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CATALYTIC ACTIVITIES OF METAL ION EXCHANGED FORMS OF FLUORO TETRASILICIC MICA FOR THE REACTION OF BUTENES

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Metal ion exchanged forms of fluoro tetrasilicic mica (M^{n+}-TSM's) showed characteristic activities of the exchanged M^{n+} ions for the reaction of butenes. It is of particular interest that Sn^{4+}- and Fe^{3+}-TSM catalyze the dehydrogenation of butenes to form butadiene in either absence or presence of hydrogen.

Recently, we found that fluoro tetrasilicic mica (TSM) which is a synthetic layer lattice silicate shows no acidity in the temperature programmed desorption of ammonia[1] and the metal ion exchanged forms of TSM (M^{n+}-TSM's) catalyze the conversion of methanol differently with the M^{n+} ions. We further investigated the catalytic activities of M^{n+}-TSM's for the reaction of butenes. The results are reported in this communication.

The preparation of most of M^{n+}-TSM's has been described previously.[2] The reaction was carried out with a conventional pulse reactor. The catalyst sample (100 mg) was pretreated for 2 h at 400 °C in a carrier gas (He; 20 ml/min) and exposed to a pulse (0.3 ml) of a mixture of butene and nitrogen or hydrogen (C_4H_8 : N_2 or H_2 = 1 : 2 or 8) at the reaction temperature.

Table 1. Results of the Reaction of 1-Butene

Cation	Conv. (%)	Product Composition (%) trans-C_4^-	cis-C_4^-	$C_4^=$
Mn^{2+}	0	-	-	-
Mg^{2+}	1	54	46	-
Co^{2+}	3	43	57	-
Al^{3+}	5	45	55	-
Sn^{4+}	8	15	12	73
Ti^{4+}	11	40	60	-
Ni^{2+}	12	54	46	-
Cr^{3+}	13	47	40	13
Cu^{2+}	16	21	27	52
Cu^{+}	17	28	26	46
Fe^{3+}	28	24	24	52
Pd^{2+}[a]	24	57	35	6
Pt^{2+}[a]	70	51	34	6

a) C_4, i-C_4^-, and C_3 were detected.

The original form of TSM (Na^+-TSM) did not show any activity for butenes. The results of the reaction of 1-butene at 380 °C are summarized in Table 1. With Pd^{2+}- and Pt^{2+}-TSM, some irreversible species seemed to be formed on the surface and the steady values shown in Table 1 were obtained after the fifth pulse. For the other samples, the results were quite independent of the pulse number. The values of conversion show that the catalytic activity of M^{n+}-TSM varies widely by the interlayer M^{n+} ions. M^{n+}-TSM with relatively low activity catalyzed only isomerization, except Sn^{4+}-TSM, while those with higher activity catalyzed dehydrogenation simultaneously to form butadiene. It is known that the isomerization of butene easily takes place over acid catalysts and the acidity of the catalysts like metal sulfates generally increases with the electronegativity of metal ions.[3)] However, the activities of M^{n+}-TSM's did not show such a correlation. It is also known that the isomerization of *cis*-2-butene over a catalyst with the higher acid strength, namely the higher activity, results in the higher ratio of *trans*-2-/1-butene in the products because of the stability of carbenium ion intermediate.[4)] We investigated the isomerization of *cis*-2-butene and found that the activity of each M^{n+}-TSM for *cis*-2-butene is identical with that for 1-butene and the ratio of *trans*-2-/1-butene in the products falls into 1 ± 0.2 independently upon the activity of M^{n+}-TSM. The facts suggest that the activity of M^{n+}-TSM is not caused by acidic hydrogen on the silicate sheet of TSM. As seen in Table 1, butene reacts scarcely over Mn^{2+}- and Mg^{2+}-TSM and considerably over Pd^{2+}- and Pt^{2+}-TSM. Considering that Mn^{2+} and Mg^{2+} are classified into hard Lewis acid and Pd^{2+} and Pt^{2+} are in soft Lewis acid, it is likely that the activity of M^{n+}-TSM represents the characteristic activity or the Lewis acidity of the M^{n+} ion.

Table 2. Results of the Reaction of 1-Butene in the Presence of Hydrogen

Cation	Conv.	Product Composition (%)			Effect of
	(%)	*trans*-C_4^{-}	*cis*-C_4^{-}	$C_4^{=}$	H_2; ΔT (°C)
Mg^{2+}	2	36	36	-	70
Co^{2+}	6	53	47	-	120
Sn^{4+}	2	27	19	54	-200
Ti^{4+}	13	49	51	-	40
Ni^{2+}	54	60	38	-	100
Cu^{2+}	76	58	38	2	170
Fe^{3+}	27	22	22	56	-20

The results of the reaction of 1-butene at 350 °C in the presence of hydrogen are summarized in Table 2, where the effect of H_2, ΔT, indicates that the conversion attained the values seen in Table 1 at the reaction temperature lower than 380 °C by ΔT °C. A small amount of butane was formed over Mg^{2+}-, Ni^{2+}-, and Cu^{2+}-TSM. The values of ΔT show that hydrogen accelerates the isomerization of butene remarkably over all M^{n+}-TSM's but Sn^{4+}- and Fe^{3+}-TSM. Since accelerating effect of hydrogen is often observed for the catalysis of the isomerization of olefins by metals or metal complexes, the results strongly suggest that the isomerization takes place on the M^{n+} ion of M^{n+}-TSM through a half-hydrogenated species.

As seen in Table 1, Sn^{4+}-, Fe^{3+}-, Cu^{2+}-, and Cu^{+}-TSM show considerable activities for the dehydrogenation to produce butadiene. This particular activity of Cu^{2+}-TSM is suppressed by hydrogen substantially, suggesting that the adsorbed butene is readily transformed into half-hydrogenated species rather than dissociative one in the presence of hydrogen. In contrast, the rate of dehydrogenation is comparable to that of isomerization over Sn^{4+}- and Fe^{3+}-TSM even in the presence of hydrogen (Table 2), suggesting that the dissociative adsorption is predominant over these ions in either absence or presence of hydrogen. Although further investigations are needed to discuss the reaction path and the working mechanism of these ions, Sn^{4+}- and Fe^{3+}-TSM are expected to develop into new catalytic system to dehydrogenate olefins.

References

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