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Short Communication

Bimetal modified ordered mesoporous carbon as a support of Rh catalyst for ethanol synthesis from syngas

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ABSTRACT

Ordered mesoporous carbons (OMCs) containing highly dispersed iron and manganese bimetal particles have been synthesized by an organic–organic self-assembly method. The characterization results showed that the ordered mesostructure of carbons still remained after the incorporation of bimetal particles into the carbon matrix. These materials were used as supports of Rh based catalysts for ethanol synthesis from CO hydrogenation reaction. The catalysts supported on the metal modified OMC exhibited much better activity and selectivity than that supported on the OMC without modified metal particles and conventional catalysts supported on silica.

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1. Introduction

Ordered mesoporous carbons (OMCs) have stimulated extensive interest due to their specific properties. Among them, the metal modified ordered mesoporous carbons (MMOMCs) have been thoroughly studied owing to their various applications such as catalysts [1], separations [2], and fuel cell [3]. There are mainly two routes for introducing the metal nanoparticles into the mesoporous carbon matrix. One method is called hard template. The main steps are as follows: firstly, dispersing the desired metal into the pore wall of silica then filling mesopore of silica with appropriate carbon source, followed by carbonization and removal of silica template [4–7]. Another way is simple, and highly effective to incorporate the metal species into the mesoporous carbon wall. This approach involves introduction of the metal precursor into the reaction mixture composed of a surfactant and an oligomer of phenolic resin. The metal particles will be dispersed throughout the mesoporous carbon framework after removal of surfactant and carbonation. Through this route, the MMOMCs containing TiC [8], MoC [9], Ir [10], and Fe [11] nanoparticles have been synthesized recently.

As a green, sustainable fuel additive, ethanol is attracting more and more attention in recent years. Currently, ethanol is produced primarily by fermentation of sugars and hydration of petroleumbased ethylene [12]. Owing to rising prices of crude oil and global foodstuff crisis, the two processes become unattractive for large scale production of ethanol. The conversion of syngas (a mixture of CO and H₂) reformed from coal, natural gas, and biomass may be a promising alternative route for the ethanol production. After extensive research efforts in the last decades, it was found that the Rh based catalysts promoted by Fe [13-15], Mn [16-18], and bimetal [19–21] exhibited accessible activity and selectivity for the ethanol synthesis from syngas. CO hydrogenation over Rh based catalyst is very sensitive to the structure of active Rh sites and CO conversion and oxygenates selectivities vary as a function of Rh particle size [22-24]. Sugi and coworkers [25] pointed out the optimum particle size of Rh cluster for C2 oxygenates synthesis was about 3-4 nm. Bao et al. found that the ethanol production was enhanced greatly when the active metal nanoparticles were confined inside carbon nanotubes (CNTs) [26]. They also investigated the carrier effects of different carbonaceous materials and suggested that the synergetic effect of nanochannels and graphitic-like structure might also greatly affect the activity and selectivity [27]. This synergetic confinement effect related to CNTs may be applied to the MMOMCs because they both have something in common such as uniform pore size, and similar graphitic structure of carbon [28,29].

Although the MMOMCs containing many different metal nanoparticles have been synthesized, the metals embedded into the mesoporous carbon matrix reported before are all single metal, almost no bimetals or trimetals. Therefore, it is a challenge to incorporate two or more metals into the mesoporous carbon and find their

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applications in some fields. Herein, we will report for the first time a facile method to synthesize highly ordered mesoporous carbon modified by Mn and Fe bimetal under an acidic medium, and then explore their catalytic properties as a support of Rh catalyst for ethanol synthesis from syngas.

