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Deactivation of $NaCl/B_2O_3/Fe_2O_3$ catalysts and their improvement for the oxidative coupling of methane

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In the present work, the deactivation of the $NaCl/B_2O_3/Fe_2O_3$ catalysts was studied for the oxidative coupling of methane. Several techniques, such as XPS, XRD, SEM, H_2-TPR, and flow-reaction, were employed to examine the function of each catalyst component, and its change during the catalytic reaction. NaCl and B_2O_3 show a synergistic effect on the Fe_2O_3 surface. B_2O_3 modifies the oxidative activity of Fe_2O_3 and makes the first reduction peak of Fe_2O_3 shift from 490 to 750°C. The NaCl modified B_2O_3/Fe_2O_3 catalyst has high reduction rate, high activity and selectivity at about 750°C. It is demonstrated that the deactivation of the $NaCl/B_2O_3/Fe_2O_3$ catalysts is a complicated process, consisting of chloride loss, sodium change, B_2O_3 loss, silica deposition and catalyst sintering. The chloride loss enhances the surface basicity, which causes the silica deposition and sodium change, and aggravates the catalyst sintering. The silica deposition and catalyst sintering cause permanent deactivation. The B_2O_3 loss is not a direct reason for catalyst deactivation. NaCl crystal diluted $NaCl/B_2O_3/Fe_2O_3$ catalysts have a better stability. The deactivated catalyst has a more stable structure. When it is regenerated by impregnating with NaCl again, a more stable catalyst can be obtained.

Keywords: alkali chloride doped ferrous oxides; characterization; deactivation; oxidative activity; oxidative coupling of methane

1. Introduction

The large amounts of natural gas (mainly methane) found worldwide have led to extensive recent research programs in the area of direct methane conversion. Although many routes are conceptually possible, the oxidative coupling of methane (OCM) can directly convert methane to useful products without extensive energy consumption [1]. A wide range of materials, such as, alkaline-earth oxides, rare-earth oxides, transition metal oxides, and these doped with alkali metal compounds, were proved to be active catalysts for the oxidative coupling of methane [2,3].

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Having done a lot of work on OCM over alkali, alkaline-earth and rare-earth oxides [4–6], we faced a common problem how to increase catalyst activity and decrease reaction temperature. The oxidation of methane over transition metal oxides is always highly active, but its products are CO and CO_2, namely the products of deep oxidation. This is because transition metal oxides, especially Fe_2O_3, have high oxidative activity to alkanes [7–9]. The strong oxidative reactivity of CH_4 over transition metal oxides such as Fe_2O_3 indicated that the activation of the C–H σ bond over transition metal oxides is much easier than that over alkaline-earth and rare-earth oxides. Furthermore, the activation of the C–H σ bond is the key step of the OCM reaction. It is the reason that we use Fe_2O_3 as the main component of the OCM catalysts. However, we have to realize that the C_2 selectivity of Fe_2O_3 is poor. We expected to improve the C_2 selectivity of Fe_2O_3 by surface modification, namely making use of the interaction between Fe_2O_3 and other components to beget a synergistic effect, in order to get better C_2 yield. Professor Amenomiya also pointed out that there was considerable untapped potential in the use of transition metal oxides or composite oxides systems for the OCM [2]. Our results on the OCM over $NaCl/B_2O_3/Fe_2O_3$ proved that idea and a synergistic effect of NaCl and B_2O_3 on Fe_2O_3 was observed.

In our previous paper [10], we have given a more detailed discussion of the synergistic effect of NaCl and B_2O_3 on Fe_2O_3, the reaction mechanism and the active sites on the catalyst surface. In this paper, the deactivation of the $NaCl/B_2O_3/Fe_2O_3$ catalysts will be discussed.

The catalyst stability is an important criterion for practical purpose because the oxidative coupling of methane is a typical high temperature reaction at about 600–800°C. Several simple catalysts can undergo the 500 h life-test [11], but their selectivity and yield are lower than the commercial need. The addition of alkali compounds, especially, alkali metal chlorides, can enhance the activity and the ethylene selectivity. The shortage of the alkali metal compound doped catalysts is their deactivation [12–14].

