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# A new supported Fe–MnO catalyst for the production of light olefins from syngas.
# I. Effect of support on the catalytic performance

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CO-TPD and $H_2$-TPD and CO/$H_2$-TPSR were used to study the effect of the support on the performance of Fe–MnO catalysts in CO hydrogenation for the production of light olefins. It was found that a Fe–MnO/MgO catalyst (based on a basic support) is capable of strongly adsorbing CO and $H_2$ favorable for the production of light olefins and CO conversion. A Fe–MnO/$Al_2O_3$ catalyst (based on an acidic support) only showed strong adsorption of $H_2$, but weaker adsorption of CO, and so, it was a poor catalyst for light olefins from syngas.

**Keywords:** Light olefins; syngas; Fe–MnO catalyst; TPSR

## 1. Introduction

Catalyst supports can improve the dispersion of the active phase, and thus, increase the catalyst activity [1]. Furthermore, their intrinsic acid–basic properties and micropore-channel structures can influence the state of the active metal [2], and even cause different support–metal interactions [3,4], which obviously have effects on catalytic behavior, especially on the selectivity [5]. In order to develop a catalyst with high catalytic activity and desirable selectivity, the proper choice of its support is important.

It is well-known that the carbon number distribution of the products observed over a classical FT catalyst can be reasonably described by a polymerization distribution law [6,7]. This imposes a severe limitation upon the selectivity. In order to enhance the selectivity of light olefins, several catalyst supports, such as $Al_2O_3$,

$SiO_2$, $TiO_2$, and zeolite have been chosen and tested. We have developed a Fe–MnO catalyst supported on a basic support, over which a high $C_2^=$–$C_4^=$ olefin selectivity (70%) and a high catalytic activity (70–90% of CO conversion) can be achieved under certain reaction conditions.

In this paper supported Fe–MnO catalysts for CO hydrogenation for the production of light olefins were evaluated in a flow reactor. TPD and TPSR were used to characterize the nature of $H_2$ and CO adspecies and their surface reaction mechanism. Combined with the results of CO hydrogenation, some information on interaction is obtained which gives us some clues into the mechanism of light olefin formation on these modified FT catalysts and allows us to develop a new catalyst.

## 2. Experimental

### 2.1. PREPARATION OF CATALYST

The catalysts were prepared by impregnation. Different supports such as MgO, $ZrO_2$, $TiO_2$, $Al_2O_3$ and $SiO_2$ with sizes of 20–30 mesh were impregnated with $Fe^{(3+)}$ and $Mn^{(n+)}$ salt solutions under vacuum condition. They were dried at 400 K for 10 h and calcined at 800 K for 16 h.

### 2.2. CO HYDROGENATION

CO hydrogenation was carried out in a flow microreactor made of stainless steel. Typically the catalyst charge was 1 ml. The reaction temperature and pressure varied in the range of 550–620 K and 1.0–2.0 MPa respectively. Syngas ($H_2/CO = 2/1$) space velocity varied in the range of 500–3000 $h^{-1}$ to give a proper CO conversion and a high olefin selectivity. Products were on line analyzed by a gas chromatograph with a TCD detector.

### 2.3. TPD AND TPSR

TPD and TPSR were carried out in a flow system equipped with a TE-150 multichannel mass spectrometer. The data were recorded, stored and processed by an IBM computer. The procedures for TPD and TPSR are as follows.

(a) *$H_2$- and CO-TPD.* A supported catalyst, after being reduced under $H_2$ at 770 K, was exposed to $H_2$ and/or CO at room temperature and then flushed with He. $H_2$- and/or CO-TPD experiments were carried out in a He stream from room temperature to 770 K at a heating rate of 16 K/min.

(b) *$CO/H_2$-TPSR.* A reduced catalyst was exposed to a CO and $H_2$ mixture and then flushed with He. The products of TPSR in a He stream were monitored by a mass spectrometer from room temperature to 770 K.

