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Catalytic Activities of La_2O_3, Y_2O_3, and CeO_2 for Decomposition of 4-Hydroxy-4-methyl-2-pentanone and Isomerization of Butenes

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The decomposition of 4-hydroxy-4-methyl-2-pentanone and the isomerization of 1-butene were carried out over La_2O_3, Y_2O_3, and CeO_2. The activities for both types of reactions were in the following order; $La_2O_3 > Y_2O_3 > CeO_2$. With La_2O_3, the change in the activity for the decomposition with the pretreatment temperature of the catalyst correlated well with the change in basicity, the activity and basicity maxima being observed when the catalyst was pretreated at 500 °C. Yttrium sesquioxide showed a maximum activity for the decomposition when pretreated at 700 °C. For the isomerizations of 1-butene and *cis*-2-butene, La_2O_3 exhibited activity maxima when pretreated at 700 °C. The *cis*/*trans* selectivities from 1-butene were considerably greater than unity, and the *trans*/1 selectivities from 2-butene were less than unity. The coisomerization of *cis*-2-butene-d_0/d_8 revealed that the reaction involved an intramolecular H(or D) transfer. The isotope effects for the formation of 1-butene from *cis*-2-butene were 4—10, while those for the formation of *trans*-2-butene were about 1.

Rare earth oxides have recently been recognized as solid base catalysts. Rosynek *et al.* studied the surface properties and catalytic behavior of La_2O_3 and reported that basic sites on La_2O_3 were essential for the isomerization of butenes.[1–3] Minachev *et al.* investigated the catalytic action of rare earth oxides for the hydrogenation of ethylene and concluded that the basicity of the oxides correlated with the activity.[4] Although the basic property was thus regarded as an important property in catalytic actions, the number of basic sites has not yet been measured.

In this study, the number of basic sites of La_2O_3 was measured and correlated with the catalytic activities for the decomposition of 4-hydroxy-4-methyl-2-pentanone and the isomerization of butenes. In the isomerization of butenes, a mechanistic study was done by the coisomerization method.[5] For a comparison with La_2O_3, oxides of elements of the same IIIa group, Y_2O_3 and CeO_2, were also studied.

Experimental

The lanthanum sesquioxide (La_2O_3), Y_2O_3, and CeO_2 were obtained by the evacuation of each hydroxide at temperatures between 400 and 800 °C for 3 h. The final pressure was in the range of 10^{-2} Pa. The hydroxides were prepared by precipitation from nitrate solutions with aqueous ammonia.

The number of basic sites (basicity) on La_2O_3 were measured by titrating the sample suspended in dry benzene with a benzene solution of 0.1 mol/dm^3 benzoic acid, 2,4,6-trinitroaniline ($pK_{BH} = 12.2$) being used as an indicator.[6] The suspension of the sample in dry benzene was performed under flowing dry nitrogen to prevent poisoning by air.

For the measurements of the IR spectra, $La(OH)_3$ was pressed into a disk and outgassed at various temperatures for 3 h *in situ*.

The decomposition of 4-hydroxy-4-methyl-2-pentanone was carried out at 30 °C in a liquid phase while magnetically stirring the reactant (10 ml) and the powdered catalyst. The reaction mixture (catalyst, reactant, and product; 1-ml portions) was periodically transferred into another vessel for the centrifugal separation of the catalyst from a solution. The solution was then analyzed by means of a gas chromatograph with a 1-m column containing polyethylene glycohol on Celite.

The isomerization of butenes was carried out in a closed circulation system (*ca.* 1370 ml) on *ca.* 0.1-g catalysts at temperatures between 0 and 200 °C and at an initial pressure of 46.6 kPa. For the coisomerization of *cis*-2-butene-d_0/d_8, a microcatalytic pulse reactor was employed and a mixture containing equal amounts of *cis*-2-butene-d_0 and *cis*-2-butene-d_8 was reacted at 0 °C. The products were gas-chromatographically separated and subjected to mass-spectrographic analysis.