In this paper, the deactivation of the $NaCl/B_2O_3/Fe_2O_3$ catalysts was studied. Several techniques, such as flow-reaction, XPS, XRD, SEM, and H_2-TPR, were employed to examine the function of each catalyst component, and its change during the catalytic reaction. It was found that the catalyst deactivation is a complicated process, comprised of chloride loss, sodium changing, B_2O_3 loss, silica deposition and catalyst sintering. These processes are closely related to each other. Methods to decrease the catalyst deactivation were suggested.

2. Experimental

2.1. CATALYST PREPARATION

The catalysts were prepared by two-step impregnation: (a) Known quantities of Fe_2O_3 were impregnated with H_3BO_3 solutions to obtain the B_2O_3/Fe_2O_3 samples with the B/Fe atomic ratio from 0, 0.01 to 0.3 (labeled as F100, FB01–FB30). (b) Then the B_2O_3/Fe_2O_3 samples were impregnated with NaCl solutions to obtain the $NaCl/B_2O_3/Fe_2O_3$ catalysts with Na/Fe atomic ratio of 0.25 (labeled as FN25, FBN0125–FBN3025). Samples at different stages of preparation, different periods of reaction and different ways of treatment were collected in order to examine the function of each catalyst component and its change during the catalytic reaction.

2.2. FLOW-REACTION

The catalytic reaction was performed in a conventional fixed-bed reactor operated in flow mode at atmospheric pressure. The general reaction conditions were: $T = 750°\mathrm{C}$, $\tau = 0.24$ g s cm^{-3}, $P_{CH_4}/P_{O_2} = 4$, $P_{CH_4} = 32$ kPa, and balanced to atmospheric pressure by helium. The reactant and product analyses were performed by on-line gas chromatography (GC) with a thermal conductivity detector and carbon zeolite columns.

2.3. XPS, XRD, SEM AND H_2-TPR CHARACTERIZATIONS

XPS data were obtained on a VG ESCALAB MKII photoelectron spectrometer using Al K_α X-ray excitation ($h\nu = 1486.6$ eV). The experimental resolution was better than 0.1 eV. The charge effect was corrected by referring to the 1s level of the background carbon at a binding energy of 284.6 eV.

XRD data were obtained on a Rigaku D/Max-rB X-ray diffractometer using a copper target at 40 kV × 100 mA and scanning speed of 8°/min.

SEM pictures were obtained on a KyKy-1000B scanning electron photomicrograph after the samples were plated by gold.

H_2-TPR profiles were recorded at a programmed temperature velocity of 16°C/min after the samples were treated in Ar flow at 700°C for 30 min.

3. Results and discussion

3.1. FUNCTIONS OF THE CATALYST COMPONENTS

In the flow-reaction, pure Fe_2O_3 (F100) as a catalyst has high activity but produces only CO_2, B_2O_3/Fe_2O_3 (FB20) has poor activity and selectivity. NaCl/Fe_2O_3 (FN25) has high activity but poor selectivity. When 8 wt% B_2O_3 was ground with NaCl as catalyst (BN*), the C_2 hydrocarbon selectivity is high, but its activity is quite low. Only NaCl and B_2O_3 co-modified Fe_2O_3 catalyst (FBN1525) has high activity and selectivity (table 1). The catalyst performance becomes better as the B_2O_3 content increases. When the additive approaches 15 at% B_2O_3, the C_2

Table 1
Performances of the modified Fe_2O_3 catalysts [a]

