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NOTE

MFI-Type Ferrisilicate Catalysts for the Oxidative Dehydrogenation of Alkanes

The catalytic properties of transition-metal ions in the framework of metallosilicate zeolites are different from those of pure transition-metal oxides (1–5). We have reported that framework Fe^{3+} in MFI-type ferrisilicate catalyzes the oxidative dehydrogenation of *n*-butane into butenes more selectively than the Fe^{3+} ions in iron oxide supported on silicalite or Fe-exchanged ZSM-5 (3). The Fe^{3+} ions in the latter two catalysts mainly catalyze the total oxidation of *n*-butane into CO_2. Iron oxide on silicalite dehydrogenates butane beyond butenes to 1,3-butadiene, while ferrisilicate exhibits a low activity for the further dehydrogenation of butenes produced. It is impossible to dehydrogenate small branched alkanes such as isobutane beyond isobutene to a conjugated diene, or lower alkane such as propane beyond propylene. Therefore, the dehydrogenation activity and selectivity of these catalysts for the oxidative dehydrogenation of isobutane and propane may differ from those for the *n*-butane reaction. In this work, we report the catalytic properties of framework iron in MFI-type ferrisilicate for the oxidative dehydrogenation of isobutane and propane. A comparison of the activity and selectivity of ferrisilicate for these reactions with those of Fe-exchanged ZSM-5 and iron oxide supported on silicalite has been made.

The preparation and characterization of catalysts used in this study have been described elsewhere (4). MFI-type ferrisilicate, silicalite, and ZSM-5 were prepared by hydrothermal crystallization. Fe-exchanged ZSM-5 (FeZSM-5) was prepared by ion exchange using an aqueous solution of $FeCl_3$, and iron oxide was supported on silicalite (FeO_x/Sil) by impregnation using an aqueous solution of $Fe(NO_3)_3$. The Si/Fe atomic ratio of ferrisilicate was 47 and the Si/Al ratio of ZSM-5 was 29. The iron content of FeO_x/Sil was 1.9 wt% (Si/Fe = 50) and for FeZSM-5, the percent of ion exchange was 48% as Fe^{3+} (Si/Fe = 177). Mössbauer spectroscopy has shown that the Fe ions in ferrisilicate are tetrahedrally coordinated Fe^{3+} and that those in FeO_x/Sil are octahedrally coordinated Fe^{3+} in the form of α-Fe_2O_3 particles (4). The particle size is much larger than the pore dimension of silicalite. Therefore, α-Fe_2O_3 should be supported on the external surface of silicalite. We could not determine the chemical states of the Fe ions in FeZSM-5 due to the low iron content of the sample.

The oxidative dehydrogenation of isobutane and propane was carried out in a fixed-bed flow-type reactor at atmospheric pressure. In a typical reaction run, the catalyst was first heated in a stream of 50 ml/min He at 773 K for 1 h. After lowering the temperature to 723 K, the reaction was commenced by introducing the feed gas. Products were analyzed by an on-line gas chromatograph using a thermal conductivity detector (TCD). The system was allowed to stabilize for 30 min before the first product sample was taken for analysis with a carbon balance always satisfied to within ±3%. The selectivity to each product was calculated on the basis of the carbon number of the hydrocarbon reacted.

Oxidative dehydrogenation of isobutane was carried out over ferrisilicate and FeO_x/Sil in order to elucidate their catalytic properties for the reaction of branched alkanes. The feed gas was a mixture of isobutane, O_2, and He in a ratio of 1 : 1 : 21 at a total flow rate of 94 ml/min. Reaction products were: isobutene produced by oxidative dehydrogenation; CO and CO_2 from deep oxidation; and propylene and ethylene as cracking products. No significant deactivation of the catalysts and no change in the selectivity with time on stream were observed. At higher temperatures and higher W/F, gas phase, blank reactions could not be neglected. Therefore, the selectivities were compared with each other at low conversions although in the case of *n*-butane reaction on ferrisilicate the selectivity to butenes was still high (47 C-%) at the conversion of 7%. Table 1 shows the conversion and selectivity measured at 723 K and time on stream of 3 h. The conversion of 1.0% corresponds to the reaction rate of 0.050 molecules of *i*-butane reacted per Fe atom per minute. Under the same reaction conditions, *n*-butane conversion was 2.3% on both catalysts (3), which is higher than the conversion of isobutane on ferrisilicate. It is generally known that branched alkanes are more reactive than straight-chain alkanes. This lower observed activity may be caused by steric hindrance between the ferrisilicate pore

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TABLE 1
Oxidative Dehydrogenation of Isobutane and Propane