Results

Basicity and IR Spectra of La_2O_3. The variations in the basicity as a function of the pretreatment temperature are shown in Fig. 1. The basicity of lanthanum sesquioxide increased on pretreatment above 400 °C, attained a maximum value when pretreated at 500 °C, and then gradually decreased as the pretreatment temperature was raised above 500 °C.

The IR spectra of La_2O_3 exhibited strong peaks around 1500—1300 cm^{-1}, which could be assigned to carbonate groups. A large number of carbonate

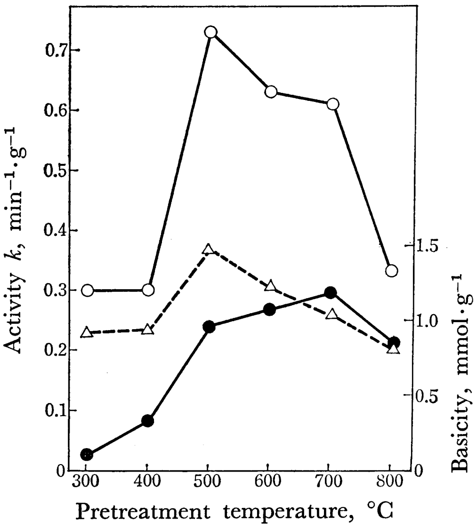

Fig. 1. Variations of basicity (—△—) of La_2O_3 as a function of pretreatment temperature and variations of activities of La_2O_3 (—○—) and Y_2O_3 (—●—) for decomposition of 4-hydroxy-4-methyl-2-pentanone at 30 °C.

Table 1. Catalytic activities and selectivities for the isomerization of 1-butene

Catalyst	Reaction temp °C	*cis*-2-Butene (%/m²·min)	*trans*-2-Butene (%/m²·min)	Selectivity
La_2O_3	0	8.6	3.3	2.8
Y_2O_3	0	2.2×10^{-2}	0.56×10^{-2}	3.9
CeO_2	0	0	0	—
CeO_2	200	3.1×10^{-2}	1.4×10^{-2}	2.2

groups still remained on the sample even when it was outgassed at 500 °C, and most of the carbonate groups was desorbed as CO_2 by raising the outgassing temperature from 500 to 600 °C.

Decomposition of 4-Hydroxy-4-methyl-2-pentanone. Only acetone was produced by the decomposition of 4-hydroxy-4-methyl-2-pentanone over La_2O_3, Y_2O_3, and CeO_2 at 30 °C. The decomposition followed the first-order rate equation with respect to the concentration of the reactant. The activity was represented by the first-order rate constant, k. Variations in the activities of La_2O_3 and Y_2O_3 on a unit of weight are also plotted as a function of the pretreatment temperature in Fig. 1. A maximum activity was obtained by pretreatment at 500 °C for La_2O_3 and at 700 °C for Y_2O_3. In the case of La_2O_3, the variation in the activity with the pretreatment temperature was similar to that of the basicity. The rate constants of CeO_2 pretreated at 700 and 800 °C were 1.02×10^{-2} and 1.17×10^{-2} $min^{-1}\cdot g^{-1}$ respectively. On comparing the maximum activities of La_2O_3 and Y_2O_3 to 1.17×10^{-2} $min^{-1}\cdot g^{-1}$ for CeO_2, the activities for the decomposition reaction are in the following order, $La_2O_3>Y_2O_3>CeO_2$.

Isomerization of Butenes. The activity was represented by a % conversion per min per unit weight or surface area of the catalyst in the initial stage of the reaction. The activities of La_2O_3, Y_2O_3, and CeO_2 pretreated at 700° for the isomerization of 1-butene are compared in Table 1 on the basis of a unit surface area, where the *cis*/*trans* selectivities in the initial stage of the reaction are also given. Cerium dioxide did not show any activity at 0 °C. The activity and the selectivity in the reaction at 200 °C are also given for the sake of comparison. The order of the activities is; $La_2O_3>Y_2O_3>CeO_2$. The *cis*/*trans* selectivities were greater than 2 for all catalysts.