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)
	CH_4	O_2	CO	CO_2	C_2H_4	C_2	C_2
F100	13.5	100	0	100	0	0	0
BN*	1.2	2	0	2.1	23	98	1.2
FB20	5.9	24	49.8	10.0	4.8	40.2	2.4
FN25	18.2	100	0.5	70	15.7	29.1	5.4
FBN0125	27.7	–	0.2	50.7	37.0	49.1	13.6
FBN0525	24.2	–	12.5	21	49	66.5	16.1
FBN1025	22.1	–	18.7	5.5	54.6	75.8	16.8
FBN1525	22.7	–	18.2	5.5	58.1	76.3	17.4
FBN2025	21.4	61	18.8	5.8	56.9	75.5	16.1
FBN3025	19.9	–	21.5	6.0	56.0	65.2	13.0

[a] $T = 750°C$, $\tau = 0.21$ g s cm^{-3}, $P_{CH_4}/P_{O_2} = 4$, $P_{CH_4} = 32$ kPa, except for BN*. BN* denotes 8 wt% B_2O_3/NaCl under reaction conditions of $T = 750°C$, $\tau = 1.20$ g s cm^{-3}, $P_{CH_4}/P_{O_2} = 4$, and $P_{CH_4} = 32$ kPa.

hydrocarbon yield and selectivity reach their maxima, 17 and 76%, respectively (fig. 1).

In the H_2-TPR profiles of the modified Fe_2O_3 catalysts (fig. 2), pure Fe_2O_3 (F100) has two reduction peaks at about 490 and 780°C, respectively. The addition of B_2O_3 adjusts the oxidative activity of Fe_2O_3. When the additive is 15 at% B_2O_3

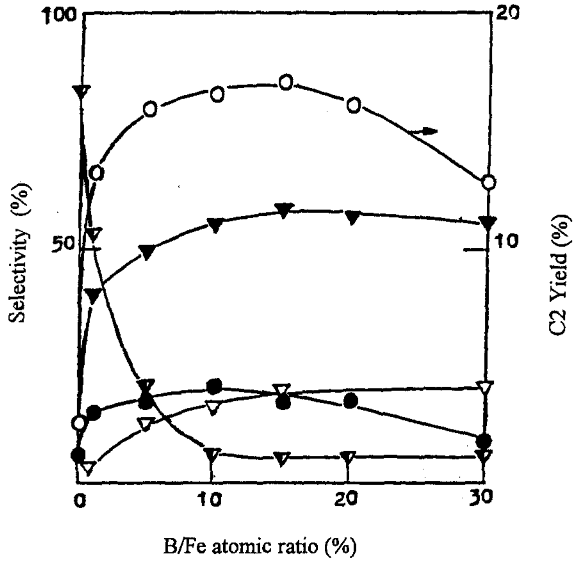

Fig. 1. Optimum amount of B_2O_3 in modified Fe_2O_3 catalysts. (○) C_2 yield, (▼) C_2H_4 selectivity, (●) C_2H_6 selectivity, (▽) CO selectivity, (▼) CO_2 selectivity. NaCl/B_2O_3/Fe_2O_3 catalysts with 25 at% Na/Fe, $T = 750°C$, $\tau = 0.24$ g s cm^{-3}, $P_{CH_4}/P_{O_2} = 4$, $P_{CH_4} = 32$ kPa.

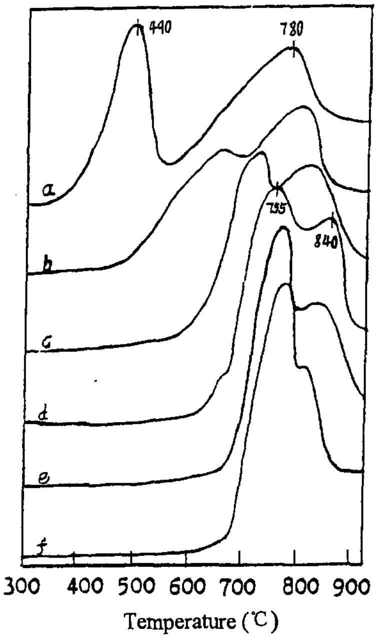

Fig. 2. H_2-TPR profiles of the modified Fe_2O_3 catalysts. (a) F100, (b) FN25, (c) FBN0525, (d) FB15, (e) FBN1525, (f) FBN3025.