## 3. Results and discussion

### 3.1. CO HYDROGENATION ON SUPPORTED Fe–MnO CATALYSTS

The effect of supports on CO hydrogenation for light olefins is shown in table 1. It is clear that different supports result in different catalytic behaviors, especially in olefin selectivity, regardless of the same metal component and the same preparation condition. The selectivity to $C_2^=$–$C_4^=$ olefins on the Fe–MnO/MgO catalyst remained 68.3% at CO conversion of 78.6% after 1000 h on stream, but the selectivity to $C_2^=$–$C_4^=$ on the Fe–MnO/$Al_2O_3$ catalyst was only 13.2%.

The effect of temperature on the behavior of the Fe–MnO/MgO catalyst (under GHSV = 1000 $h^{-1}$) is outlined in fig. 1. The catalytic activity increases rapidly with reaction temperature and the selectivity to $C_2^=$–$C_4^=$ olefins exhibits a maximum at 590 K, and then decreases remarkably. The effect of temperature on catalytic reactivities of the supported Fe–MnO catalysts is different under different space velocities of syngas.

The effect of syngas space velocity on the reactivity of the Fe–MnO/MgO catalyst (at $T = 580$ K) is shown in fig. 2. With an increase in the space velocity, the selectivity to $C_2^=$–$C_4^=$ olefins exhibits a little increase while the catalytic activity clearly decreases. It is necessary to choose a proper reaction condition so that the yield of light olefins from syngas will be a maximum.

### 3.2. CO-TPD AND $H_2$-TPD

The CO-TPD spectra for the Fe–MnO/MgO, Fe–MnO/$Al_2O_3$ and Fe–MnO/$ZrO_2$ catalysts (fig. 3) illustrate that the supported catalysts have completely different CO adsorption/desorption behaviors. The CO-desorption peak appeared at a lower temperature for the Fe–MnO/$Al_2O_3$ catalyst, accompanying CO disproportionation on the catalyst surface. This means that the Fe–MnO/$Al_2O_3$ catalyst has a weaker capability for CO adsorption. The Fe–MnO/$ZrO_2$ catalyst is capable of a stronger CO adsorption than Fe–MnO/$Al_2O_3$, since the peak temperature

Table 1
The effects of the support on the catalytic performance of Fe–MnO catalyst for CO hydrogenation [a]

| Support | CO conv. | HC product distribution | | | | | | | Sel. $C_2^=$ – $C_4^=$ (wt%) |
|---|---|---|---|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $C_4H_8$ | $C_4H_{10}$ | |
| $Al_2O_3$ | 83.0 | 40.3 | 0.8 | 14.3 | 2.3 | 15.7 | 10.1 | 16.5 | 13.2 |
| $ZrO_2$ | 71.0 | 32.6 | 8.3 | 2.7 | 18.6 | 2.1 | 19.4 | 16.3 | 46.3 |
| MgO | 78.6 | 23.1 | 22.4 | 2.6 | 24.3 | 2.3 | 21.6 | 3.7 | 68.3 |
| $TiO_2$ | 69.4 | 28.1 | 15.1 | 3.6 | 22.5 | 3.2 | 18.8 | 8.7 | 56.4 |
| $SiO_2$ | 65.1 | 35.2 | 5.2 | 17.3 | 12.4 | 12.7 | 9.9 | 7.3 | 27.5 |

[a] Reaction condition: 593 K, 2.0 MPa, 2000 $h^{-1}$.

