Promotion effect of K_2O and MnO additives on the selective production of light alkenes via syngas over Fe / silicalite-2 catalysts

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The addition of K_2O and MnO promoters enhances catalyst activity and selectivity to light alkenes during CO hydrogenation over silicate-2 (Si-2) supported Fe catalysts. The results of CO hydrogenation and CO-TPD, CO/H_2-TPSR, C_2H_4/H_2-TPSR and C_2H_4/H_2 pulse reaction over Fe/Si-2 catalysts with and without promoters clearly show that the MnO promoter mainly prohibits the hydrogenation of C_2H_4 and C_3H_6. Therefore, it enhances the selectivity to C_2H_4 and C_3H_6 products. Meanwhile further incorporating the K_2O additive into the FeMn/Si-2 catalyst leads to a remarkable increase in both the capacity and strength of the strong CO adspecies. These produce much more $[C_{ad}]$ via their dissociation and disproportionation at higher temperatures. This results in an increase in the CO conversion and the selectivity to light olefins. Moreover, the K_2O additive modifies the hydrogenating reactivity of $[C_{ad}]$ and suppresses the disproportionation of C_2H_4 that occurs as a side-reaction. Both K_2O and MnO promoters play key roles for enhancing the selective production of light alkenes from CO hydrogenation over Fe/Si-2 catalyst.

Keywords: Fe–MnO catalyst; silicalite-2; light alkenes; carbon monoxide

1. Introduction

Recently, research interest in heterogeneous catalytic CO hydrogenation has focused on the production of light alkenes. This reaction will provide an alternative route to produce basic chemical feed stocks such as ethylene and propylene [1,2]. Therefore, it is important from both the academic and practical points of view, to

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control the reaction pathway of CO hydrogenation to obtain desirable products with high selectivity. Usually, researchers selected a Fe-containing catalyst for the production of hydrocarbons via CO hydrogenation. Unfortunately, the reaction product follows the Flory-Schulz distribution ranging from CH_4 to hydrocarbons with much higher molecular weights. The addition of promoters and the use of different supports are two available approaches to remarkably change the reactivity and selectivity of CO hydrogenation. Much progress has been made in the selective CO hydrogenation for the production of light olefins from syngas. An unsupported iron catalyst, for example, promoted with alkali metal and manganese oxide, will result in a large increase in alkene yields [3,4]. Studies on supported iron catalyst also achieved improvement in the selective production of light alkenes from syngas [5,6]. Again, the supported Fe catalyst with the addition of alkali metal and MnO exhibited a good activity and selectivity [7,8].

In our previous study on the development of a new supported Fe catalyst, we have reported that a silicalite-2 (Si-2) zeolite supported Fe catalyst promoted by alkali metal and MnO additive displayed as high as 70% selectivity to light alkenes at 70% CO conversion, therefore the yield of light alkenes is about 49%. Moreover, this catalyst showed a good stability in its life test. However, the production of light alkenes from syngas with the necessary high reactivity and selectivity for its application in industry still remains a big challenge to catalytic chemists, since its lower price and the relative easiness of oil to handle and process. In an effort to further improve the activity and selectivity of the catalyst, we have studied the mechanism of the promotional effect of K_2O and MnO additives for the selective production of light alkenes via syngas over Si-2 supported Fe catalysts [9]. In this paper, we have focused on the evaluation of Si-2 supported Fe catalyst with different amounts of K_2O and MnO additives for the production of light alkenes from CO hydrogenation. We also use CO-TPD and COH_2-TPSR, $C_2H_4H_2$-TPSR as well as $C_2H_4H_2$ pulse reaction techniques in order to gain insight into the promotional effects of K_2O and MnO on the enhancement of the activity and selectivity of the Fe/Si-2 catalyst. By understanding the mechanism of the promotional effect, a new generation of K–Fe–Mn/Si-2 catalysts has been developed with the selectivity to C_2C_4 light olefins of about 70% and the CO conversion of about 90% can be maintained for longer than 200 h in a life test. The yield of light alkenes is about 63% compared to that of 49% with the previous K–Fe–Mn/Si-2 catalyst.

