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Combination-type MgO/CNTs Composites as Effective Supports for CO Hydrogenation to Light Olefin

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Abstract: A series of Magnesia-carbon nanotubes (abbreviated as MgO-CNTs) nanocomposites with different weight ratio were prepared by impregnation of CNTs and used for Fischer-Tropsch synthesis. The results indicated that most of the MgO-CNTs supported catalysts showed high CO conversion and the olefin selectivity was higher than the others when the MgO/CNTs ratio was 2 : 1 under 2 MPa at 350 °C. The catalysts were characterized by scanning electron microscope (SEM), temperature programmed reduction (TPR) of H₂, X-ray diffraction (XRD) and N₂ desorption.

Key words: Fischer-Tropsch synthesis; CO conversion; MgO-CNTs

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To solve the shortage of the cruel oil and meet the ever growing demand for chemical feedstocks, considerable attention was being paid to the design of Fischer-Tropsch catalysts with high selectivity for the lower alkenes^[1-3]. The Fe-base catalysts were particularly attractive due to good activity and their high selectivity of alkenes from syngas^[4]. The effect of support on iron catalysts for light alkenes, such as Al₂O₃, SiO₂, MgO, and Zeolite etc., has been investigated^[4-9]. It has been stated that basicity of the support influenced the selectivity of the light alkenes. MgO was usually adopted as the support due to its basicity and stability, however, a strong metal-support interaction was usually generated and even led to the formation of mixed compounds of FeO-MgO^[10] that were reducible only at very high temperatures. To avoid these problems, the use of carbon as a support has been explored^[11, 12].

Carbon supported iron catalysts were considered to be able to maintain high activities and high selectivities to olefins in the F-T reaction. Thus carbon nanotubes (CNTs) have been used as a novel catalyst support media for heterogeneous catalysts. Earlier studies have indicated that using CNTs as a support to provide an inert, poorly interaction surface could promote the catalytic behavior of metals such as iron, cobalt and ruthenium^[13-15]. Previous work also has shown that CNTs allowed a better metal dispersion control and minimized the metal phase interaction (formation of mixed compounds) with the support^[13, 14, 16]. Although the discovery extended the application of CNTs material in heterogeneous catalysis, there were disadvantages in the use of CNTs in the CO hydrogenation reaction, e. g. high cost and methanation.

In view of the advantage of MgO and CNTs, we prepared MgO-CNTs nanocomposite and used the mate-

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rial as a support for CO hydrogenation. In this letter, a series of catalysts were prepared and applied for CO hydrogenation to light alkenes. The catalysts were characterized by N₂ physisorption, power X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR), H₂, CO and CO₂ temperature-programmed desorption (H₂-, CO- and CO₂-TPD).

1 Experimental

1.1 MgO-CNTs preparation

The MgO-CNTs samples were prepared according to the follow steps. An appropriate amount of CNTs was added to a solution of Mg(NO₃)₂. A NaOH solution was continuously doped into the suspension under stirring. Then the Mg(OH)₂-CNTs precipitated mass was filtered and washed thoroughly with deionized water until excess of Na⁺, NO₃⁻ and OH⁻ was completely removed. The precipitate was dried at 100 °C for 12 h, and then calcined at 500 °C in a N₂ flow for 6 h. A series of chemical compositions of MgO-CNTs (weight ratio = 1 : 1, 2 : 1, 3 : 1, 5 : 1, 10 : 1, 15 : 1) were prepared by using the synthesis technique above.