(FB15), the two reduction peaks shift to higher temperatures, at about 755 and 860°C, respectively. NaCl also has some effect on the oxidative activity of Fe_3O_3 (FN25), but its oxidative activity is still high. The modification of B_2O_3/Fe_2O_3 by NaCl (FBN1525) makes the first reduction peak become more narrow and higher comparing with FB15. The narrow peak width indicates that the NaCl/B_2O_3/Fe_2O_3 catalyst has high reduction velocity at about 750°C. The width of the first peak becomes more narrow as the B_2O_3 content increases. When 15 wt% B_2O_3 is added the width and height of the first peak reach their maxima.

The reduction properties of the modified Fe_2O_3 catalysts well explain the catalytic performance. Pure Fe_2O_3 has high oxidative activity. The addition of B_2O_3 suppresses the oxidative activity of Fe_2O_3, but no new active species are formed, thus its activity and selectivity are both poor. NaCl cannot inhibit the deep oxidation capability of Fe_2O_3. When NaCl and B_2O_3 co-modify Fe_2O_3, the catalyst has high activity and selectivity, and this catalyst has high reduction velocity. The synergic effect of NaCl and B_2O_3 on Fe_2O_3 was described elsewhere [10].

3.2. EFFECT OF CHLORIDE AND ITS LOSS

Chloride containing catalysts have high ethylene selectivity. Several papers [15–31] described the significance of chloride and believed that chloride participates in the methane activation and coupling processes. In this paper, it is shown that the cation, especially the matching of the cation and anion in the salt doped oxide catalysts, is critical to the catalytic performance. The performances of the sodium containing salts and the chloride containing salts modified B_2O_3/Fe_2O_3 catalysts are given in table 2. $Na_2B_2O_7$ doped catalyst has very low activity. The activities and selectivities of the Na_2CO_3 and $Na_2P_2O_7$ doped catalysts, or the $CaCl_2$ and $LaCl_3$ doped catalysts, are relatively low. Only NaCl doped B_2O_3/Fe_2O_3 catalyst has high activity and selectivity.

In the flow-reaction, pulsing CH_2Cl_2 into the feed gas, pure Fe_2O_3 having high activity, produces also mainly CO_2 and some CO. The activity of B_2O_3/Fe_2O_3 becomes a little better after the CH_2Cl_2 injection, but the product is mainly CO. The activity and selectivity of the $Na_2O/B_2O_3/Fe_2O_3$ catalyst increase significantly after the CH_2Cl_2 injection, and maintain for more than 30 min, but return to the original levels 1 h later. The same changes were observed when the CH_2Cl_2 injections were repeated. This shows that (a) chloride is chemisorbed on the catalyst surface, (b) the chemisorbed chloride improves the catalyst performance, and (c) the chemisorbed chloride is lost during the reaction. Those results agree with earlier work [32–34]. From the different effects of CH_2Cl_2 on the modified Fe_2O_3, it is noted that the existence of sodium is significant. The chemisorption of chloride on the catalyst surface was also proved by XPS examination of the samples after CH_2Cl_2 injection (fig. 3). Sugiyama and co-workers also prove that by using XPS [25,32,33].

The most serious problem of the chloride containing catalysts is their deactivation. In the published papers [15–31], this is attributed to the loss of chloride during reaction. Using XPS to follow the deactivation processes it is noted that the surface concentration of chloride decreases initially by 12.5% but the CH_4 conversion and C_2 selectivity also decrease by 7.2 and 5.4% respectively during the first 10 h of reaction. However, after 40 h of reaction, the surface concentration of chloride