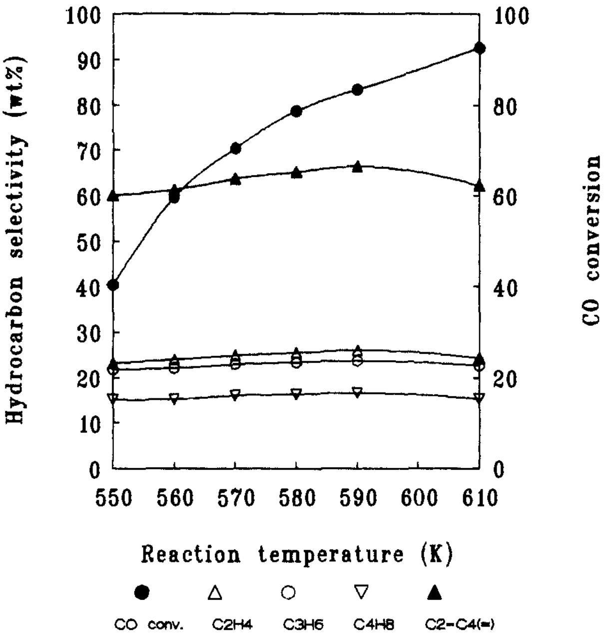

Fig. 1. Effect of reaction temperature on the behavior of the Fe–MnO/MgO catalyst.

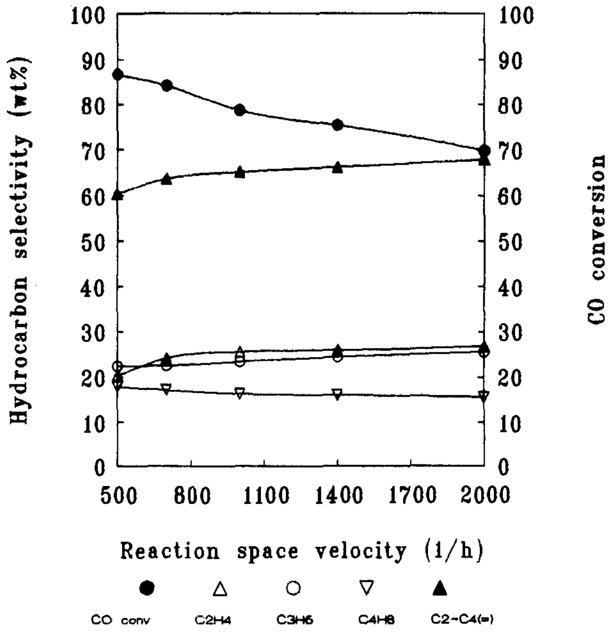

Fig. 2. Effect of reaction space velocity on the performance of the Fe–MnO/MgO catalyst.

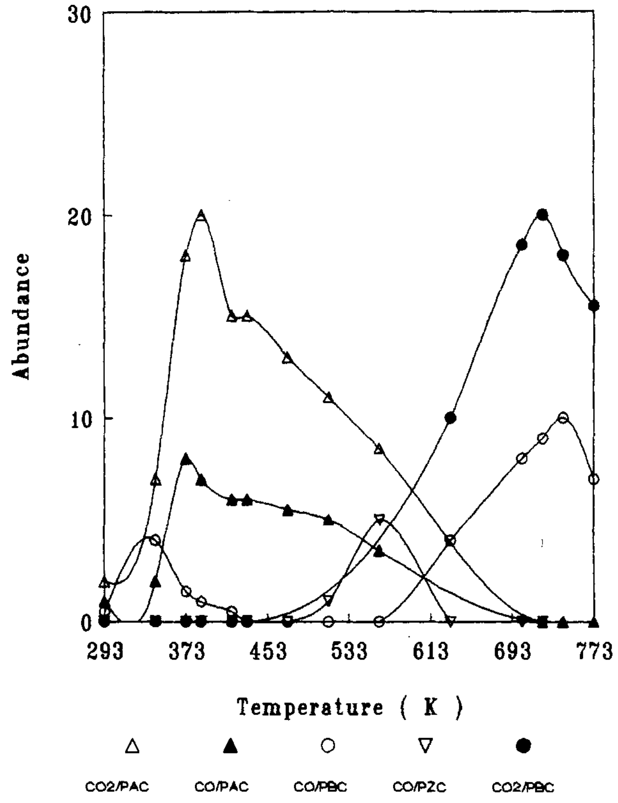

Fig. 3. CO-TPD profiles from the catalysts.

for CO desorption shifts to a higher temperature (570 K) without $CO_2$ being detected. This also suggested that no CO disproportionation takes place on the Fe–MnO/$ZrO_2$ surface. Two kinds of CO-adsorption states can be detected on the Fe–MnO/MgO surface. A small amount of weak CO adsorption desorbed at a lower temperature range, while a large amount of strong CO adsorption desorbed at a higher temperature range. Combining these results with that of CO hydrogenation, we suggest that the strong adsorption state of CO may play an important role for the formation of light olefins.

