A new supported Fe–MnO catalyst for the production of light olefins from syngas.
II. Effect of support on the secondary reactions of C_2H_4

Xu-Yide, Huang-Jiasheng

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,
Academia Sinica, Dalian 116023, PR China

Xu-Longya and Wang-Qingxia

Dalian Institute of Chemical Physics, Academia Sinica,
Dalian 116023, PR China

Received 19 April 1993; accepted 17 September 1993

The TPSR technique was used to investigate the effect of the support on the secondary reactions of ethylene formed during CO hydrogenation. Based on the results of CO hydrogenation and CO/H_2-TPSR characterization, it was found that different supports induced different secondary reactions, and thus affected the selectivity to light olefins directly. The Fe–MnO/MgO catalyst (based on basic support) causes disproportionation of C_2H_4, and thus, leads to the formation of C_3H_6. The Fe–MnO/Al_2O_3 catalyst (based on acidic support) showed obvious hydrogenation of C_3H_6. The disproportionation of C_2H_4 was also promoted by the Fe–MnO/Al_2O_3 catalyst, but because of its activity for C_3H_6 hydrogenation, a large amount of C_3H_8 was produced. The different C_2H_4 secondary reactions are relevant to different CO/H_2 reaction pathways over the catalyst surface, so the Fe–MnO/MgO catalyst is a desirable catalyst for the production of light olefins from CO/H_2 while the Fe–MnO/Al_2O_3 catalyst was not so.

Keywords: Ethylene; secondary reaction; TPSR

1. Introduction

It is clear from our previous study on reaction mechanism by using TPD and TPSR techniques that the primary products of FT reactions on supported Fe–MnO catalysts are CH_4 and light olefins (especially C_2H_4) [1]. Due to its reactivity, C_2H_4 on the catalysts gives many reactions, such as hydrogenation, disproportionation and polymerization, and therefore, leads to various by-products [2,3], which is unfavourable for the selective production of C_2H_4 from CO/H_2. To enhance the selectivity to light olefins, it is necessary to prevent the formation of CH_4 and suppress the secondary reactions of C_2H_4. For a supported catalyst, selectivity to products can be influenced by the properties of the metal active component and the support [4]. It is found that the nature of the support sometimes plays a crucial role, especially, for the catalytic selectivity.

In the present work, the TPSR technique was employed to investigate the effect of the support on secondary reactions of ethylene. Based on the results of CO/H_2-TPSR, the different selectivities to light olefins of differently supported catalysts were explained in terms of various secondary reactions of C_2H_4 over the catalyst surfaces. The study on the secondary reactions of C_2H_4 also gives insight into the mechanism for the production of light olefins, and gives some information to guide the development of a new catalyst.

2. Experimental

2.1. CATALYST PREPARATION

Different supports such as basic support-MgO and acidic support-Al_2O_3 (20–30 meshes) were calcined, and then impregnated with $Fe(NO_3)_3$ and $Mn^{(n+)}$ solution under vacuum conditions. The unsupported Fe–MnO catalyst was prepared by co-precipitation procedures using $Fe^{(3+)}$ and $Mn^{(n+)}$ as precursors. The samples were dried at 400 K for 8 h and then calcined at 800 K for several hours.

2.2. C_2H_4/H_2 PULSE REACTION

In order to directly study the secondary reactions of C_2H_4 over catalyst surface, mixtures of C_2H_4/H_2 with different mole ratios were pulsed through differently supported catalysts at 670 K using He as a carrier. Pulse reaction products were analyzed with on-line gas chromatography.

2.3. TPSR

(a) *C_2H_4-He-TPSR.* A supported catalyst, after being reduced at 770 K, was flushed with He at room temperature, and then exposed to C_2H_4. Temperature-programmed surface reaction (TPSR) was then carried out under a He stream from room temperature to 770 K with a heating rate of 16 K/min. The products were monitored with a multichannel mass spectrometer.

(b) *C_2H_4-H_2-TPSR.* A supported catalyst, after being reduced at 770 K, was exposed to C_2H_4 directly at room temperature. TPSR was performed under a H_2 stream from room temperature to 770 K.