2. Experimental

2.1. CATALYST PREPARATION

Si-2 was synthesized as described in ref. [10]. Supported Fe–MnO catalysts were prepared by impregnating a solution with desirable amount of Fe^3 and Mn^n and K ions (as shown in table 1) onto Si-2 zeolite (with the addition of a binder)

Table 1
Chemical composition of Si-2 supported K–Fe–Mn catalysts

Catalyst No.	Composition of active element (wt%)			Support composition (wt%)	
	Fe	Mn	K	Si-2	binder
Fe-1	9.5	0.0	0.0	60.0	40.0
FeMn-2	9.4	1.2	0.0	60.0	40.0
FeMn-3	9.3	3.8	0.0	60.0	40.0
FeMn-4	9.6	9.5	0.0	60.0	40.0
KFeMn-5	9.4	9.7	1.2	60.0	40.0
KFeMn-6	9.4	9.5	5.2	60.0	40.0
KFeMn-7	9.5	9.6	8.3	60.0	40.0
KFe-8	9.4	0.0	8.5	60.0	40.0

under vacuum condition. Catalyst particles with size of 1.2 mm (diameter) ×1.5 mm (length) were dried at 400 K for 8 h and calcined at 800 K for 10 h. Catalysts were then reduced in H_2 at 700 K, 1.2 MPa, 2000 h^{-1} for several hours before CO hydrogenation [4,7]. The chemical compositions of the catalysts used in this paper were listed in table 1.

2.2. CO HYDROGENATION

The activity and selectivity of a catalyst were evaluated in a small continuous flow fixed-bed reactor which was made of stainless steel. Usually, the catalyst charge was 6 ml and the evaluation was performed under fixed reaction conditions. After a series of primary tests, the reaction parameters, such as reaction temperatures, gas space velocities as well as reaction pressures, were set as follows: reaction temperature: 620 K, pressure: 2.0 MPa, space velocity: 1000 h^{-1} and the molar ratio of $CO/H_2 = 1/2$. The tail gas was on-line separated and analyzed by gas chromatography with a TCD detector.

2.3. TEMPERATURE PROGRAMMED DESORPTION AND SURFACE REACTION

CO-TPD and CO/H_2- and C_2H_4/H_2-TPSR were carried out in a flow reactor system equipped with a TE-150 multichannel mass spectrometer and an IBM computer. Each desorption species was monitored and recorded by one channel of the TE-150 mass spectrometer at a set sensitivity which remained the same for all experiments. Therefore, the results were comparable. The recorded data were processed and stored using an IBM computer.

CO-TPD: 0.5 g catalyst, after being reduced in situ under H_2 at 720 K, was exposed to CO for 10 min at room temperature. It was then switched to a He stream and CO-TPD was performed from room temperature to 780 K at a heating rate of 16 K/min.

CO/H_2- and C_2H_4/H_2-TPSR: 0.5 g catalyst, after being reduced in situ, was exposed to CO or C_2H_4 for 10 min at room temperature. The gas flow was then switched to H_2, and CO/H_2- or C_2H_4/H_2-TPSR were carried out at a heating rate of 16 K/min. The reaction products and desorption species were monitored with a multichannel mass spectrometer.

2.4. THE PULSE REACTION OF C_2H_4/H_2

A catalyst, after being reduced under H_2 at 720 K, was used for the C_2H_4/H_2 (with the molar ratio of 1/1) pulse reaction in a He stream at 670 K. Reaction products were on-line separated and analyzed with gas chromatography.

3. Results and discussion

3.1. CO HYDROGENATION OVER K–Fe–Mn/Si-2 CATALYSTS

Table 2 lists the catalytic performances of CO hydrogenation over K–Fe–Mn/Si-2 catalysts for the production of light olefins. Over the unpromoted Fe-1 catalyst the selectivity to $C_2^=-C_4^=$ alkenes is 14.9% at the CO conversion of 76.3%. The addition of MnO promoter onto the Fe-1 results in an improvement in the selectivity to light alkenes. The selectivity to light alkenes is about 39% over the FeMn-4 catalyst. This is about 24% higher than that over the Fe-1 catalyst. While the formation of CH_4 and the CO conversion seem to be hardly affected by incorporating MnO additive as shown in table 2.

The addition of K_2O promoter onto the Fe-1 catalyst results in a remarkable improvement in many aspects, as we can see from table 2. The selectivity to light alkenes is about 56% over the KFe-8 catalyst. This is about 40% higher than that over the Fe-1 catalyst, as far as the selectivity to light alkenes is concerned. Moreover, the formation of CH_4 is obviously suppressed as we can see from table 2. In addition, there is a little increase in the CO conversion.

