MOF-199 to be reused many times.

MOF-199 exhibited activity in methanol synthesis from synthesis gas, while ZnO@MOF-199 and Cu,ZnO@MOF-199 catalysts have lower activity on this reaction. However, it is active in investigated conditions for about 60 minutes, after that the structure of MOF-199 will be collapsed.

Acknowledgements

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