Table 2
Performances of different salts modified catalysts

Salt	Conversion of CH_4 (%)	Selectivity (%)				Yield (%) C_2
		CO	CO_2	C_2H_4	C_2H_6	
NaCl	27.9	22.0	7.3	60.3	10.5	19.7
LiCl	24.1	26.3	17.6	53.0	3.0	13.5
$CaCl_2$	16.8	44.0	26.3	19.0	10.7	5.0
$LaCl_3$	4.3	–	51.3	15.5	33.2	2.1
Na_2O	15.2	30.1	21.4	12.1	36.4	7.4
Na_2CO_3	11.5	22.1	40.2	9.5	28.2	4.3
$Na_4P_2O_7$ [a]	12.7	21.6	63.8	3.9	10.7	1.9
$Na_2B_2O_7$ [a]	2.1	54.2	27.5	5.2	13.1	0.4

[a] Salts were added to Fe_2O_3 directly. Other salts were added to B_2O_3/Fe_2O_3. $T = 750°C$, $\tau = 0.24$ g s cm^{-3}, $P_{CH_4}/P_{O_2} = 4$, $P_{CH_4} = 32$ kPa.

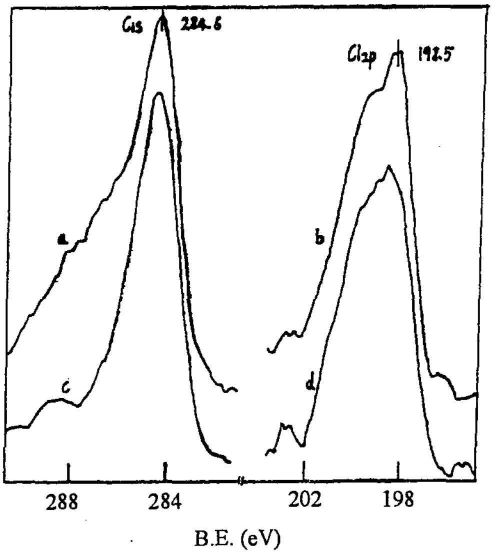

Fig. 3. XPS spectra of FB15 after CH_2Cl_2 treatment. (a) C 1s, (b) Cl 2p, treated at 25°C and 10^{-6} Torr. (c) C 1s, (d) Cl 2p, treated at 600°C and 10^{-6} Torr.

decreases by 62.9%, and CH_4 conversion and C_2 selectivity decrease by 57.4 and 17.6% respectively (table 3). In order to compensate for the chloride loss, CH_2Cl_2 was added to the feed gas, but no evident effect was observed on the catalyst deactivation. These imply that the catalyst deactivation is not simply due to the chloride loss. The chloride loss is, nevertheless, one of the important deactivation factors; e.g., about 20% of chloride on FBN1025 catalyst was lost as HCl after 40 h of reaction.

3.3. EFFECT OF SODIUM AND ITS CHANGES

The significant effect of sodium on the catalyst performance is evident. XPS data show that the surface sodium concentration remains constant during the first 10 h of reaction. However, it decreases by 55.0% after 40 h of reaction (table 3). It is therefore suggested that sodium change is another factor causing the catalyst

Table 3
Changes of surface composition and catalytic performance [a]

Reaction time (h)	Conv. of CH_4 (%)	Sel. to C_2 (%)	Yield of C_2 (%)	Surface composition (%)					
				O	Fe	Cl	B	Na	Si
0.5	29.1	65.3	19.0	34	8.1	24	35	4.0	–
10	27.0	61.8	16.7	28	8.2	21	23	4.0	15
40	12.4	53.8	6.7	35	4.4	8.9	10	1.8	40

[a] FBN1025 catalyst, $T = 750°C, \tau = 1.2$ g s cm^{-3}, $P_{CH_4}/P_{O_2} = 4$, $P_{CH_4} = 32$ kPa.

deactivation [13,35–37]. In a study of the deactivation of Li/MgO catalyst, Kaminsky [12] discovered that it is due to the lithium loss through the evaporation of LiOH, and the formation of Li_2SiO_3 or $LiAlO_2$.