1.2 Catalysts preparation

The Fe-K-Mn/S (S = MgO, CNTs, MgO-CNTs) catalysts were prepared by incipient wetness impregnation of S with KNO₃ (Xilong Chemical Reagent Co. Ltd, A R, China) in an aqueous solution first. The slurry was spray dried at 100 °C and then calcined in N₂ at 450 °C for 6 h. The manganese promoted catalysts were prepared by further addition of the requisite amount of a Mn(NO₃)₂ (Spinopharm Group Chemical Reagent Co. Ltd, A R, China) aqueous solution and calcined at the same condition to obtain the 5% K- 5% Mn/S. Fe(CO)₅ (synthesized in our lab) dissolved in acetone was mixed with equal mole pyridine with Fe(CO)₅ under constant stirring and then impregnated onto the K-Mn/S. In the absence of light for 12 h, the sample was decomposed under H₂ atmosphere at 450 °C and then we obtained the 10% Fe- 5% K- 5% Mn/S.

1.3 Catalytic measurements

The catalysts were sieved into particle diameter 0.450 ~ 0.280 mm particles. Sample of 3 mL was loaded in a 9-mm-i. d. tube. Prior to the testing, cata-

lysts were reduced with H₂ at 450 °C for 6 h and then fed with the synthesis gas. The reaction conditions were adjusted to 350 °C, 2 MPa, 1 000 h⁻¹ and H₂/CO = 2. Gaseous products (H₂, CO, CH₄ and CO₂) were measured on a shimadzu GC-9A with a TDX-01 column (3 m × 3 mm i. d.) and a TCD detector. C₁-C₄ hydrocarbons were analyzed with an Al₂O₃ capillary column (30 m × 0.53 mm, N₂ carrier) and a flame ionization detector (FID). Oil phase component was determined by an OV-101 capillary column (2.5 mm i. d., He carrier).

1.4 Characterization of supports and iron catalysts

H₂ temperature-programmed reduction (H₂-TPR) (TPR, TP-5080, China) was carried out in a quartz tube reactor using 5% H₂/95% Ar as the reactant. The catalysts of 50 mg were kept at 450 °C for 30 min in a flowing Ar. After the temperature has dropped to the ambient temperature, the catalysts were reduced by raising the temperature from ambient temperature to 900 °C at the rate of 10 °C/min.

The H₂, CO and CO₂ temperature-programmed desorption (H₂-, CO- and CO₂-TPD) (TP-5080, China) were performed in the same system as used in TPR, with Ar (in H₂-TPD, CO₂-TPD) or He (in CO-TPD) as the carrier gas. Note that, particularly for the H₂-TPD, CO-TPD experiments, the catalysts of 50 mg were first reduced with H₂ at 450 °C for 4 h. And then the samples were cooled to the ambient temperature. In the subsequent steps, H₂, CO or CO₂ adsorption on the catalysts was performed for 30 min until the baseline leveled off, and then the samples were flushed by the carrier gas for 30 min to remove the physical adsorbed species at 120 °C. After that, H₂-, CO- or CO₂-TPD was carried out while the temperature was increased to 900 °C at ramp of 40 °C/min.

X-ray powder diffraction (XRD, X'pert, PANalytical, Dutch) with Cu K α radiation was used to analyze the crystalline structure of the samples. The 2 θ angles were scanned from 15° ~ 80°.

Nitrogen adsorption measurements were carried at -196 °C with a Micromeritics ASAP 2010 instrument. The BET surface area and the pore size distribution were determined from the isotherms.

The surface morphology was observed by the scanning electronic microscopy (SEM, JSM-6701F, JEOL).

2 Results and discussion

2.1 SEM

The morphology of the MgO-CNTs compounds is shown in Fig. 1. We could observe that the CNTs were

composed of fibrous structures and the MgO mainly consisted of sheetlike structures. After the addition of CNTs to MgO, the particle size of MgO became smaller and the CNTs were well penetrated among the MgO materials. The SEM implied that the nanocomposite might be not a simple mixture of CNTs and MgO, but rather a special material composed of strongly interacting CNTs and MgO.