Table 2
Catalytic performance on K–Fe–Mn/Si-2 catalysts [a]

Catalyst	CO conv. (%)	Selectivity (wt%)							
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	$C_2^=-C_4^=$
Fe-1	76.3	48.9	4.2	17.2	5.6	9.7	5.1	9.3	14.9
FeMn-2	77.4	48.1	10.4	12.4	13.5	6.1	5.5	4.0	29.4
FeMn-3	76.9	46.6	13.8	7.9	15.5	3.8	7.2	3.2	36.5
FeMn-4	77.8	45.0	12.5	7.3	17.7	4.0	8.8	4.7	39.0
KFeMn-5	82.3	38.6	16.6	6.8	21.1	3.8	10.1	3.0	47.8
KFeMn-6	88.6	28.9	20.8	4.3	23.5	3.3	16.8	2.4	61.1
KFeMn-7	90.4	22.4	23.7	3.2	26.0	2.5	19.9	2.3	69.6
KFe-8	80.2	29.9	17.5	5.8	22.3	4.2	16.8	3.5	56.6

[a] Reaction conditions: 620 K, 2.0 MPa, 1000 h^{-1} and $CO/H_2 = 1/2$.

The addition of K_2O as a second promoter further enhances the activity and selectivity of the Fe–Mn/Si-2 catalysts, as shown in table 2. With increasing K_2O amount (from FeMn-4 to KFeMn-7 in table 2), the CO conversion increases from 77.8 to 90.4%, while the formation of CH_4 decreases from 45 to 22.4%. Selectivities for $C_2^=-C_4^=$ alkenes as high as 69.6% at the CO conversion of 90.4% can last as long as 200 h during the life test as shown in table 2 and fig. 1. Therefore, both K_2O and MnO and promoters are crucial and of significance for enhancing the activity and selectivity of the Fe/Si-2 catalyst.

3.2. THE EFFECT OF K_2O AND MnO ADDITIVES ON CO-TPD

Fig. 2 shows the CO-TPD profiles obtained on the Fe-1, FeMn-4 and KFeMn-7 catalysts. There are two desorption peaks for both CO and CO_2 desorption species that appear during CO-TPD, one located at the low temperature of about 343 K that corresponds to the weak CO adsorption, and another at the high temperature of at least 573 K that corresponds to the strong CO adsorption. The distinct feature over the KFeMn-7 and the FeMn-4 catalysts revealed with the CO-TPD profiles gives us a clear picture that helps us to understand the different function of K_2O and MnO promoters incorporated into the Fe-1 catalyst for the selective CO hydrogenation. First, the co-existence of CO and CO_2 implies that the reaction of CO disproportionation (the Boudouard reaction) takes place during CO-TPD over the tested catalysts, evolving CO and CO_2 while C_{ad} is deposited on

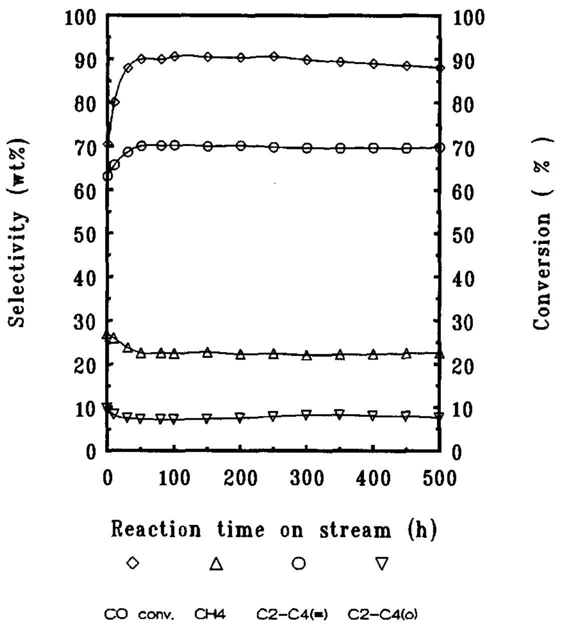

Fig. 1. The life test over the KFeMn-7/Si-2 catalyst.