On the NaCl/B_2O_3/Fe_2O_3 catalysts, the surface sodium loss occurs also through two ways, i.e., the evaporation of NaCl or NaOH, which can be detected in the reactor downstream the catalyst bed, and the formation of $Na_2FeSi_2O_6$, which can be detected by XRD in the FBN1025 catalyst after 40 h reaction (fig. 4). The silica is deposited from the corrosion of the quartz reactor wall. NaCl/B_2O_3/Fe_2O_3 catalysts do not directly react with quartz at the reaction temperature. As the chloride is lost, the surface basicity increases, which then causes the corrosion of the quartz reactor wall. This chain process would be general in the deactivation of alkali metal chloride containing catalysts.

3.4. EFFECT OF B_2O_3 AND ITS LOSS

The effect of B_2O_3 is to inhibit the oxidative activity of Fe_2O_3. The addition of B_2O_3 does not create new active sites. Thus the activity of B_2O_3/Fe_2O_3 (FB15) is low. NaCl/Fe_2O_3 (FN25) without modification by B_2O_3 has a high deep oxidation activity. Only NaCl doped B_2O_3/Fe_2O_3 catalyst (FBN1525) has high activity and selectivity (table 1). It is demonstrated elsewhere [38] that B_2O_3 and NaCl have a synergistic effect on the Fe_2O_3 surface, which results in the high activity and selectivity.

From fig. 1 it is seen that the optimum content of B_2O_3 is 15 at%. The catalyst with this B_2O_3 content has a high reduction rate and good catalytic performance. This effect can be understood from the XPS data (fig. 5). After 200 min reaction,

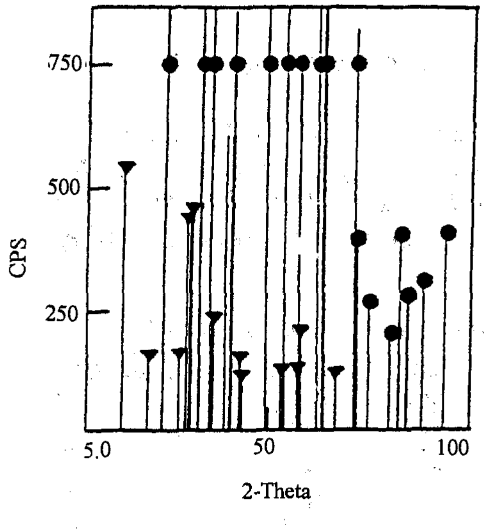

Fig. 4. A new formed compound detected by XRD. (▼) $NaFeSi_2O_6$, (●) Fe_2O_3, FBN1025 catalyst after 40 h of reaction.

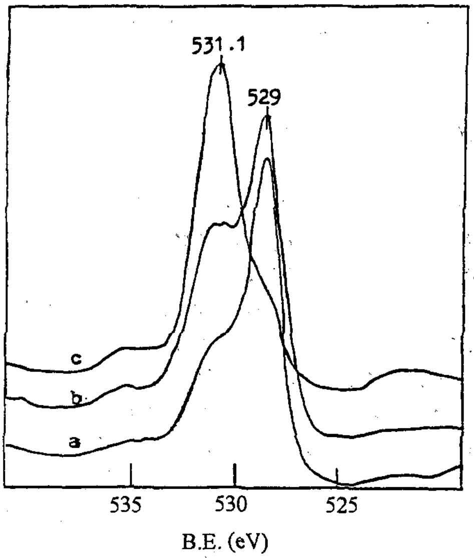

Fig. 5. O 1s XPS spectra of FBN catalysts. (a) FBN0125, (b) FBN1025, (c) FBN3025, after 200 min of reaction.

the lattice oxygen (BE 529 eV) is the major oxygen species on the surface of the FBN0125 catalyst, which has high activity but low C_2 selectivity. On the surface of FBN1025, another surface oxygen species (BE 531.1 eV) modifies the property of the lattice oxygen. This results in better catalytic performance. When the additive oxygen becomes dominant, e.g. on the FBN3025 catalyst, the total activity is quite low (table 1, fig. 5). The C 1s XPS data indicated that there were no carbonates existing over reacted FBN catalysts. So, the O 1s XPS peak at BE 531.1 eV is not due to the existence of carbonates but attributable to a mixture of different species including OH^-, O^-, O_2^{2-} [39].

