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Hydrogenation of Carbon Monoxide to Form Light Olefins over an Iron-modified Crystalline Silica

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Synopsis. Iron-modified crystalline silicas prepared from an Fe(II) compound were more active than those prepared from an Fe(III) compound. The (C_2H_4+C_3H_6) selectivity of the former was lower than that of the latter. By the addition of alkaline earth metals, the (C_2H_4+C_3H_6) selectivity of the catalysts prepared from the Fe(II) compound increased remarkably.

An intensive research effort is now being directed towards the development of highly selective Fischer-Tropsch catalysts. Recently, there has been considerable interest involving the use of zeolites supports for such catalysts.[1—3] Among these zeolite-based catalysts are the modified crystalline silica catalysts in which a portion of the silicon atoms in the crystal lattice were replaced by iron, ruthenium *et al.*[4—7] These catalysts have improved the product distribution.

From this point of view, the authors have also prepared zeolite-based catalysts modified with iron.[8] In this paper the hydrogenation of CO over such modified crystalline silica catalysts prepared from Fe(II), $FeSO_4$, and Fe(III), $Fe(NO_3)_3$ compounds is discussed.

The syntheses conditions regarding the various crystalline silica catalysts are shown in Table 1 together with some analytical data determined by atomic-absorption spectrophotometry.

The synthetic iron-modified crystalline silica catalyst had a well defined crystalline ZSM-5 type structure, as demonstrated by an X-ray powder diffraction pattern and a scanning electron micrograph. Peaks corresponding to iron oxide were not observed. The iron may have been highly dispersed in the catalysts.

These catalysts were used for the hydrogenation of CO after being reduced under hydrogen at 450 °C for 15 h. Hydrogenation of CO was carried out in a flow reactor at 420 °C and 10 kg/cm² (H_2:CO:Ar=45:45:10). Conversion and carbon-based selectivity (excluding CO_2 yield) were calculated on the basis of argon as an internal standard. Figure 1-(A) shows the CO conversion plotted against the Fe/Si atomic ratio. On the other hand, Fig. 1-(B) shows the selectivity to CH_4, (C_2H_4+C_3H_6) and (C_2H_4+C_2H_6+C_3H_6+C_3H_8) plotted against the selectivity to total gaseous hydrocarbons (C_1—C_5). It should be noted that both the catalytic activity and the product selectivity are affected by the source of iron. The catalysts prepared from an Fe(II) compound are more active than those prepared from an Fe(III) compound. The selectivity to total gaseous hydrocarbons decreased much after using the Fe(II) compound instead of the Fe(III) compound as a source of iron and by increasing the amount of the Fe(II) compound. However, a linear relationship exists between the selectivity to CH_4, (C_2H_4+C_3H_6) and (C_2H_4+C_2H_6+C_3H_6+C_3H_8) and the selectivity to gaseous hydrocarbons. This suggests that each selectivity in the gaseous hydrocarbons is constant. It may be concluded that the C_1 to C_5 hydrocarbons are produced over the same active sites.

In order to elucidate these differences involving the activity and the selectivity, X-ray powder diffraction patterns of various catalysts (after preparation) were measured using silicon as an internal standard. As shown in Fig. 2, in the case of the crystalline silica catalysts prepared from the Fe(III) compound, the d(084)-spacing sharply increased with the Fe/Si atomic ratio. On the other hand, in the case of the catalysts

TABLE 1. PREPARATION OF THE VARIOUS IRON-MODIFIED CRYSTALLINE SILICA CATALYSTS[a)]

Cat. No.	Source of Fe	Atomic ratios of reaction mixture[b)]		Atomic ratios of product		BET
		Si/Fe	Si/M[c)]	Si/Fe	Si/M[c)]	Surface area (m²/g)
1	$Fe(NO_3)_3$	25		56		351
2		15		34		
3		7.5		20		
4		25	25(Mg)	58	58	
5		25	10(Ca)	52	19	
6		25	10(Sr)	78	21	353
7		25	10(Ba)	54	14	
8	$FeSO_4$	25		60		
9		15		32		361
10		7.5		18		352
11		3.5		9		
12		7.5	150(Mg)	18	180	361
13		7.5	150(Ca)	19	210	354
14		7.5	150(Sr)	25	244	352
15		7.5	150(Ba)	19	183	356

a) Crystallization was carried out in a 300 ml stainless steel autoclave at 150—160 °C for 20—40 h. b) OH^-/SiO_2=0.2, H_2O/SiO_2=40, $(n\text{-}C_3H_7)_4NBr/SiO_2$=0.10. c) An alkaline earth metal acetate.