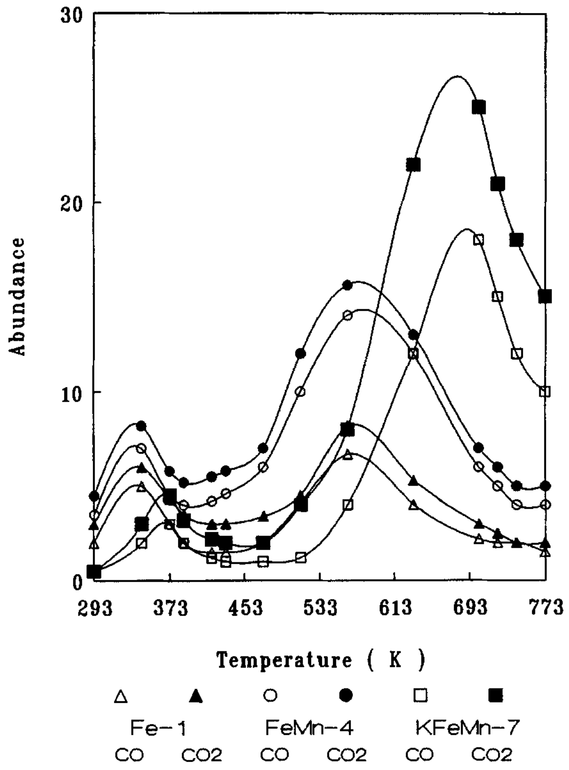

Fig. 2. The CO-TPD profiles obtained on the Fe-1, FeMn-4 and KFeMn-7 catalysts.

the catalyst surface. Secondly, the CO adsorption capacities at low and high temperatures are affected by the MnO promoter as shown in fig. 2. The desorption peak areas corresponding to the CO and CO_2 desorption on the FeMn-4 catalyst are much larger than on the Fe-1 catalyst. Since the two peak temperatures of the CO and CO_2 desorption on the FeMn-4 catalyst are almost the same as that on the Fe-1 catalyst, this means that the MnO promoter, once incorporated into the Fe-1 catalyst, only causes the CO adsorption capacity to increase remarkably.

When K_2O promoter was added into the Fe–Mn/Si-2 catalyst, we observed that both of the desorption peak temperatures shifted to higher temperatures, one from about 343 to about 373 K and the other from 573 to 683 K, as shown in fig. 2. Also the areas of the high temperature peaks for CO and CO_2 desorption increased significantly. The CO-TPD profiles illustrate that the KFeMn-7 catalyst adsorbs more CO and adsorbs it more strongly than the FeMn-4 catalyst does. We notice that, over the KFeMn-7 catalyst, the area corresponding to the CO_2-desorption peak at the high temperature is much larger than that of the CO-desorption peak at the high temperature. This is evidence that the KFeMn-7 catalyst favors CO disproportionation of the strongly adsorbed CO on the catalyst surface, resulting in an increase in both the C_{ad} concentration and the area of CO_2 desorption peak. There is evidence [11] that the subsequent hydrogenation of C_{ad} species is responsible for the formation of methane and ethylene. The higher the C_{ad} concentration is, the more favorable is the formation of ethene on the catalyst surface. So the functions of K_2O additive on the FeMn-4 catalyst are to enhance the capacity and the strength of CO adsorption, and to increase the reactivity of the strong CO adspecies.

Since the CO hydrogenation is performed at 620 K, we believe that the capacity for CO adsorption and the reactivity of CO adspecies at the high temperature are two key factors that are relevant for enhancing the light alkene production from syngas over a catalyst. Combining these TPD results with those of CO hydrogenation, we are able to discuss and explain what is the promotional effect of K_2O and MnO additives on the activity and especially, the alkene selectivity of the Fe-1 catalyst in terms of the enhancement of the capacity and strength of the CO adsorption at the high temperature.

The addition of MnO promoter on the Fe-1 catalyst causes an increase in proportion of the CO adsorption capacity at both low and high temperatures, but does not enhance the strength since the desorption peak temperatures remain the same on the FeMn-4 catalyst as it does on the Fe-1 catalyst. Therefore, MnO additive will affect neither the formation of methane nor the CO conversion. Later, we will show that the MnO additive inhibits the hydrogenation of ethylene via the study of the C_2H_4/H_2 pulse reaction. So the selectivity to light alkenes can increase without any obvious effect on the CO conversion and CH_4 formation after adding MnO promoter to the Fe-1 catalyst. Meanwhile a remarkable decrease in CH_4 formation and an obvious increase in CO conversion caused by adding K_2O promoter to the FeMn-4 catalyst can be attributed to the higher capacity and stronger strength of CO adsorption on the KFeMn-7 catalyst.