Fig. 4 shows the profiles of $H_2$-TPD on differently supported catalysts. The Fe–MnO/MgO catalyst exhibits a stronger capability for $H_2$ adsorption than the Fe–MnO/$ZrO_2$ and Fe–MnO/$Al_2O_3$ catalysts. Since the Fe–MnO/MgO catalyst is able to strongly adsorb CO, giving a high concentration of $C_{ad}$, and to strongly adsorb $H_2$, it avoids carbon deposition and has a long life time, and so it is favorable for the formation of light olefins.

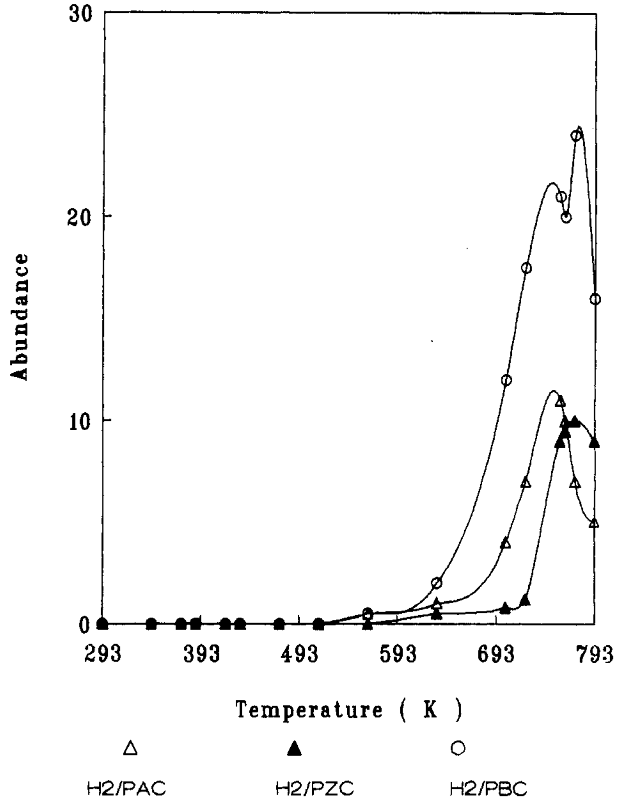

Fig. 4. $H_2$-TPD profiles from the catalysts.

### 3.3. CO/$H_2$-TPSR

CO/$H_2$-TPSR over supported Fe–MnO catalysts were performed to study the nature of CO hydrogenation. Figs. 5–7 show CO/$H_2$-TPSR results on the Fe–MnO/$Al_2O_3$, Fe–MnO/$ZrO_2$ and Fe–MnO/MgO catalysts respectively. For the Fe–MnO/$Al_2O_3$ catalyst (fig. 5), the formation of $C_2H_4$ and $C_3H_6$ is easier than the formation of $CH_4$ at about 340 K. According to its CO-TPD profile the adsorbed CO began to desorb at 340 K, while the adsorbed $H_2$ did not. The amount of $CH_4$ released increases while the amount of $C_2H_4$ and $C_3H_6$ released decreases with temperature. Therefore, the Fe–MnO/$Al_2O_3$ catalyst was not good for CO hydrogenation for the production of light olefins. For the Fe–MnO/$ZrO_2$ catalyst (fig. 6), both the selectivities of $C_2H_4$ and $C_3H_6$ and the amount of $CH_4$ appeared in an increasing trend with temperature till 710 K. When the temperature was higher than 710 K, the selectivity of light olefins decreased and the formation of $CH_4$ increased. During the whole TPSR, selectivities of $C_2H_4$ and $C_3H_6$ were much lower than that of $CH_4$. So the Fe–MnO/$ZrO_2$ catalyst was still not proper for the