3. Results and discussion

3.1. C_2H_4-He-TPSR

It was found that the profiles recorded from C_2H_4-He-TPSR on the Fe–MnO/MgO catalyst (fig. 1) was very different from that on the Fe–MnO/Al_2O_3 catalyst (fig. 2). For the Fe–MnO/MgO catalyst (fig. 1), the amounts of CH_4 and C_3H_6 increased simultaneously and then decreased in the same way with temperature, which suggested that the formations of CH_4 and C_3H_6 are from C_2H_4 disproportionation. Moreover, dimerization of C_2H_4 may occur, but it is much less than disproportionation. No hydrogenation of light olefins takes place over the Fe–MnO/MgO catalyst, since saturated hydrocarbons could not be detected. For the Fe–MnO/Al_2O_3 catalyst (fig. 2), the secondary reactions of ethylene were much more complicated. Besides the disproportionation and polymerization of C_2H_4, C_3H_8, which is from C_3H_6 hydrogenation, can be detected. The differences in C_2H_4 secondary reaction on the two kinds of catalysts can be attributed to the different catalyst supports. The Fe–MnO/MgO catalyst based on a basic support can prevent

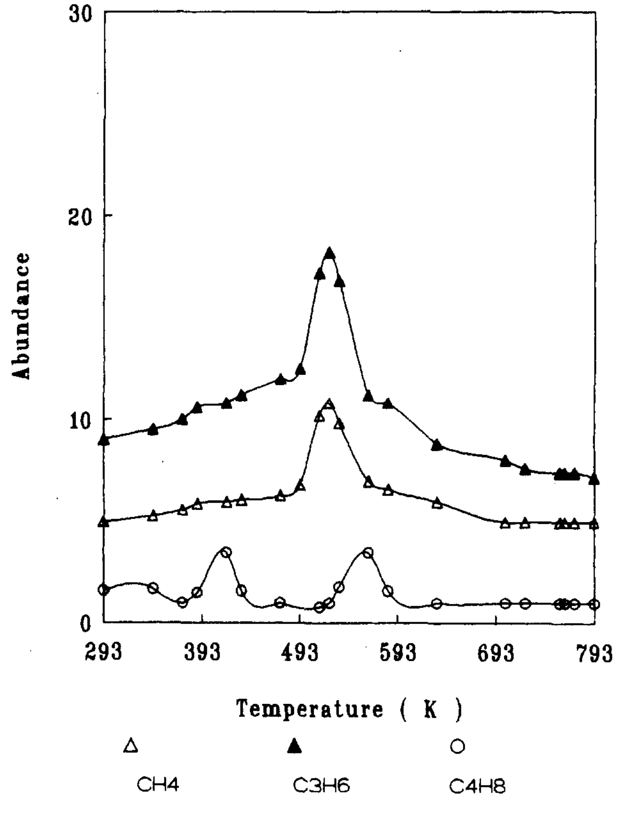

Fig. 1. C_2H_4-He-TPSR profiles from the Fe–MnO/MgO catalyst.