3.3. THE EFFECT OF K_2O AND MnO ADDITIVES ON THE PROFILES OF CO/H_2-TPSR

CO/H_2-TPSR over Si-2 supported Fe catalysts with K_2O and MnO promoters are performed to investigate the surface reaction of CO hydrogenation. Figs. 3, 4 and 5 show the profiles of CO/H_2-TPSR on the Si-2 supported Fe-1, FeMn-4 and KFeMn-7 catalysts, respectively. Again on all the tested catalysts, they evolve CO profiles with two peaks during CO/H_2-TPSR. These can be used to deduce what the functions are of the K_2O and MnO promoters. For both the Fe-1 and FeMn-4 catalysts the two peak temperatures are almost the same, one is about 373 K and the other is about 643 K. Compared with the peak temperatures of CO-TPD (one is about 343 K, the other is about 573 K), we know that the CO desorption is inhibited by the presence of H_2. Moreover, CH_4 and C_2H_6 are formed on both catalysts, starting at almost the same temperatures (353 K for CH_4 and 483 K for C_2H_6 respectively). The major differences appearing in the CO/H_2-TPSR are the areas corresponding to the formation of C_2H_4 and C_3H_6, starting from the same temperature of 583 K. These areas are much larger on the FeMn-4 catalyst than on the Fe-1 catalyst. At the same time the area corresponding to the formation of C_2H_6

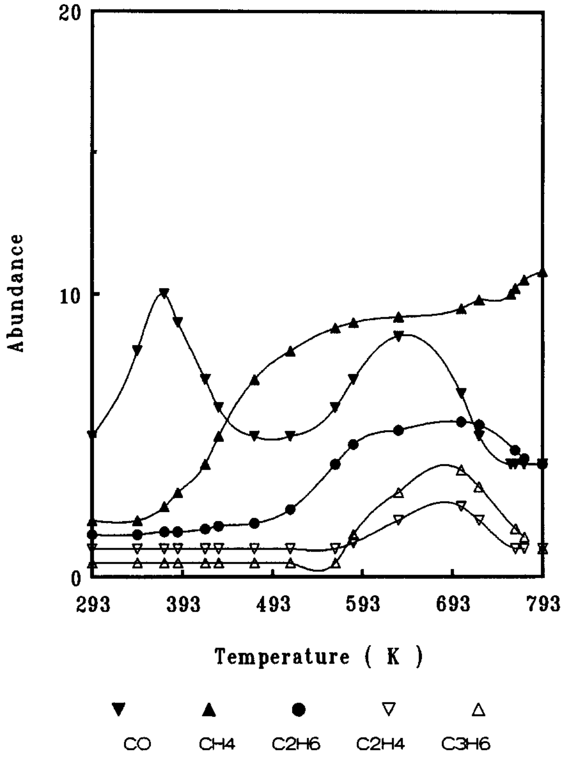

Fig. 3. The CO/H_2-TPSR profiles obtained on the Fe-1 catalyst.

on the FeMn-4 catalyst is less than that on the Fe-1 catalyst. This illustrates that the formation of C_2H_6 is inhibited by the addition of MnO promoter to the Fe-1 catalyst. This is in agreement with the results obtained during the evaluation of CO hydrogenation over the catalysts.

The CO/H_2-TPSR spectra obtained on the KFeMn-7 catalyst are quite different from those obtained on the Fe-1 and FeMn-4 catalysts. The peak temperature of the second peak in the CO spectrum is 693 K on the KFeMn-7 catalyst, which is about 50 K higher than for both Fe-1 and FeMn-4 catalysts. The main products of CO/H_2-TPSR over the KFeMn-7 catalyst are C_2H_4 and C_3H_6, with much lower amount of CH_4 and C_2H_6. The results again give us evidence that the K_2O additive plays an important role in inhibiting the formation of CH_4 and promoting the production of light alkenes.

3.4. THE EFFECT OF K_2O AND MnO ADDITIVES ON THE SECONDARY REACTION OF C_2H_4

It is generally accepted that the Fischer–Tropsch synthesis occurs on iron-containing catalysts by the following reaction sequences [12–15]:

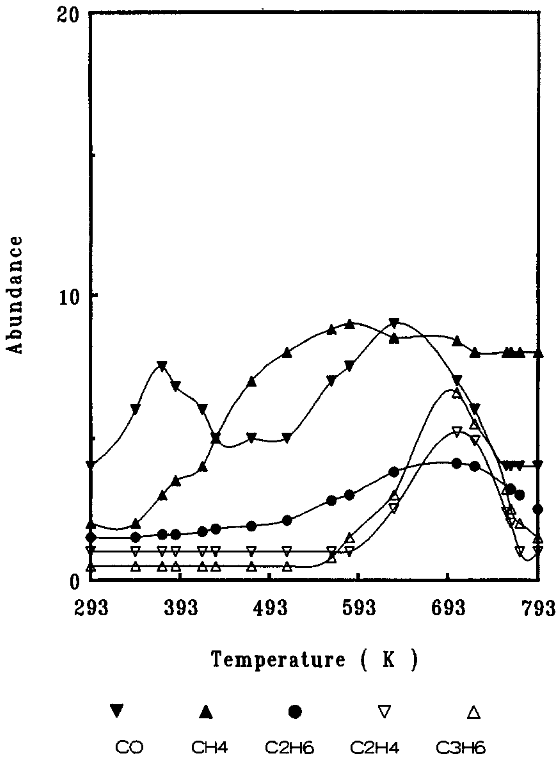

Fig. 4. The CO/H_2-TPSR profiles obtained on the FeMn-4 catalyst.