B_2O_3 is a low melting-point oxide (m.p. 450°C). Its evaporation at the reaction temperature is unavoidable. XPS data show that the B_2O_3 loss during the reaction is serious (table 3). The deposition of silica also causes the B_2O_3 loss. Using XPS to observe the deactivation processes it is noted that the surface concentration of B decreases from 35 to 23%, while that of Si increases from 0 to 15% during the first 10 h reaction. Furthermore, the surface concentration of B decreases to 10% while that of Si increases to 40% (table 3).

3.5. CATALYST SINTERING

The oxidative coupling of methane is a typical high temperature reaction at about 600–800°C. The catalyst sintering is expected, especially for the alkali metal compounds doped catalysts. SEM shows that the sintering of the NaCl/B_2O_3/Fe_2O_3 catalysts is serious, i.e., the catalyst crystals grew larger during the reaction.

The silica deposition would aggravate the catalyst sintering, which causes the permanent catalyst deactivation.

3.6. IMPROVEMENT OF THE CATALYST ACTIVITY

The deactivation of $NaCl/B_2O_3/Fe_2O_3$ catalysts is a complicated process, comprised of chloride loss, sodium changing, B_2O_3 loss, silica deposition and catalyst sintering. These processes are closely related to each other, e.g., the chloride loss increases the surface basicity, which causes the silica deposition and the sodium change, then aggravates the catalyst sintering. The silica deposition and catalyst sintering cause permanent deactivation. The component loss can be recovered by adding them again. The B_2O_3 loss is special to the deactivation. The effect of B_2O_3 is to inhibit the oxidative activity of Fe_2O_3. The B_2O_3 loss itself should enhance the catalyst activity with the sacrifice of selectivity. Thus the B_2O_3 loss is not a direct reason for the catalyst deactivation. But the B_2O_3 loss and the silica deposition would change the active sites formed by the synergistic effect between NaCl and B_2O_3, and then lead to catalyst deactivation.

It would be difficult to avoid the deactivation of the alkali metal chloride doped catalysts. In published papers [13,14,16,17,19–31], chloride containing organic compounds, e.g. bichloromethane, were added to the feed gas. This can compensate the chloride loss on some catalysts. Because the organic compounds decompose to CO, its concentration should be limited. On the $NaCl/B_2O_3/Fe_2O_3$ catalysts the addition of CH_2Cl_2 to the feed gas does not show evident effect on the original rapid catalyst deactivation.

To inhibit the catalyst sintering and chloride loss, the FBN1025 catalyst was ground with NaCl to prepare a NaCl diluted catalyst. Its activity and stability are significantly improved (fig. 6). The activity reaches a stable level after 1 h which was maintained for more than 10 h with a high ethylene selectivity.

The deactivated FBN1025 catalyst was regenerated by impregnating with NaCl again. It is shown that the regenerated catalyst has high stability and selectivity (fig. 7). The methane conversion and C_2 hydrocarbon selectivity maintain at 15 and 82%, respectively, at the reaction conditions: $T = 750°\mathrm{C}$, $\tau = 0.24$ g s cm^{-3}, $P_{CH_4}/P_{O_2} = 4$ and $P_{CH_4} = 32$ kPa. The high stability of the regenerated catalyst would be due to the slow catalyst re-sintering and the slow silica re-deposition. After the first run, the deactivated catalyst has a more stable structure, from which a more stable catalyst can be obtained.