2. Experimental section

2.1. Preparation of catalysts

The detailed steps of bimetal modified OMC synthesis route demonstrate as follows: 12.5 g F127 (Triblock poly (ethylene oxide)-bpoly (propylene oxide)-b-poly (ethylene oxide) copolymer Pluronic F127) and 16.5 g resorcinol were together dissolved in a 100 g mixture of water/ethanol (50/50 vol.%) under stirring at room temperature, then 7.5 g hydrated manganese nitrate $(Mn(NO_3)_2 \cdot 4H_2O)$ and 1.5 g hydrated iron nitrate (Fe(NO₃)₃·9H₂O) were added into the mixture. When a uniform solution formed after about half an hour continuous stirring, 12.5 g formaldehyde (37 wt.%) was dropped into the solution in 30 min. After adjusting the pH value to 0.8 and 1.0 using HCl (37 wt.%), the mixture was kept standing until it began to separate into two layers. Further aging for 60 h, the upper layer was discarded. The lower layer was mechanically stirred overnight and the formed material was further thermal polymerized at 100 °C for 48 h. Finally, the template agent was decomposed at 350 °C for 3 h and the phenolic resin was carbonized at 850 °C for 3 h under an argon atmosphere. The resulted composite was designated as MnFeOMC. For comparison, some single metal modified OMCs and a pure OMC were synthesized by the same method and designated as MnOMC, FeOMC and OMC respectively.

The catalysts were prepared by impregnation method with ethanol solution of the precursor. The detailed steps are as follows: The Rh loading of all the catalysts was 2.0 wt.%. The MnFeOMC sample was impregnated with RhCl₃ solution. The MnOMC support was impregnated with RhCl₃ solution and different amounts of FeCl₃ solution to explore the optimum Fe loading on the RhFe/MnOMC catalysts. The same method was used to optimize the Mn loading on the RhMn/ FeOMC catalysts. Besides RhCl₃ solution, the OMC support was impregnated with Mn and Fe solution with their optimum loading. The impregnated catalysts were further dried at 120 °C overnight. The catalysts were separately denoted as Rh/MnFeOMC, RhFe/ MnOMC, RhMn/FeOMC and RhMnFe/OMC.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm), operated at 40 kV and 150 mA. Transmission electron microscopy (TEM) images were taken on a JEOL2000 EX electronic microscope with an accelerating voltage of 120 kV, while high resolution transmission electron microscopy (HRTEM) was performed on a Tecnai G² F30 S-Twin transmission electron microscopy operating at 300 kV. N₂ adsorption–desorption isotherms were measured by a Micromeritics ASAP-2010 at 77 K. TPR and CO chemisorption experiments were performed on a Micromeritics Autochem 2910 apparatus. The metal contents were determined by inductively coupled plasma (ICP) on an IRIS Intrepid II XPS instrument. Before ICP measurements, the samples were calcined at 600 °C for 6 h, then dissolved by nitric acid.

2.3. Catalytic activation and test

CO hydrogenation was carried out in a fixed bed micro-reactor under 573 K, 5.0 MPa (H_2 /CO=2) and GHSV=12,000 h⁻¹. Before the reaction, the catalysts were reduced in situ in a pure H_2 flow at 623 K for 1.5 h. The effluent passed through a condenser and

subsequently analyzed on-line by Agilent 3000A Micro GC with TCD detector. The produced oxygenates completely dissolved in deionized water were analyzed off-line by Varian 3800 GC with FID detector, using n-pentanol as an internal standard. The syngas conversion and product selectivity were calculated according to the following equations:

$$\text{CO conversion} \ [\%] = \frac{\sum n_i M_i}{M_{\text{CO}}} \times 100, \text{Selectivity} \ [\%] = \frac{n_i M_i}{\sum n_i M_i} \times 100$$

where n_i is the number of carbon atoms in product i, M_i is the total mole number of product i during a certain reaction time, and M_{CO} is the total mole number of carbon monoxide in the feed during a certain reaction time.