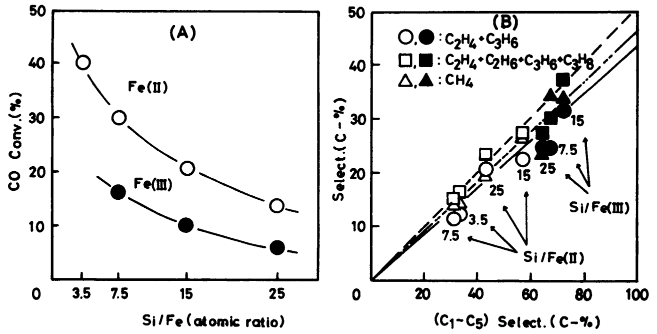

Fig. 1. Results of CO hydrogenation over the iron-modified crystalline silica catalysts prepared from Fe(II) and Fe(III) compounds as a source of iron.
Reaction conditions: Temp=420 °C, SV=1000 h^{-1}, P=10 Kg/cm^2, CO/H_2=1.
Arabic number denotes Si/Fe atomic ratio of reaction mixture in Table 1.

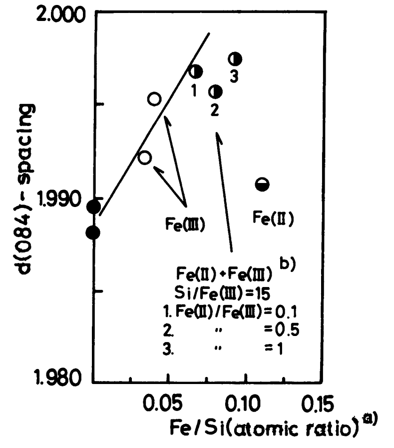

Fig. 2. Spacing d(084) of the various catalysts.
a) Determined by atomic absorption spectrophotometry, b) atomic ratios of reaction mixture in preparing catalysts.

prepared from the Fe(II) compound, the spacing remained unchanged.

From these results, it may be concluded that only Fe(III) can replace a portion of the silicon atoms in the crystal lattice and that Fe(II) is present in an enveloped form with the crystalline silica. The differences of both the catalytic activity and the product selectivity may be attributed to the amount of iron which does not replace a portion of the silicon atoms.

This concept can be supported by the following fact. The crystalline silica catalyst prepared from the Fe(III) compound was treated with 3 M HCl (1 M=1 mol dm^{-3}) at room temperature for 2 d with vigorous stirring. The catalyst, thus obtained, did not show any activity in spite of a considerable amount of iron present in the catalyst.

It may also be considered that a part of the iron enveloped with crystalline silica can easely be moved to the external surface of a crystal upon treatment with hydrogen. This iron will produce higher carbon-

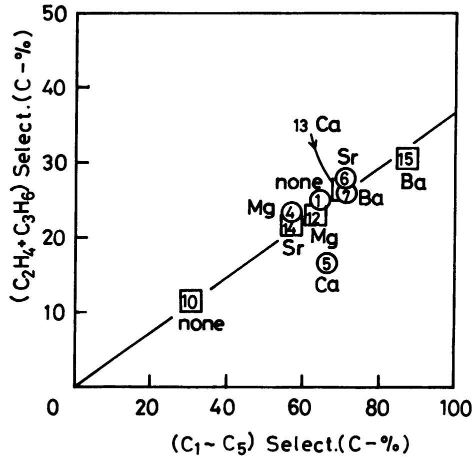

Fig. 3. Effect of alkaline earth metals on the selectivity to (C_2H_4+C_3H_6) over the iron-modified crystalline silica catalysts prepared from Fe(II) and Fe(III) compounds.
○: Prepared from Fe(III) compound, □: prepared from Fe(II) compound.
Reaction conditions: Temp=420 °C, SV=1000 h^{-1}, P=10 Kg/cm^2, CO/H_2=1.
Arabic number denotes Cat. No. in Table 1.

number hydrocarbons (C_6^+) because of the lack of restrictions caused by the zeolitic structure. Therefore, to restrict this moving of iron, an alkaline earth metal (acetate) was added. Figure 3 shows the effect of alkaline earth metals on the selectivity. A remarkable increase in total gaseous hydrocarbons was observed over the alkaline earth metal-modified crystalline silica catalysts prepared from the Fe(II) compound. The selectivity to (C_2H_4+C_3H_6) also increased in the order: Sr<Mg<Ca<Ba. However, this effect was not observed for catalysts prepared from the Fe(III) compound. The activity of these catalysts were about 30 percent lower than those of catalysts containing no alkaline earth metals. Moreover, the activity and the selectivity of these catalysts hardly changed at 420 °C even after 50—60 h.

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