$$\mathrm{CO(g)} \rightarrow \mathrm{CO(s)} \tag{1}$$

$$\mathrm{H_2(g)} \rightarrow \mathrm{2H(s)} \tag{2}$$

$$\mathrm{CO(s)} \rightarrow \mathrm{C(s)} + \mathrm{O(s)} \tag{3}$$

$$\mathrm{O(s)} + \mathrm{H(s)} \rightarrow \mathrm{OH(s)} \tag{4}$$

$$\mathrm{OH(s)} + \mathrm{H(s)} \rightarrow \mathrm{H_2O(s)} \tag{5}$$

$$\mathrm{C(s)} + \mathrm{H(s)} \rightarrow \mathrm{CH(s)} \tag{6}$$

$$\mathrm{CH(s)} + \mathrm{H(s)} \rightarrow \mathrm{CH_2(s)} \tag{7}$$

$$\mathrm{CH_2(s)} + \mathrm{H(s)} \rightarrow \mathrm{CH_3(s)} \tag{8}$$

$$\mathrm{CH_3(s)} + \mathrm{H(s)} \rightarrow \mathrm{CH_4(g)} \tag{9}$$

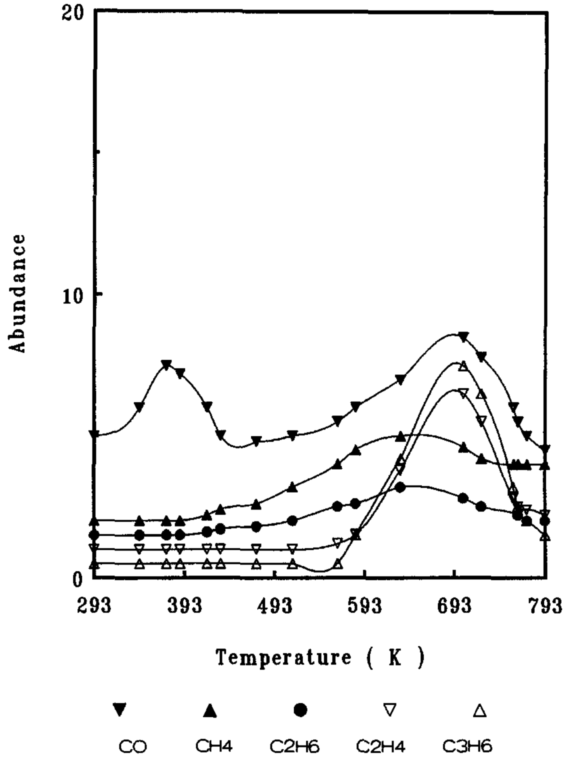

Fig. 5. The CO/H_2-TPSR profiles obtained on the KFeMn-7 catalyst.

$$CH_3(s) + CH_2(s) \rightarrow CH_3CH_2(s) \quad (10)$$

$$CH_3CH_2(s) + H(s) \rightarrow CH_3CH_3(g) \quad (11)$$

$$CH_3CH_2(s) \rightarrow CH_2CH_2(g) + H(s) \quad (12)$$

$$CH_3CH_2(s) + CH_2(s) \rightarrow CH_3CH_2CH_2(s) \quad (13)$$

$$C_nH_{(2n+1)}(s) + CH_2(s) \rightarrow C_{(n+1)}H_{(2(n+1)+1)}(s) \quad (14)$$

$$C_nH_{(2+1)}(s) + H(s) \rightarrow C_nH_{(2n+2)}(g) \quad (15)$$

$$C_nH_{(2n+1)}(s) \rightarrow C_nH_{2n}+H_2 \quad (16)$$

The C_2H_4 (and/or other olefin products), once produced, can undergo several side-reactions, such as hydrogenation, disproportionation and polymerization. These side-reactions will result in the formation of saturated and long-chain hydrocarbons [16]. Obviously, all of these side-reactions decrease the selectivity to light olefins. Therefore, on the basis of above mentioned reaction mechanism another