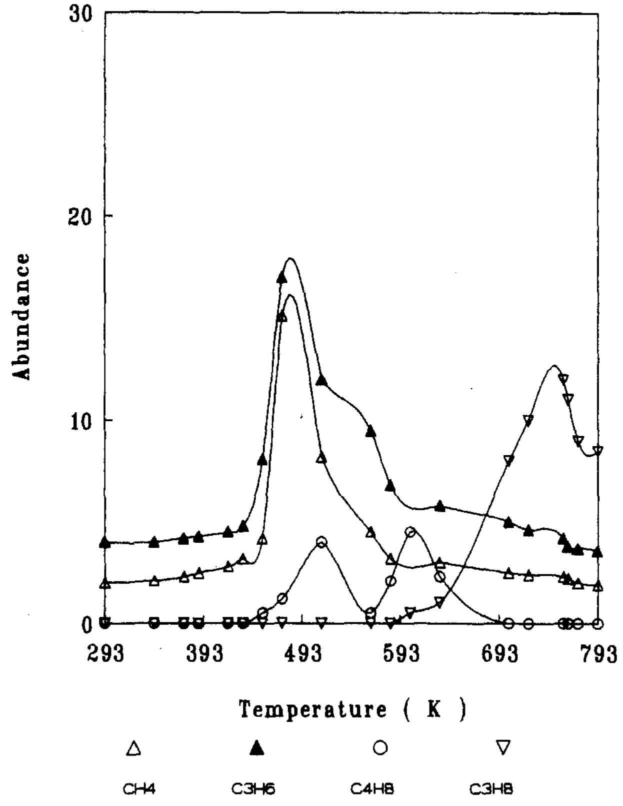

Fig. 2. C_2H_4-He-TPSR profiles from the Fe–MnO/Al_2O_3 catalyst.

hydrogenation of light olefins which would take place over the Fe–MnO/Al_2O_3 catalyst based on an acidic support.

During the reduction of the catalyst, a little amount of H_2 might be adsorbed on the catalyst surface, which may be the source of H_2 for the disproportionation of C_2H_4 and the hydrogenation of C_3H_6.

3.2. C_2H_4-H_2-TPSR

C_2H_4-H_2-TPSR profiles of the Fe–MnO/MgO, Fe–MnO/Al_2O_3 and unsupported Fe–MnO catalysts are shown in figs. 3–5. For the Fe–MnO/MgO catalyst, ethylene hydrogenation occurs to a small extent, in addition to its disproportionation and polymerization. We did not find C_3H_8 in the products during C_2H_4-H_2-TPSR on the Fe–MnO/MgO catalyst, which showed that no C_3H_6 hydrogenation reaction takes place. While for the Fe–MnO/Al_2O_3 catalyst, various complicated secondary reactions of light olefins take place over the Fe–MnO/Al_2O_3 catalyst. Large amounts of CH_4 and C_3H_8 were produced simultaneously. This leads to a conclusion that the hydrogenation of C_3H_6 produced from ethylene disproportio-

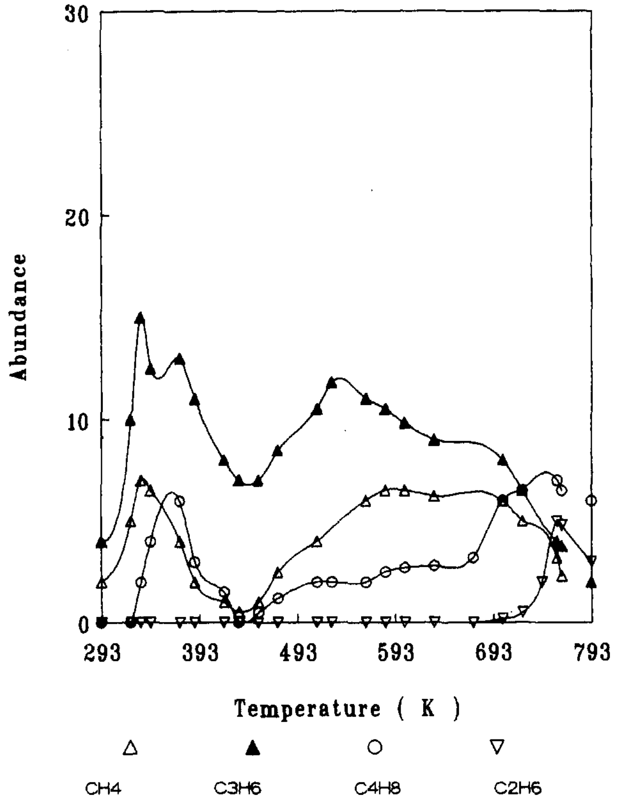

Fig. 3. C_2H_4-H_2-TPSR profiles from the Fe–MnO/MgO catalyst.

nation occurs to a large extent. The strong hydrogenation of C_3H_6 can promote disproportionation of C_2H_4 in turn, while preventing the polymerization and hydrogenation of ethylene. So the main products during its C_2H_4-H_2-TPSR were CH_4 and C_3H_8, with the formation of little amounts of C_4H_8 and C_2H_6.