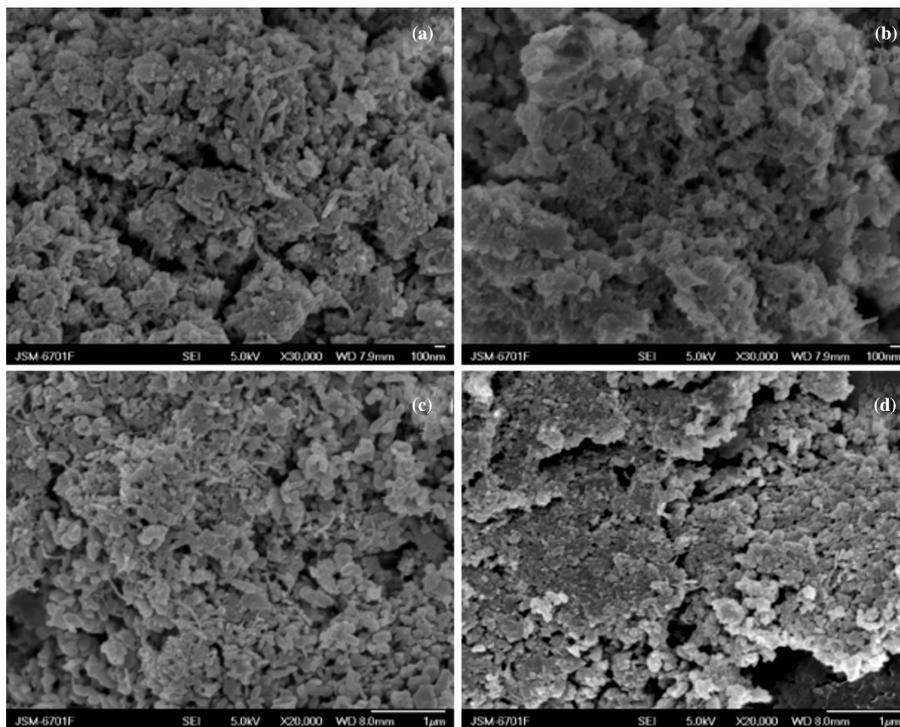


Fig. 1 SEM images of MgO-CNTs compounds

(a) MgO : CNTs = 2 : 1; (b) MgO : CNTs = 3 : 1; (c) MgO : CNTs = 5 : 1; (d) MgO : CNTs = 15 : 1.

2.2 BET surface area

Table 1 gives the results of N₂ physisorption for the catalysts. The BET surface area and pore volume of

the catalysts decreased with the decreasing CNTs content, while the average pore diameter increased slightly.

Table 1 N₂ physisorption results

Supports	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	Pore volume/ $(\text{cm}^3 \cdot \text{g}^{-1})$	Pore diameter/nm
CNTs	156.6	0.62	15.8
MgO	19.2	0.14	28.7
MgO : CNTs = 1 : 1	79.4	0.29	14.8
MgO : CNTs = 2 : 1	68.9	0.30	17.1
MgO : CNTs = 3 : 1	57.6	0.29	20.4
MgO : CNTs = 5 : 1	30.8	0.19	24.1
MgO : CNTs = 10 : 1	19.4	0.12	25.5
MgO : CNTs = 15 : 1	24.3	0.16	25.6

2.3 XRD

The XRD patterns of various catalysts are shown in Fig. 2. For all the catalysts, the small peaks located at 25.7 and 43.8 could be attributed to carbon nanotubes, while the peaks at two-theta values of 42.8, 36.8, 62.1, 74.4 and 78.3 corresponded to the MgO phase. However, in the XRD pattern of MgO-CNTs ([10 : 1] [15 : 1]) catalysts, very strong MgCO₃ peaks were observed at 32.6, 35.8, 38.8, 46.8, 66.3, 69.1 and 70.2, indicating that the MgO-CNTs supports became unstable with a small quantity of CNTs. The peaks at two-theta values of 35.3, 41.0 and 59.3 were assigned to the characteristic peaks of FeO-MnO [17, 18]. We implied that the strong interaction between the metal and the support led to the formation of FeO-MnO during the reduced progress. Moreover, no characteristic diffraction peaks for Fe, K and Mn species were detected, indicating that the metal particles were smaller in diameter than the detection limit (4 nm) of the diffractometer, or that large metal particles were amorphous on the support.