			Selectivity (C-%)				
Catalyst[a]	Reactant[b]	Conversion (%)	i-C_4H_8	C_3H_6	Cracked products[c]	CO	CO_2
Ferrisilicate	i-C_4H_{10}	1.6	39.6	—	14.1	16.8	29.5
	C_3H_8	2.2	—	65.8	0.0	18.2	16.0
FeO_x/Sil	i-C_4H_{10}	2.7	8.0	—	0.3	6.7	85.0
	C_3H_8	1.7	—	0.0	0.0	5.9	94.1
FeZSM-5	C_3H_8	3.5	—	0.0	25.0	34.4	40.6

[a] Catalyst weight: 0.1 g (ferrisilicate and FeO_x/Sil), 0.4 g (FeZSM-5).

[b] Reactant mixture: i-C_4H_{10} (or C_3H_8)/O_2/He = 1/1/21 (molar ratio).

[c] C_2H_4 and C_3H_6 (isobutane reaction), C_2H_4 and CH_4 (propane reaction). Reaction temperature, 723 K; time on stream, 3 h; and total flow rate, 94 ml/min.

and the branched hydrocarbon. Conversely, the increased conversion on FeO_x/Sil is caused by the fact that the active species, probably particles of α-Fe_2O_3, are located on the external surface of the silicalite crystallite. As with the n-butane reaction, the selectivity differed between the two catalysts. Ferrisilicate showed a much higher selectivity for the oxidative dehydrogenation of isobutane to isobutene than FeO_x/Sil. FeO_x/Sil mainly catalyzed total oxidation into CO_2. The high selectivity of ferrisilicate framework Fe^{3+} ions for oxidative dehydrogenation was again exhibited in the reaction of isobutane.

In order to clarify the differences in selectivity for the reaction of lower alkanes, the oxidative dehydrogenation of propane was carried out at 723 K on these catalysts and FeZSM-5. The feed consisted of propane, oxygen and He in a ratio of 1 : 1 : 21 at a total flow rate of 94 ml/min. Weights of the catalysts were adjusted to obtain the same amount of iron in all cases. The products were: propylene produced by oxidative dehydrogenation; CO and CO_2 from deep oxidation; and ethylene and methane as cracking products. No oxygenated products were detected under these reaction conditions. A decrease in propane conversion on FeZSM-5 was observed in the initial stages, which can be attributed to a high activity for cracking on the acid sites of FeZSM-5 and consequent carbon deposition. Table 1 reveals the conversion and selectivity for the oxidative dehydrogenation of propane on ferrisilicate, FeO_x/Sil and FeZSM-5, measured at a steady state after 3 h on stream. Compared with the reaction of n-butane under the same reaction conditions where conversions were 2.3%, 2.3%, and 7.1% on ferrisilicate, FeO_x/Sil and FeZSM-5, respectively (3), the conversions of propane on FeO_x/Sil and FeZSM-5 were significantly lower. The conversion of propane on ferrisilicate was also slightly lower. The above results are consistent with the fact that for the oxidative dehydrogenation of alkanes the relative reactivity of different alkane molecules increases with the carbon number (6). Selectivities also differed among the catalysts. Ferrisilicate catalyzed the oxidative dehydrogenation of propane selectively to propylene. However, no dehydrogenation products were observed in the case of FeO_x/Sil and FeZSM-5. FeO_x/Sil produced only carbon oxides, mainly CO_2. Unlike ferrisilicate and FeO_x/Sil, FeZSM-5 produced a significant amount of cracking products, such as ethylene and methane. The activity for cracking on FeZSM-5 may be attributed to the acid sites of the catalyst. Selectivity for the deep oxidation of propane to carbon oxides was also very high on FeZSM-5. Higher activity of FeO_x/Sil observed in the further dehydrogenation of butenes (3) results in the deep oxidation of propylene produced on FeO_x/Sil. This suggests that, as in the case of n-butane to butenes, the tetrahedrally coordinated Fe^{3+} in the ferrisilicate framework catalyzes the oxidative dehydrogenation of propane to propylene selectively. On the other hand, the octahedrally coordinated Fe^{3+} in iron oxide (FeO_x/Sil) catalyzes only the deep oxidation of propane into carbon oxides, and the isolated Fe^{3+} in FeZSM-5 also mainly catalyzes the deep oxidation of propane into carbon oxides.

Therefore, we conclude that the framework Fe ions in ferrisilicate catalyze the oxidative dehydrogenation of lower alkanes into alkenes more selectively than those of iron oxide supported on silicalite or Fe-exchanged ZSM-5.

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