It is concluded that the intrinsic property of the catalyst support is responsible for the different ethylene secondary reactions on differently supported Fe–MnO catalysts. Hydrogenation of C_3H_6 was very strong over the Fe–MnO/Al_2O_3 surface, while it was not seen on the Fe–Mn/MgO catalyst, which promoted disproportionation of ethylene giving large amounts of CH_4 and C_3H_6. Fe–MnO/Al_2O_3 was not a proper catalyst for producing light olefins from syngas. The secondary reactions of ethylene over Fe–MnO/MgO catalyst were weaker than Fe–MnO/Al_2O_3, and Fe–MnO/MgO shows high selectivity to light olefins, so the Fe–MnO/MgO catalyst was a desirable catalyst for conversing synthesis gas to light olefins.

From the study of the secondary reactions of ethylene over the unsupported Fe–MnO catalyst (fig. 5 C_2H_4-H_2-TPSR of Fe–MnO catalyst characterization), it is interesting to note that both C_2H_4 and C_3H_6 could hydrogenate to form C_2H_6 and C_3H_8 and that C_3H_6 were easier to hydrogenate than C_2H_4. It is also found that

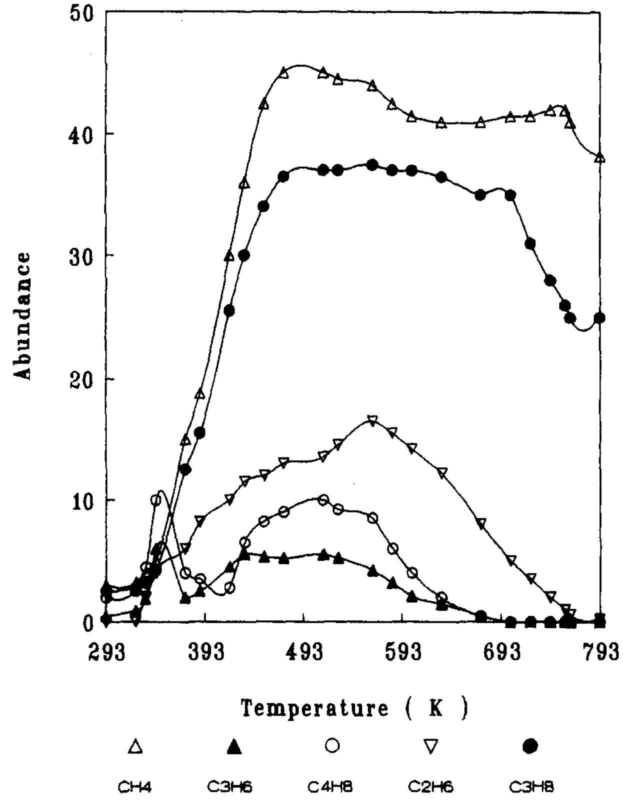

Fig. 4. C_2H_4-H_2-TPSR profiles from the Fe–MnO/Al_2O_3 catalyst.

the polymerization of C_2H_4 is more difficult than the other secondary reactions. Based on the above results, it is suggested that the secondary reactions of ethylene over the Fe–MnO catalyst can be changed by its support, different supports causing different C_2H_4 secondary reactions.

3.3. INFLUENCE OF DIFFERENT C_2H_4/H_2 RATIO ON ETHYLENE SECONDARY REACTIONS

The results of pulse reactions of C_2H_4/H_2 over the different catalysts are shown in figs. 6 and 7. There are many reactions of ethylene such as ethylene hydrogenation, ethylene disproportionation and ethylene polymerization which can proceed over the catalysts. Reaction pathways depended on different catalyst supports and different reaction gas environments. For the Fe–MnO/MgO catalyst, the production of C_2H_6 and C_4H_8 increases a little, with a little decrease in the amount of CH_4 and C_3H_6 with increasing of the mole percentage of H_2. It showed that the existence of H_2 promoted hydrogenation and polymerization of ethylene and prevented disproportionation of ethylene, but the influences of H_2 on all kinds of C_2H_4 secondary reactions over Fe–MnO/MgO were not obvious. For the Fe–MnO/