3. Results and discussion

3.1. Characterization

In the low-angle XRD spectra (Fig. 1 insets), the diffraction peak at 2θ range of 0.5–1° can be observed from the curves of all the samples, which proves the existence of 2-D hexagonally ordered mesostructure. The quite close peak intensity of these four samples suggests that the incorporation of metal particles hardly destroy the ordered mesostructure of the samples. The wide-angle XRD patterns of all samples exhibit two broad diffraction peaks centered at 22.5° and 43.5°, which are in accordance with an amorphous carbon framework [9]. In the case of FeOMC sample, a distinguishable diffraction peak at 35.8° can be assigned to the (311) diffraction of γ -Fe₂O₃ (JCPDS 00-039-1346). The weak intensity of the peak may be caused by the low content (Table 1) and the high dispersion of Fe species. An intensive diffraction peak at $2\theta = 34.9^{\circ}$, along with three resolved diffraction peaks at $2\theta = 40.5^{\circ}$, 58.6°, and 70.1° can be observed in the XRD pattern of MnOMC sample, which can be indexed as the (111), (200), (220), and (311) diffraction of cubic MnO (JCPDS 01-075-1090), respectively.

The XRD pattern of MnFeOMC sample possesses some new characteristics. Firstly, a narrow peak located at 26.47° which is a characteristic peak of graphite-like carbon superimposes on a broad profile [4]. This suggests that MnFeOMC composite contains a small quantity of graphitized carbon. It is well known that certain metal nanoparticles such as Fe, Co, Ni, and Mn can catalyze the conversion of amorphous carbon toward graphitic carbon at high temperature in an inert gas atmosphere [28,29]. Secondly, the original weak resolved peak belonging to γ -Fe₂O₃ disappeared. Thirdly, compared with the MnOMC sample, almost all the diffraction peaks of manganese species shift right about 0.3°, indicating that a new species has formed



Fig. 1. Low-angle (inset) and wide-angle XRD patters of (a) OMC, (b) FeOMC, (c) MnOMC, and (d). MnFeOM.

 Table 1

 Textural property of the four samples

Sample	$\frac{S_{BET}{}^{a}}{\left(m^{2}/g\right)}$	V _M ^b / (cm ³ /g)	$V_T^c/$ (cm ³ /g)	D _P ^d / (nm)	Mn content (wt.%) ^e	Fe content (wt.%) ^e			
OMC	743	0.15	0.75	5.2	0.0	0.0			
MnOMC	683	0.12	0.65	4.9	2.45	0.0			
FeOMC	675	0.12	0.63	4.9	0.0	0.35			
MnFeOMC	664	0.12	0.62	4.9	2.26	0.25			

^a Brunauer-Emmet-Teller (BET) surface area.

^b Micropore volume determined by t-plot.

 $^{\rm c}$ Total pore volume calculated from the amount of nitrogen adsorbed at a relative pressure (p/p_0) of 0.99.

^d Pore diameter calculated by the Barrett–Joyner–Halenda (BJH) method using desorption branches.

^e The metal contents were analyzed by ICP method.

when manganese and iron bimetals were together introduced into the OMC material. The four peaks can be respectively indexed as (111), (200), (220), and (311) diffraction of cubic iron manganese oxide ($Fe_{0.099}Mn_{0.901}O$) (JCPDS 01-077-2362). The chemical formula of iron manganese oxide ($Fe_{0.099}Mn_{0.901}O$) was also consistent with the element analysis result.

Nitrogen sorption isotherms of the four samples show representative type IV curves with an obvious H₁-type hysteresis loops (Fig. 2), indicating the mesoporous structure of the materials. Clear capillary condensation is observed between the relative pressures P/ P₀=0.5–0.8 corresponding to a narrow and uniform pore distribution, which could be observed from the pore size distribution curves (Fig. 2 inset) calculated by BJH method based on the desorption branch. The average pore size of MMOMCs becomes a little small due to the incorporation of metal particles and the BET surface area also slightly reduced (see Table 1).

