

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<sup>1)</sup> 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.<sup>2)</sup> 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 (%)		
		<i>trans</i> - $C_4^-$	<i>cis</i> - $C_4^-$	$C_4^-$
Mn <sup>2+</sup>	0	-	-	-
Mg <sup>2+</sup>	1	54	46	-
Co <sup>2+</sup>	3	43	57	-
Al <sup>3+</sup>	5	45	55	-
Sn <sup>4+</sup>	8	15	12	73
Ti <sup>4+</sup>	11	40	60	-
Ni <sup>2+</sup>	12	54	46	-
Cr <sup>3+</sup>	13	47	40	13
Cu <sup>2+</sup>	16	21	27	52
Cu <sup>+</sup>	17	28	26	46
Fe <sup>3+</sup>	28	24	24	52
Pd <sup>2+a)</sup>	24	57	35	6
Pt <sup>2+a)</sup>	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.<sup>3)</sup> 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.<sup>4)</sup> 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  $1 \pm 0.2$  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 $H_2$ ; $\Delta T$ ( $^{\circ}C$ )
		<i>trans</i> - $C_4^-$	<i>cis</i> - $C_4^-$	$C_4^-$	
$Mg^{2+}$	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  $^{\circ}C$  in the presence of hydrogen are summarized in Table 2, where the effect of  $H_2$ ,  $\Delta T$ , indicates that the conversion attained the values seen in Table 1 at the reaction temperature lower than 380  $^{\circ}C$  by  $\Delta T$   $^{\circ}C$ . A small amount of butane was formed over  $Mg^{2+}$ -,  $Ni^{2+}$ -, and  $Cu^{2+}$ -TSM. The values of  $\Delta T$  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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