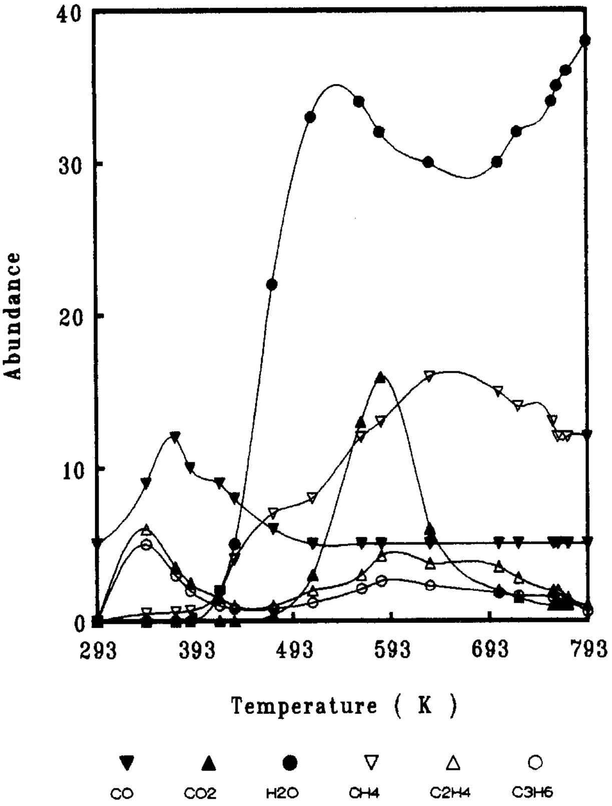

Fig. 5. CO/$H_2$-TPSR profiles from the Fe–MnO/$Al_2O_3$ catalyst.

production of light olefins from syngas. For the Fe–MnO/MgO catalyst (fig. 7), the TPSR spectra were quite different from the Fe–MnO/$Al_2O_3$ and Fe–MnO/$ZrO_2$ catalysts. Product of TPSR mainly was $CH_4$ with a little amount of $C_2H_4$ and $C_3H_6$ at lower temperatures. When the temperature was over 710 K, the selectivities of $C_2H_4$ and $C_3H_6$ increase rapidly, and then decrease with temperature. Combining with its CO-TPD result (fig. 3), we found that the most proper temperature favorable for the formation of light olefins on the Fe–MnO/MgO catalyst is just within the temperature range of CO desorption.

It is interesting to note that no $C_2H_6$ and $C_3H_8$ could be detected in the products released during the CO/$H_2$-TPSR on all three catalysts. We can, therefore, conclude that the primary products of CO hydrogenation are $CH_4$ and light olefins. The primary olefins will suffer severe secondary reactions on the catalyst surface producing $C_2H_6$, $C_3H_8$ and $C_{4+}$. It is important, therefore, to prohibit the secondary reactions of light olefins during the CO hydrogenation in order to achieve a high selectivity to light olefins.