TEM images of the samples clearly show large domains of ordered stripe-like and hexagonally arranged patterns (Fig. 3), which are consistent with the analysis of the low-angle XRD patterns. From TEM images of the OMC sample (Fig. 3a), parallel channels with pore size of about 5 nm and pore wall thickness of ca. 7 nm can be observed. It can be noticed that the nanoparticles (the dark spots) about 6–14 nm are highly dispersed and dominantly imbedded in the carbon walls although some of the large particles can penetrate the pore walls through the mesochannels. Moreover, from the HRTEM images (Fig. 3e, f), one can clearly see the lattice fringes with d spacing of 2.52 Å and 2.22 Å, which correspond respectively to the [311]



Fig. 2. Nitrogen sorption isotherms and pore size distributions (inset) of OMC, MnOMC, FeOMC, and MnFeOMC.

plane of cubic γ -Fe₂O₃ and the [200] plane of cubic Fe_{0.099}Mn_{0.901}O. We believe that the embedded structure can avoid metallic particles aggregation in some level due to the growth restriction caused by the nanopore.

3.2. Catalytic activity

In order to further study the catalytic properties of the fabricated materials, we used them as the supports of Rh based catalysts for the ethanol synthesis from syngas. The performance of CO hydrogenation over the catalysts was summarized in Table 2. It was found that the CO conversion and ethanol selectivity of catalyst supported on the metal modified OMC were significantly improved, particularly in the case of the Rh/MnFeOMC sample. The CO conversion and ethanol selectivity of the Rh/MnFeOMC catalyst increased about 8 times and 1.5 times respectively by contrast with those of the RhMnFe/ OMC catalyst, while the selectivity for the main by-product CH₄ decreased from 41% to 30%. Compared with sample supported on bimetal modified OMC, the activity and ethanol selectivity of catalysts supported on the single metal modified OMCs decreased a little, but still far exceeded those of the catalyst supported on pure OMC. Compared with previously reported similar recipe catalyst supported on silica, the catalysts supported on the MMOMCs still exihibited better activity and higher ethanol selectivity under the similar reaction conditions (Table 2). The performance of CO hydrogenation was strongly influenced by the presence of promoters [30]. A strong interaction between the active promoters and the Rh particles creates tilted adsorption mode of CO, which can be described as $(Rh_x^0Rh_y^+)$ -O-Mⁿ⁺ where a part of Rh atom which have intimate contact with promoter (M^{n+}) exists as Rh⁺ [31]. A tilted adsorption of CO facilitates the dissociation of CO to form an adsorbed – CH_x – species. Furthermore, it is believed that Rh⁺ was more active for undissociated CO insertion than Rh⁰ to form C₂ oxygenates [32].

In Fig. 4, The twoTPR peaks of FeOMC sample may be induced by the reduction from Fe₂O₃ to FeO and FeO to Fe. The first TPR peak of MnOMC sample reflected the reduction of MnO. The first peak of MnFeOMC sample which located bentween the first peak of FeOMC sample and that of MnOMC sample should be attributed to the reduction of Fe_{0.099}Mn_{0.901}O. By contrast with the FeOMC, MnOMC, and MnFeOMC three carriers, most corresponding peaks of their Rh catalysts shift toward low temperature, the shift suggests the intimate contact between the embedded metal nanoparticles and Rh particles. In the cases of RhMnFe/OMC, RhMn/FeOMC, and RhFe/MnOMC catalysts, the interaction between metals can exist in various modes, such as Rh and Mn, Rh and Fe, Mn and Fe, Rh and Mn and Fe. On the TPR patterns of the above three catalysts, the first peak could be attributed to the reduction of Rh³⁺. While in the case of Rh/ MnFeOMC catalyst, due to the only interaction between Rh and iron manganese oxide particles, the original low reduction temperature peak of Rh and the high temperature of iron manganese oxide overlapped in the middle. Because of the intimate contact, the embedded metal oxide nanoparticles can hinder the reduction of Rh ion. Thus, more formation of the $(Rh_x^0Rh_y^+)$ –O–Mⁿ⁺ active sites during reduction facilitates the more CO activation and more insertion into adsorbed $-CH_x$ - species. From Table 2, we can observe that the CO2 selectivity of the catalysts supported on the MMOMCs was obviously higher than that of the catalyst supported on the pure OMC. This indicates the embedded metal particles could promote the water-gas shift reaction which would produce a partial higher concentration of H₂ inside the nanochannel of MMOMCs and will further accelerate the hydrogenation of acetaldehyde and acetic acid. Accordingly, the CO conversion and ethanol selectivity can be greatly increased. In addition, the pore size distribution of MMOMCs channels concentrates at 3-6 nm, which is the optimum size of Rh particles to form C₂ oxygenates. And the Rh particle sizes are calculated about 2.4 nm from CO chemisorptions, which is in accordance with



