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Catalytic Properties of Framework Iron in MFI-Type Ferrisilicate for the Oxidative Dehydrogenation of n-Butane

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The catalytic properties of MFI-type ferrisilicate for the oxidative dehydrogenation of n-butane were compared with those of iron-oxide impregnated silicalite (FeO_x/Sil) and Fe^{3+} exchanged ZSM-5 (FeZSM-5). The framework Fe^{3+} in ferrisilicate showed much higher dehydrogenation selectivity than Fe^{3+} in FeO_x/Sil and FeZSM-5.

It has been reported that Ti^{4+} ions in titanosilicate can be catalytically active centers for the hydroxylation of phenol.1) However, few studies have been carried out on the catalytic properties of the framework cations of metallosilicates. In this communication, we report that Fe^{3+} present in ferrisilicate exhibits much higher selectivity for oxidative dehydrogenation of n-butane than Fe^{3+} in iron-oxide impregnated silicalite and Fe ion-exchanged ZSM-5.

Ferrisilicate,2) ZSM-53), and silicalite4) with an MFI structure were synthesized by a hydrothermal crystallization technique. Iron-oxide impregnated silicalite (FeO_x/Sil) was obtained using silicalite and an aqueous solution of $Fe(NO_3)_3$. The FeZSM-5 was prepared by an ion-exchange technique using NaZSM-5 (Si/Al=29) and an aqueous solution of $FeCl_3$. The Si/Fe atomic ratios were 47, 50 and 177 for ferrisilicate, FeO_x/Sil and FeZSM-5, respectively.

The oxidative dehydrogenation of n-butane was carried out in a fixed-bed flow-type reactor under atmospheric pressure. The amounts of catalyst used were 0.1 g, 0.1 g, and 0.39 g for ferrisilicate, FeO_x/Sil, and FeZSM-5, respectively, so that the amount of iron would be about the same in all three cases. The catalytic reaction was performed at 723 K by introducing a gas mixture containing O_2 (4 ml min^{-1}), n-butane (4 ml min^{-1}) and helium (84 ml min^{-1}). The products in gas phase were analyzed by gas chromatography.

Table 1 shows the conversion and selectivities in the oxidative dehydrogenation of n-butane on the three catalysts. The reaction products were 1-butene, trans- and cis-2-butene (oxidative dehydrogenation); further dehydrogenated 1,3-butadiene; and CO and CO_2 (deep oxidation). A small amount of cracking products (C_2H_4 and C_3H_6) was also observed. The selectivity to each product was calculated on the basis of the carbon number of n-butane reacted. The conversion and selectivity changed slightly with time on stream in the initial stages of the reaction; however, they became constant later. The values shown in the table were taken in this steady state at 3 h time on stream. FeZSM-5 was active with a conversion of 7.1% com-

Table 1. Oxidative dehydrogenation of n-butane

Catalyst	n-Butane Conversion / %	Selectivity / %			
		C_4H_8	C_4H_6	C_3H_6, C_2H_4	CO, CO_2
Ferrisilicate	2.3	54.0	6.8	9.3	29.9
FeO_x/Sil	2.3	2.0	23.6	0.0	74.4
FeZSM-5	7.1	7.2	3.1	4.1	85.6

pared with 2.3% for both ferrisilicate and FeO_x/Sil. The selectivities were completely different from each other. On ferrisilicate, butenes were the main products. The selectivity to butadiene was low. The total selectivity for oxidative dehydrogenation (butene + butadiene) was ca. 61%. On the other hand, in the case of FeO_x/Sil, the main product was CO_x. Unlike ferrisilicate, the selectivity to butadiene was higher than that to butenes. The main product on FeZSM-5 was also CO_x. The selectivity for oxidative dehydrogenation was extremely low.

To clarify the cause of the differences in the dehydrogenation selectivities of ferrisilicate and FeO_x/Sil, the oxidative dehydrogenation of 1-butene was performed under the same reaction conditions, except for the use of 1-butene instead of n-butane. The conversions of 1-butene were almost the same, 62% for ferrisilicate and 67% for FeO_x/Sil, but the selectivity varied markedly. On ferrisilicate, the isomerization into trans- and cis-2-butene occurred predominantly (88%), while on FeO_x/Sil, the selectivity for dehydrogenation into 1,3-butadiene was significantly high (39%). This indicates that for the n-butane reaction the high selectivity to butenes on ferrisilicate is due to the low activity for the further dehydrogenation of the butenes produced, and that the rather high selectivity to butadiene on FeO_x/Sil is due to the high activity for the production of butadiene from butenes.

From Mössbauer spectra, we have found that Fe^{3+} ions are located in the framework of ferrisilicate with tetrahedral coordination.5) Therefore, we concluded that the tetrahedrally coordinated Fe^{3+} in ferrisilicate framework catalyzed the oxidative dehydrogenation of n-butane to butenes more selectively than the octahedrally coordinated Fe^{3+} in iron oxide (FeO_x/Sil) or the isolated Fe^{3+} in the ion-exchange site of FeZSM-5.

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