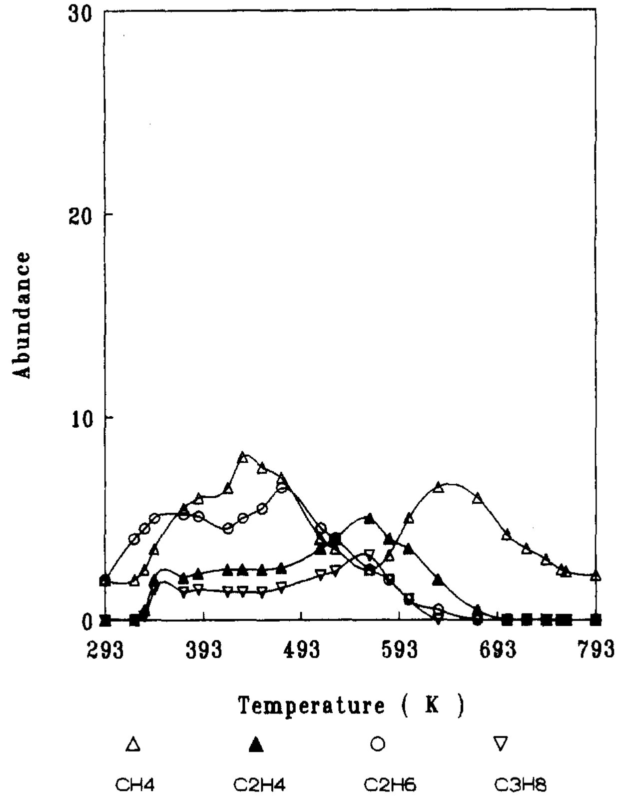

Fig. 5. C_2H_4-H_2-TPSR profiles from the unsupported Fe–MnO catalyst.

Al_2O_3 catalyst, H_2 can affect strongly the secondary reactions of ethylene. Hydrogenations of C_2H_4 and C_3H_6 produced from ethylene disproportionation were weaker with $H_2/C_2H_4 = 0$ as pulse reaction gas, while ethylene could be polymerized easily forming C_4H_8. The distribution of reaction products will change a lot with an increase in H_2 concentration. For example, the productions of CH_4 and C_3H_8 were increased while the formation of C_3H_6 was decreased obviously, meanwhile productions of C_2H_6 and C_4H_8 were also prevented. It could be suggested that the introduction of H_2 would speed up hydrogenation of C_3H_6 and so promote the disproportionation and prevent the hydrogenation and polymerization of ethylene. The influence of H_2 on ethylene secondary reaction was very strong from above point.

The secondary reactions of ethylene occurring over a catalyst surface are not only affected by the catalyst support, but also by the mole ratio of H_2/C_2H_4. On the other hand, the influence of H_2 concentration on secondary reactions of ethylene also depends on different catalyst supports. For the Fe–MnO/MgO catalyst, we can prevent its catalytic reactivity from carbon deposition on the surface by using a high H_2/CO ratio as reaction syngas.

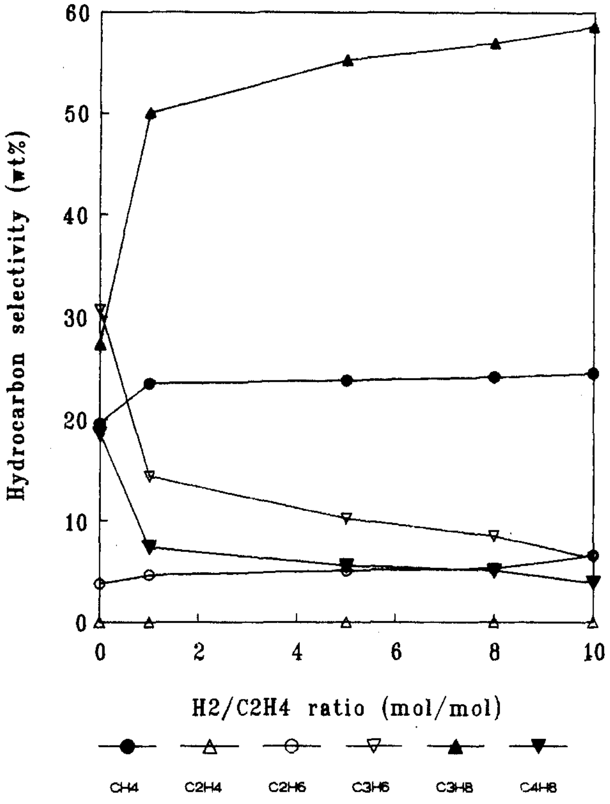

Fig. 6. Effect of H_2/C_2H_4 ratio on the secondary reactions of C_2H_4 over the Fe–MnO/Al_2O_3 catalyst.