Table 3
The distribution of hydrocarbons of C_2H_4/H_2 reaction over K–Fe–Mn catalyst with different C_2H_4/H_2 ratio

Catalyst	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8
Fe-1	20.1	42.3	12.9	12.3	9.7	2.8
FeMn-2	19.4	44.1	9.4	16.6	7.2	3.3
FeMn-4	18.4	47.5	6.2	19.8	5.0	3.1
KFeMn-5	10.7	68.1	3.2	11.6	2.2	4.2
KFeMn-7	3.5	90.2	0.5	4.6	0.0	1.2

important factor improving the alkene selectivity is to bring side-reactions of light olefins occurring on the catalyst surface under control [12]. The C_2H_4/H_2 pulse reaction and C_2H_4/H_2-TPSR techniques were employed to investigate the effect of K_2O and MnO promoters on controlling the side-reactions of C_2H_4 formed during the CO hydrogenation. It is the KFeMn-7 catalyst that exhibits the largest capacity and the highest disproportionation activity, and the largest strengths for the CO adsorption among the tested catalysts, it should produce more C_{ad} adspecies that are responsible for the formation of light olefins.

Table 3 lists the results of C_2H_4/H_2 pulse reaction over Fe/Si-2 catalysts modi-

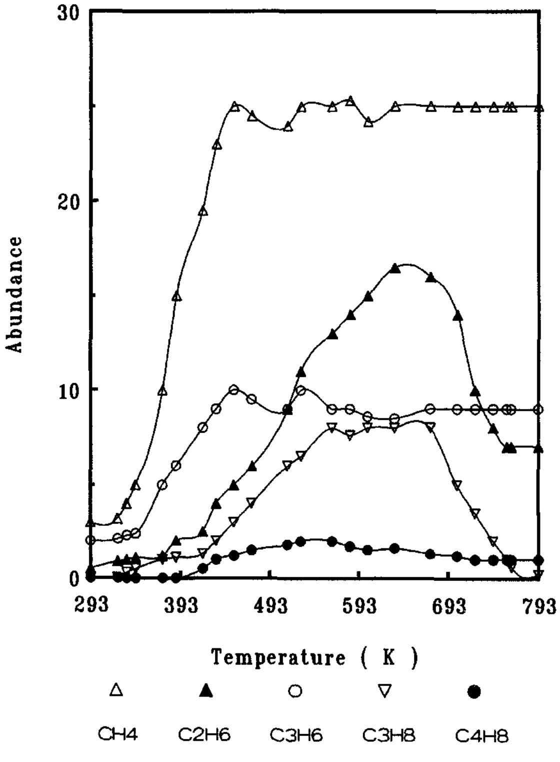

Fig. 6. The profiles of C_2H_4/H_2-TPSR obtained on the Fe-1 catalyst.

fied by K_2O and/or MnO promoters. With increasing amounts of the MnO additive, the reactivity of C_2H_4 hydrogenation on the catalyst decreases. We also observe decreases in C_3H_8 accompanied by increases in C_3H_6 formation while the CH_4 yield does not change much. This is evidence that the MnO promoter prohibits the hydrogenation of C_2H_4 and C_3H_6. We notice that there is a sharp decrease in the formation of CH_4 when K_2O is added, along with a distinct decrease in the reactivity of C_2H_4 hydrogenation. Clearly, the side-reactions of C_2H_4, such as C_2H_4 hydrogenation, C_2H_4 disproportionation and dimerization, were remarkably suppressed by K_2O addition. We conclude that the promotional effect of MnO additive mainly is in prohibiting the hydrogenation of C_2H_4 and C_3H_6 to C_2H_6 and C_3H_8, respectively, and no obvious effect on C_2H_4 disproportionation. The function of the K_2O additive is to suppress the C_2H_4 disproportionation to a large extent, giving rise to a marked decrease in C_2H_4 conversion and in the formation of CH_4 and C_3H_6. That means the K_2O additive decreases not only the formation of CH_4 during Fischer–Tropsch reaction, as evidenced by CO/H_2-TPSR, but also the disproportionation of C_2H_4 that is the primary product for the reaction studied. Therefore, on the basis of the above results and discussion, it is understandable that with the K–Fe–Mn/Si-2 catalyst such higher CO conversion and selectivity to light alkenes can be achieved.