2.4 TPR

The reduction behaviors of the catalysts were measured by H₂-TPR. The reduction profiles for the catalysts are present in Fig. 3. For the unmodified catalysts, the CNTs supported catalyst exhibited one broad peak at 300 ~ 500 °C. However, the MgO supported catalyst exhibited another peak at high temperature. In supported catalysts, the reducibility of Fe species often depended on the extent of the metal-support interaction. Boudart et al. [19] have reported that the formation of the mixed compound of FeO-MgO could form because of the strong metal-support interaction and this strong interaction suppressed the reduction of Fe²⁺ to metal iron. For comparison, CNTs could facilitate the Fe²⁺ reduction to some degree. For the modified iron catalysts, the TPR peaks at 300 ~ 500 °C became stronger and stronger and the peak at high temperature became weaker and weaker with the increase of the CNTs. In addition we could observe that the platform peaks appeared on MgO-CNTs catalysts at 450 ~ 700 °C because of the different interaction between the Fe and the support.

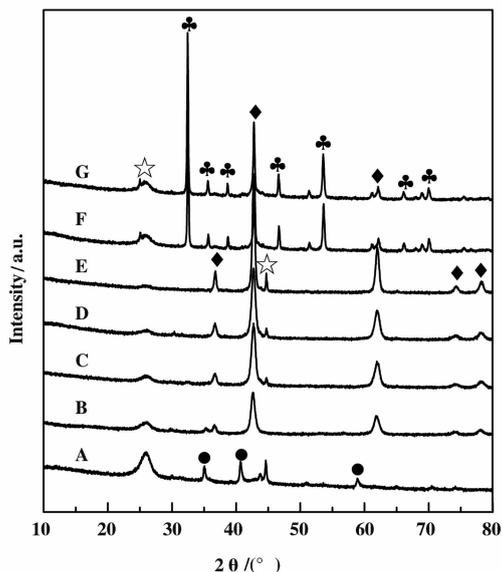


Fig. 2 XRD patterns of the catalysts

- (A) Fe-K-Mn/CNTs; (B) Fe-K-Mn/MgO-CNTs [1 : 1];
 (C) Fe-K-Mn/MgO-CNTs [2 : 1]; (D) Fe-K-Mn/MgO-CNTs [3 : 1]; (E) Fe-K-Mn/MgO-CNTs [5 : 1];
 (F) Fe-K-Mn/MgO-CNTs [10 : 1]; (G) Fe-K-Mn/MgO-CNTs [15 : 1]; (☆) CNTs; (◆) MgO;
 (●) FeO-MnO; (♣) MgCO₃

2.5 TPD

Fig. 4 shows the CO₂-TPD profiles for the catalysts. It was observed that there were two CO₂ desorption peaks on the MgO supported catalyst. These two peaks could be attributed to desorption of the weakly and strongly chemisorbed CO₂, respectively. For the CNTs supported catalyst and MgO-CNTs ([2 : 1]) supported catalyst, there was only one peak at the high temperature. Apparently, the CO₂ desorption temperature on the MgO-CNTs supported catalyst was higher than that on the CNTs supported catalyst. There was no peak at the low temperature on the CNTs and MgO-CNTs supported catalyst because of the poorly interaction between Fe and the support. Fisher et al. [20] have suggested that the CNTs had excellent electronic properties which could made the charge disturbed throughout the catalyst and led to the strong CO₂ adsorption. After the addition of CNTs to the MgO, the synergistic effect of the electronic properties of CNTs and the basicity of MgO promoted the degree of the CO₂ adsorption.