Another interesting phenomenon is that a large amount of water is produced

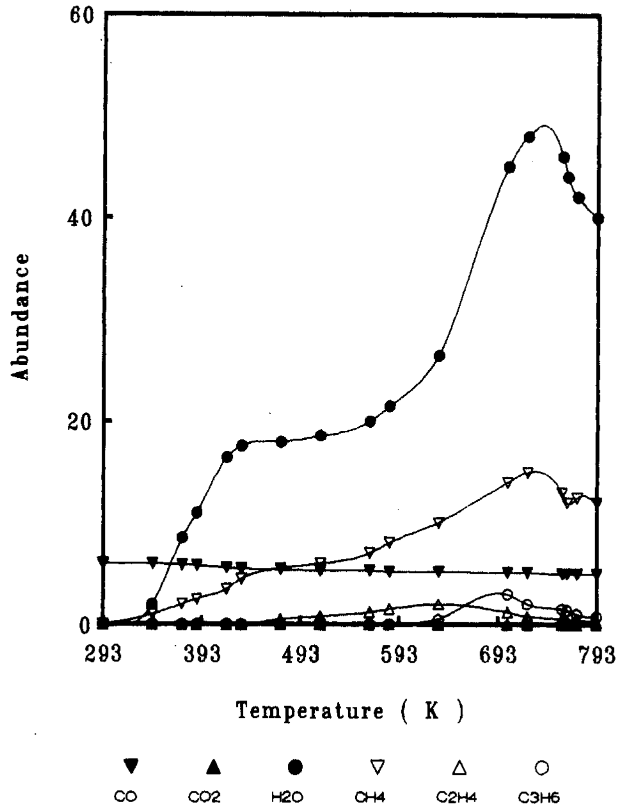

Fig. 6. $CO/H_2$-TPSR profiles from the Fe–MnO/$ZrO_2$ catalyst.

during $CO/H_2$-TPSR accompanying formation of $CO_2$ over Fe–MnO/$Al_2O_3$ (fig. 5) and Fe–MnO/MgO (fig. 7) catalysts, while for Fe–MnO/$ZrO_2$ catalyst, only $H_2O$ without $CO_2$ formed during $H_2/CO_2$-TPSR. The formation of $CO_2$ suggests the existence of water–gas-shift reaction over Fe–MnO/$Al_2O_3$ and Fe–MnO/MgO catalysts which is not observed over Fe–MnO/$ZrO_2$ catalyst.

## 4. Conclusions

(1) In order to produce light olefins selectively, the catalyst must have a strong capability for CO adsorption.

(2) Primary products of CO hydrogenation over the catalysts are $CH_4$, $C_2H_4$ and $C_3H_6$. In order to get a high selectivity to light olefins, it is important to prevent secondary reactions of light olefins and $CH_4$ formation during $CO/H_2$ reaction.

(3) The Fe–MnO/MgO catalyst (based on basic support) adsorbs CO strongly and therefore can selectively produce light olefins. The Fe–MnO/$Al_2O_3$ catalyst (based on acidic support) weakly adsorbs CO and is not a good catalyst.

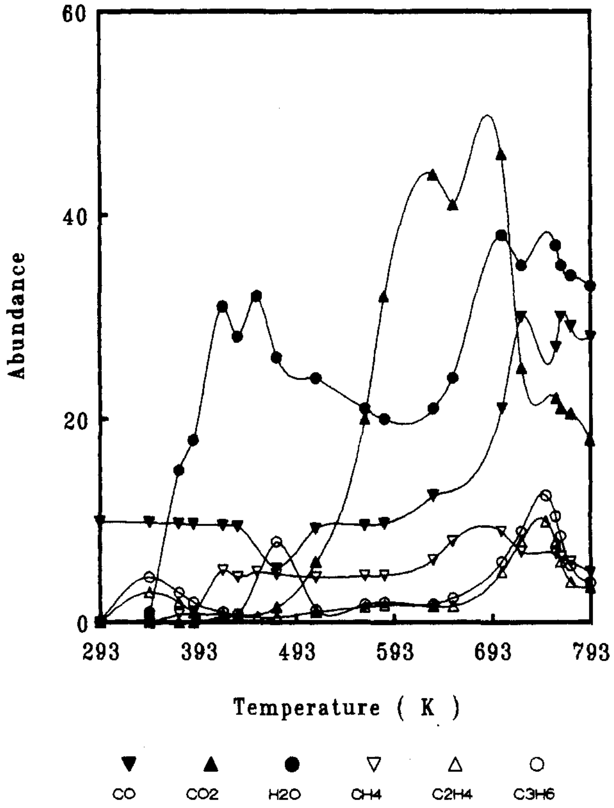

Fig. 7. $CO/H_2$-TPSR profiles from the Fe–MnO/MgO catalyst.

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