Fig. 3. TEM and HRTEM images of (a) OMC, (b) FeOMC, (c) MnOMC, (d) MnFeOMC, (e)Fe particles embedded in FeOMC, (f) Fe0.099 Mn0.901 O particles embedded in MnFeOMC.

the spatial limitation of the nano-channel (Table 2). The synergistic effect of the difficult reduction of embedded metal oxide nanoparticles, their intamite interaction with Rh particles, nano-channel, and

graphitic structure might be the reasons for the high activity and ethanol selectivity of Rh based catalyst supported on the bimetal modified OMC.

Tal	ole 2				
CO	hydrogenation da	ata on	different	catalysts.	

Catalysts ^a	Particle size	Т	Р	GHSV	СО	Selectivity (%)						Ref.
	d (nm)	(K)	(MPa)	(h ⁻¹)	Con%	$C2 + oxy^{c}$	EtOH	CH ₄	CH ^d	CO ₂	MeOH	
RhMnFe/OMC	2.4	573	5.0	12,000	3.2	38.0	24.0	41.8	47.6	4.5	9.9	This work
RhFe/MnOMC	2.6	573	5.0	12,000	16.2	44.6	28.7	29.4	34.9	11.9	8.6	This work
RhMn/FeOMC	2.8	573	5.0	12,000	15.5	41.9	28.8	27.7	34.7	16.4	7.0	This work
Rh/MnFeOMC	2.5	573	5.0	12,000	25.5	46.3	34.5	30.7	38.5	11.5	3.7	This work
RhMnFe/SiO2	_ ^e	593	3.0	12,000	8.9	40.2	22.7	_e	58.2	_e	1.6	[20]

^a Fe loading on RhFe/MnOMC, Mn loading on RhMn/FeOMC and Mn, Fe loadings on OMC have been optimized (see Fig. S1).

^b Assuming CO/Rh_{surface} = 1.

 c C2 + oxy denotes oxygenates containing two and more carbon atoms such as ethanol, acetaldehyde, and acetic acid.

^d CH denotes all the hydrocarbons.

^e The data in the indexed paper was not given.



Fig. 4. H₂-TPR profiles of (a) RhFeMn/OMC, (b) RhMn/FeOMC, (c) RhFe/MnOMC, (d) Rh/MnFeOMC, (e) FeOMC, (f) MnOMC, and (g) MnFeOMC.

4. Conclusions

In summary, we have developed a one-pot route for imbedding highly dispersed nanoparticles of iron, manganese, and bimetal iron manganese oxide into the carbon framework of OMC materials. These materials were used as the carriers of Rh catalysts for ethanol synthesis from CO hydrogenation reaction and exhibited excellent performance, particularly, over the Rh catalyst supported on the bimetal modified OMC material.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.catcom.2011.12.015.

References

- [1] A.H. Lu, W.C. Li, Z.S. Hou, F. Schuth, Chemical Communications (2007) 1038.
- Y. Zhai, Y. Dou, X. Liu, B. Tu, D. Zhao, Journal of Materials Chemistry 19 (2009) [2] 3292