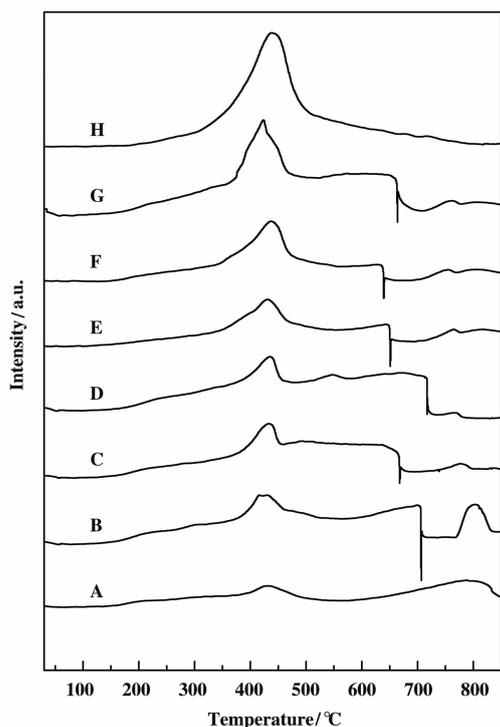


Fig. 3 H₂-TPR profiles for the catalysts

(A) Fe-K-Mn/MgO; (B) Fe-K-Mn/MgO-CNTs [15 : 1];
 (C) Fe-K-Mn/MgO-CNTs [10 : 1]; (D) Fe-K-Mn/MgO-CNTs [5 : 1]; (E) Fe-K-Mn/MgO-CNTs [3 : 1]; (F) Fe-K-Mn/MgO-CNTs [2 : 1]; (G) Fe-K-Mn/ CNTs [1 : 1];
 (H) Fe-K-Mn/ CNTs

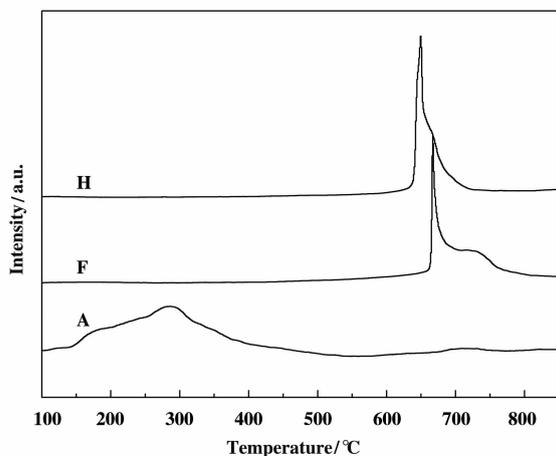


Fig. 4 CO₂-TPD profiles for the catalysts

(A) Fe-K-Mn/MgO; (F) Fe-K-Mn/MgO-CNTs [2 : 1];
 (H) Fe-K-Mn/ CNTs

Fig. 5a shows the H₂ adsorption behavior of the catalysts. It was observed that MgO supported catalyst showed two peaks; one at low temperature correspon-

ding to the weak H₂ adsorption on the metal Fe or Fe oxide surface, the other one at high temperature was attributed to the strong H₂ adsorption on the cleavage of OH species on the difficultly reduced oxide surface in catalysts. For the CNTs catalyst, there peaks appeared; two kinds of H₂ adsorption were the same with that on the MgO supported catalyst although the peaks appeared in advance due to the electronic effect, and the third peak could be attributed to the H₂ adsorption inside the CNTs. For the MgO-CNTs catalyst, there was only one strong peak at the high temperature, which might be attributed to the H₂ adsorption inside the CNTs. From the H₂-TPD, we concluded that the interaction between Fe and the support was changed in the CNTs-modified catalyst and further changed the H₂ adsorption.

Fig. 5b shows the CO-TPD adsorption behavior of the catalysts. For the MgO supported catalyst, the CO desorption curves located at 370°C and 700°C, while there were two peaks at the high temperature on the CNTs supported catalyst, both of which located in a high temperature range. However, for the MgO-CNTs ([2 : 1]) supported catalyst, it was interesting to note that the MgO-CNTs supported catalyst also had two strong peaks at the high temperature except for the two weak peaks below 600°C.