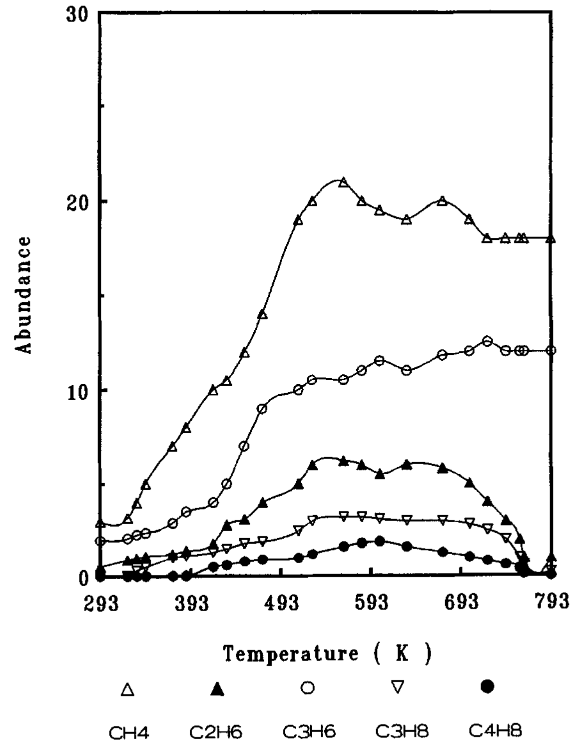

Fig. 7. The profiles of C_2H_4/H_2-TPSR obtained on the FeMn-4 catalyst.

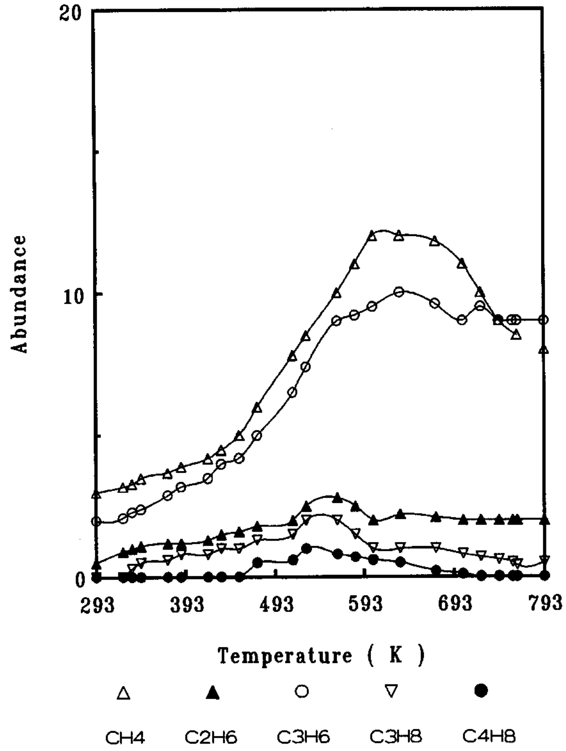

Fig. 8. The profiles of C_2H_4/H_2-TPSR obtained on the KFeMn-7 catalyst.

In the C_2H_4/H_2-TPSR experiments, the Fe-1 catalyst (fig. 6) produces large amounts of CH_4, C_2H_6, C_3H_6 and C_3H_8. The main products of C_2H_4/H_2-TPSR on the FeMn-4 catalyst are CH_4 and C_3H_6 with lower selectivities to C_2H_6 and C_3H_8 (fig. 7). This shows the inhibition of the hydrogenation reaction by MnO. With the KFeMn-7 catalyst, the secondary reactions of C_2H_4 are diminished even more. Less CH_4 and C_3H_6 were formed during the C_2H_4/H_2-TPSR over the KFeMn-7 catalyst (fig. 8). The results from C_2H_4/H_2-TPSR again confirm the above mentioned function of K_2O and MnO promoters.

4. Conclusions

(1) The activity of the Fe/Si-2 catalyst can be improved along with the selectivity to light alkenes for CO hydrogenation by the addition of K_2O and MnO promoters.

(2) The MnO additive mainly prohibits the hydrogenation of C_2H_4 and C_3H_6. This enhances the selectivity to C_2H_4 and C_3H_6 by decreasing the formation of C_2H_6 and C_3H_8.

(3) The addition of K_2O to the FeMn/Si-2 catalyst leads to the largest capacity

for and the highest strength of CO adsorption among the tested catalysts. We believe this is the reason for the observed increase in the CO conversion and alkene selectivity and for the decrease in the formation of CH_4. Moreover, the K_2O additive inhibits the disproportionation and hydrogenation of C_2H_4 occurring as a side-reaction on the catalyst. All of these factors enhance the selective production of light alkenes from CO hydrogenation.

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