- [3] I. Grigoriants, L. Sominski, H. Li, I. Ifargan, D. Aurbach, A. Gedanken, Chemical Communications (2005) 921.
- A.B. Fuertes, T.A. Centeno, Journal of Materials Chemistry 15 (2005) 1079. [4]
- S.M. Holmes, P. Foran, E.P.L. Roberts, J.M. Newton, Chemical Communications (2005) 1912
- [6] S.H. Liu, R.F. Lu, S.J. Huang, A.Y. Lo, S.H. Chien, S.B. Liu, Chemical Communications (2006) 3435
- [7] A.H. Lu, J.J. Nitz, M. Comotti, C. Weidenthaler, K. Schlichte, C.W. Lehmann, O. Terasaki, F. Schuth, Journal of the American Chemical Society 132 (2010) 14152.
- [8] T. Yu, Y.H. Deng, L. Wang, R.L. Liu, L.J. Zhang, B. Tu, D.Y. Zhao, Advanced Materials 19 (2007) 2301.
- [9] H. Wang, A. Wang, X. Wang, T. Zhang, Chemical Communications (2008) 2565.
- I. Tvang, J. Tvang, X. Vang, J. Zhang, Chemistry of Materials 20 (2008) 1200.
 P. Gao, A. Wang, X. Wang, T. Zhang, Chemistry of Materials 20 (2008) 1881.
 J. Li, J. Gu, H. Li, Y. Liang, Y. Hao, X. Sun, L. Wang, Microporous and Mesoporous Materials 128 (2010) 144.
- V. Subramani, S.K. Gangwal, Energy & Fuels 22 (2008) 814. [12]
- R. Burch, M.J. Hayes, Journal of Catalysis 165 (1997) 249. [13]
- [14] M. Haider, M. Gogate, R. Davis, Journal of Catalysis 261 (2009) 9.
- [15] M.R. Gogate, R.J. Davis, Catalysis Communications 11 (2010) 901.
- [16] H. Trevino, G.D. Lei, W.M. Sachtler, Journal of Catalysis 154 (1995) 245.
- [17] M. Ojeda, M.L. Granados, S. Rojas, P. Terreros, F.J. Garcia, J.L. Fierro, Applied Catalysis A 261 (2004) 47
- X. Ma, H.Y. Su, H. Deng, W.X. Li, Catalysis Today 160 (2011) 228. [18]
- [19] H.M. Yin, Y.J. Ding, H.Y. Luo, L. Yan, T. Wang, L.W. Lin, Energy & Fuels 17 (2003) 1401
- [20] H.M. Yin, Y.J. Ding, H.Y. Luo, H.J. Zhu, D.P. He, J.M. Xiong, L.W. Lin, Applied Catalysis A 243 (2003) 155.
- [21] H. Ngo, Y. Liu, K. Murata, Reaction Kinetics, Mechanisms and Catalysis 102 (2010) 425
- [22] H. Arakawa, K. Takeuchi, T. Matsuzaki, Y. Sugi, Chemistry Letters 13 (1984) 1607.
- [23] M. Ojeda, S. Rojas, M. Boutonnet, F.J. Perez-Alonso, F.J. Garcia, J.L. Fierro, Applied Catalysis A 274 (2004) 33.
- [24] S.T. Zhou, H. Zhao, D. Ma, S.J. Miao, M.J. Cheng, X.H. Bao, Zeitschrift für Physikalische Chemie 219 (2005) 949.
- [25] T. Tago, T. Hanaoka, P. Dhupatemiya, H. Hayashi, M. Kishida, K. Wakabayashi, Catalysis Letters 64 (2000) 27.
- [26] X.L. Pan, Z.L. Fan, W. Chen, Y.J. Ding, H.Y. Luo, X.H. Bao, Nature Materials 6 (2007) 507
- [27] Z. Fan, W. Chen, X. Pan, X. Bao, Catalysis Today 147 (2009) 86.
- Ì28Ì M. Sevilla, A. Fuertes, Carbon 44 (2006) 468.
- [29] H. Huwe, M. Froba, Carbon 45 (2007) 304.
- [30] J.J. Spivey, A. Egbebi, Chemical Society Reviews 36 (2007) 1514.
- Y. Wang, Z. Song, D. Ma, H.Y. Luo, D.B. Liang, X.H. Bao, Journal of Molecular Catalysis [31] A: Chemical 149 (1999) 51.
- [32] S.C. Chuang, R.W. Stevens, R. Khatri, Topics in Catalysis 32 (2005) 225.