In generally, the adsorption capability of CO/H₂ was important for the catalytic activity and the selectivity because of the competitive adsorption between CO and H₂. Compared to the MgO and CNTs supported catalysts, the MgO-CNTs ([2 : 1]) supported catalyst improved the H₂/CO chemisorption, which was beneficial for the activity and the selectivity of the production.

2.6 Fischer-Tropsch synthesis (FTS)

The results of catalytic performance for FTS are listed in Table 2. The CO conversion was used as a measure of FTS activity in the current study. As shown in Table 2, two trends were apparent; (1) with the increasing the CNTs content, the CO conversion and the methane selectivity of the CNTs-modified catalysts increased, while the C₅₊ selectivity decreased all the time. (2) the CO conversion of MgO-CNTs [1 : 1,

2 : 1, 3 : 1, 5 : 1] supported catalysts was much higher than that of unmodified iron catalysts, howev-

er, the CO conversion was lower when the MgO/CNTs ratio and CNTs was 10 and 15.

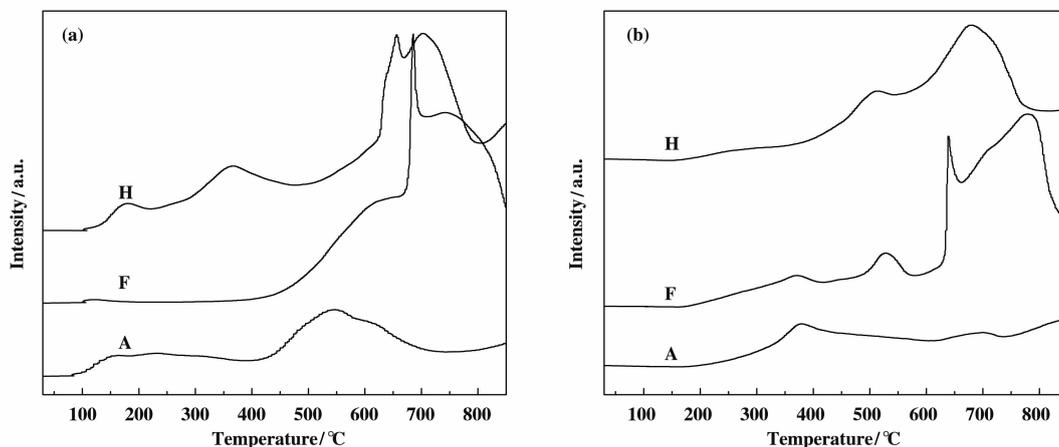


Fig. 5 H₂-TPD and CO-TPD profiles for the catalysts

(A) Fe-K-Mn/MgO; (F) Fe-K-Mn/MgO-CNTs [2 : 1]; (H) Fe-K-Mn/ CNTs

Table 2 Activity of selectivity of the Fe-K-Mn/MgO-CNTs catalysts

Supports MgO : CNTs	CO conversion /%	Selectivity /%				
		CH ₄	C ₂	C ₃	C ₄	C ₅₊
MgO	59.6	12.4	13.0	14.6	8.2	51.8
CNTs	75.0	18.9	25.0	27.5	15.0	13.6
1 : 1	93.5	28.3	28.6	28.7	14.5	–
2 : 1	90.8	21.1	27.5	32.1	19.2	–
3 : 1	89.1	19.9	26.4	30.2	14.1	9.4
5 : 1	82.2	18.8	25.9	28.3	11.9	15.1
10 : 1	39.6	18.2	16.5	16.2	11.2	37.9
15 : 1	16.3	10.9	10.1	9.1	3.2	67.2

Reaction condition: T=350 °C, P=2.0 MPa, GHSV=1 000 h⁻¹, H₂/CO=2

It has been suggested that the activity of the catalyst was directly depended on the catalyst reducibility for FTS^[18]. As indicated by the H₂-TPR findings and the reduction behavior, CNTs-modified catalysts improved the reducibility of the iron oxides. Thus, the trend in variation of CO conversion with CNTs content was similar to that of percentage reduction of the catalysts.