4. Conclusion

Pure Fe_2O_3 has a high oxidation activity. NaCl and B_2O_3 have a synergistic effect on the Fe_2O_3 surface. B_2O_3 inhibits the oxidative activity of Fe_2O_3, and makes the first reduction peak of Fe_2O_3 shift from 490 to 750°C. The NaCl modi-

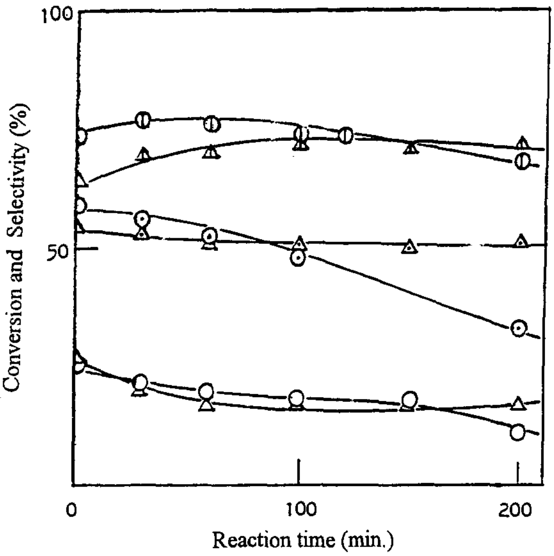

Fig. 6. Effect of NaCl dilution on the performance. (○) CH_4 conversion, (⊙) C_2H_4 selectivity, (⦶) C_2 selectivity, FBN1025 catalyst. (△) CH_4 conversion, (◬) C_2H_4 selectivity, (◬) C_2 selectivity, NaCl diluted FBN1025 catalyst, $T = 750°C$, $\tau = 1.2$ g s cm^{-3}, $P_{CH_4}/P_{O_2} = 4$, $P_{CH_4} = 32$ kPa.

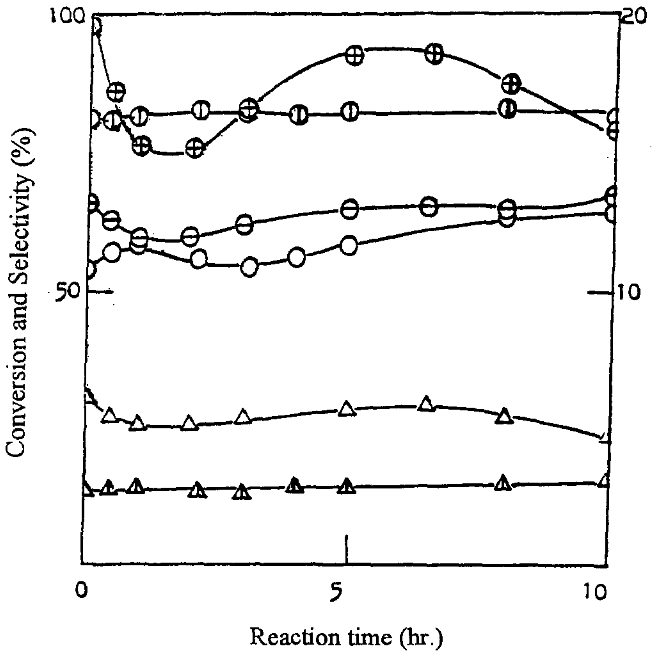

Fig. 7. Stabilities of the FBN1025 and reactivated FBN1025 catalysts. (△) CH_4 conversion, (⊖) C_2 selectivity, (⊕) C_2 yield, FBN1025 catalyst. (◬) CH_4 conversion, (⦶) C_2 selectivity, (○) C_2 yield, reactivated FBN1025 catalyst.

fied B_2O_3/Fe_2O_3 catalyst has a high reduction rate, high activity and selectivity at about 750°C.

The deactivation of the $NaCl/B_2O_3/Fe_2O_3$ catalysts is a complicated process, consisting of chloride loss, sodium changing, B_2O_3 loss, silica deposition and catalyst sintering. These processes are closely related to each other. The chloride loss enhances the surface basicity, which causes the silica deposition and sodium change, and then aggravates the catalyst sintering. The silica deposition and the catalyst sintering cause permanent deactivation. The B_2O_3 loss is not a direct reason for catalyst deactivation.

NaCl crystal diluted $NaCl/B_2O_3/Fe_2O_3$ catalysts have better stability. The deactivated catalyst has a more stable structure. When it is regenerated by impregnation with NaCl again, a more stable catalyst can be obtained.

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