4. Conclusions

(1) Hydrogenation, disproportionation and polymerization reactions of ethylene proceeded easily over a catalyst surface during FT reactions. The reaction pathway and the extent of ethylene secondary reaction occurring on various catalysts depend on the nature of support. For the Fe–MnO/MgO catalyst based on a basic catalyst support, the main secondary reaction of ethylene is ethylene disproportionation, while for the Fe–MnO/Al_2O_3 catalyst using an acidic support, the hydrogenation of C_3H_6 produced from the disproportionation of ethylene is considerable, which, in turn promoted ethylene disproportionation giving large amount of C_3H_8.

(2) Hydrogenation and polymerization of ethylene are promoted by increasing the H_2/C_2H_4 ratio, while the disproportionation of ethylene is inhibited for the Fe–MnO/MgO catalyst. For the Fe–MnO/Al_2O_3 catalyst, the disproportionation of ethylene and hydrogenation of C_3H_8 are much stronger with increasing H_2 concentration in the H_2/C_2H_4 mixture gas.

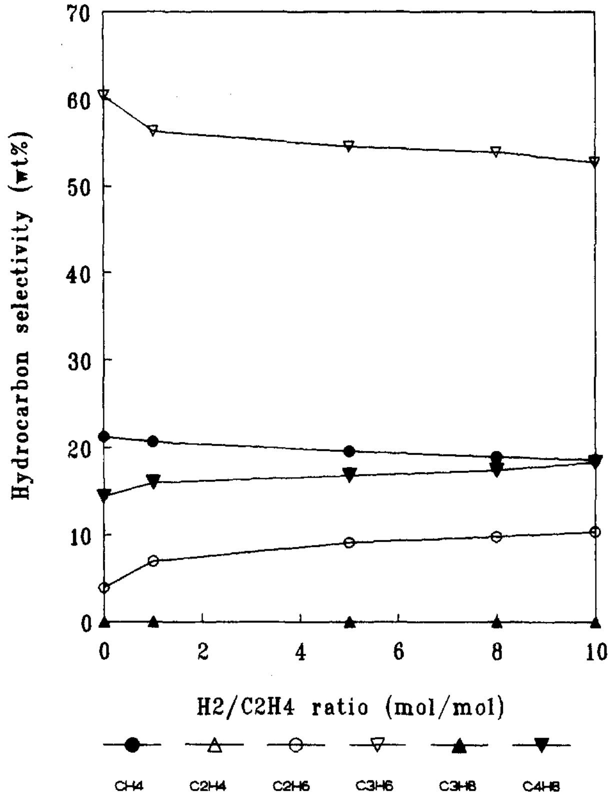

Fig. 7. Effect of H_2/C_2H_4 ratio on the secondary reactions of C_2H_4 over the Fe–MnO/MgO catalyst.

(3) Fe–MnO/MgO is a desirable catalyst for the production of light olefins from syngas. Its catalytic stability can be prolonged by increasing the H_2 concentration in syngas, because high H_2 concentration can prevent the carbon deposition on the catalyst.

References

[1] P. Biloen, J.N. Helle and W.M.H. Sachtler, J. Catal. 58 (1979) 95.
[2] D.J. Dwyer and G.A. Somorjai, J. Catal. 56 (1979) 249.
[3] J.P. Reymond, P. Meriaudean, B. Pommier and C.O. Bennett, J. Catal. 64 (1980) 163.
[4] Longya Xu, Guongyu Cai, Qingxia Wang and Guoquan Chen, Fuel Chem. Xue Bao. 29 (1992) 252.