Compared to the MgO and CNTs supported catalysts, the MgO-CNTs supported catalyst had higher CO conversion. As shown in Fig. 5, the addition of CNTs

to MgO improved the H₂/CO adsorption, which was beneficial for CO conversion. As stated above, the CNTs also had excellent electronic properties, the appropriate addition of CNTs increased the charge transfer which could further promoted the CO dissociation. However, the small number of the CNTs led to the instability of the catalysts which affected the activity negatively.

Fig. 6 showed the olefin selectivity of the catalysts. We could see that the C₂⁼-C₄⁼ selectivity increased with the addition of CNTs at the beginning and

then decreased when the MgO/CNTs weight ratio was up to 1. The appropriate interaction between Fe and the supports played a dominant role in the selectivity of the catalysts. It was considered that the MgO-CNTs composite had new surface properties compared with the MgO and CNTs, such as the optimized interaction between the supported Fe and the support. When used in catalysis, the MgO-CNTs not only had the electronic properties of the CNTs but also the basicity of MgO. We concluded that the synergistic effect of the electronic properties of the CNTs and the basicity of MgO were beneficial for the olefin selectivity when the MgO/CNTs weight ratio was 2.

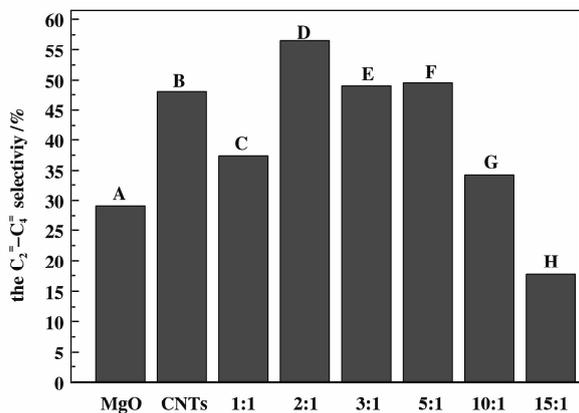


Fig. 6 The $C_2=C_4$ selectivity of catalysts

(A) Fe-K-Mn/MgO; (B) Fe-K-Mn/CNTs; (C) Fe-K-Mn/MgO-CNTs [1 : 1]; (D) Fe-K-Mn/MgO-CNTs [2 : 1]; (E) Fe-K-Mn/MgO-CNTs [3 : 1]; (F) Fe-K-Mn/MgO-CNTs [5 : 1]; (G) Fe-K-Mn/MgO-CNTs [10 : 1]; (H) Fe-K-Mn/MgO-CNTs [15 : 1]

3 Conclusion

CO hydrogenation was investigated over Fe catalysts supported on MgO-CNTs composite. The appropriate ratio MgO-CNTs ([2 : 1]) supported catalysts revealed high CO conversion and olefin selectivity. The reason might be that the advantageous interactions between Fe/MgO and Fe/CNTs were well engaged.

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MgO-CNTs 复合载体负载的铁基催化剂用于 CO 加氢制备低碳烯烃催化性能研究

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摘 要: 通过将 $\text{Mg}(\text{NO}_3)_2$ 沉淀于碳纳米管(CNTs)上, 制备了一系列质量比不同的 MgO-CNTs 混合物并用于费托合成的载体. 实验结果表明, 在 2 MPa, 350 °C 条件下大部分以 MgO-CNTs 为载体制备的催化剂有着很高的 CO 转化率, 同时, 当 MgO : CNTs 的比例为 2 : 1 时, 烯烃的选择性高于其它载体制备的催化剂. 我们还用扫描电镜 (SEM), 程序升温还原(H_2 -TPR), X 射线衍射 (XRD) 和 N_2 物理吸附对催化剂进行了表征.

关键词: 费托合成; CO 转化率; MgO-CNTs