The activity and *cis*/*trans* and *trans*/1 selectivities in the isomerizations of 1-butene and *cis*-2-butene are plotted against the pretreatment temperature in Figs. 2 and 3. The activities for both reactions appeared on pretreatment above 400 °C. The maximum activities were observed when La_2O_3 was pretreated at 700 °C for both reactions. The *cis*/*trans* and *trans*/1 selectivities were markedly changed by raising pretreatment temperature from 600 to 700 °C. In all cases, the *cis*/*trans* selectivities were greater than 2 and the *trans*/1 selectivities were less than 1.

The results of the coisomerization of *cis*-2-butene-d_0/d_8 over La_2O_3 pretreated at 600 and 700 °C are summarized in Table 2. Non-exchanged products were predominant. This indicates that the reaction

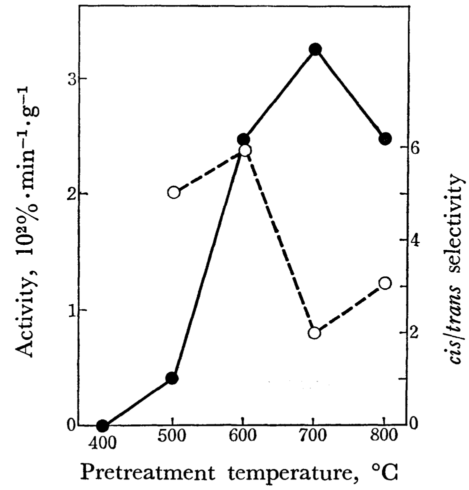

Fig. 2. Activity and *cis*/*trans* selectivity in isomerization of 1-butene over La_2O_3 at 0 °C. ●: Activity, ○: selectivity.

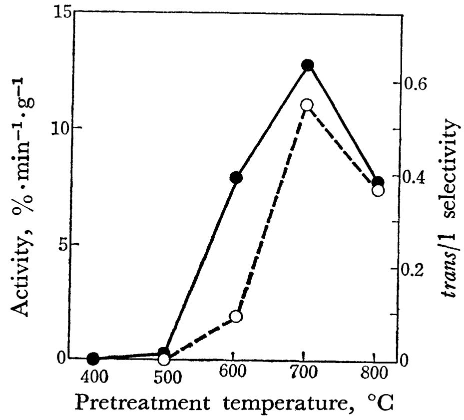

Fig. 3. Activity and *trans*/1 selectivity in isomerization of *cis*-2-butene over La_2O_3 at 0 °C. ●: Activity, ○: selectivity.

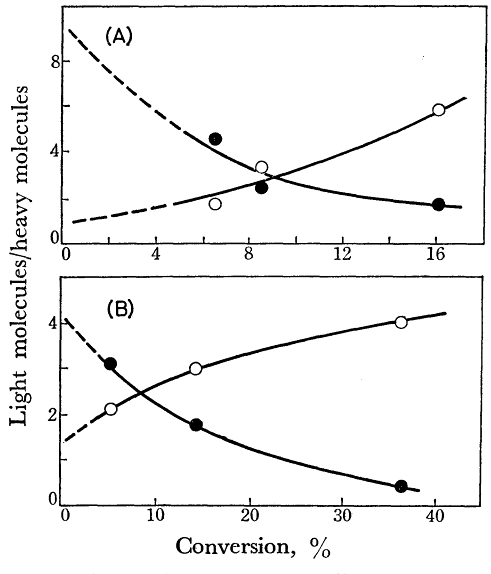

Fig. 4. Ratios of "light molecules" to "heavy molecules" produced in coisomerization of *cis*-2-butene-d_0/d_8. (A) La_2O_3 pretreated at 600 °C. (B) La_2O_3 pretreated at 700 °C. ●: 1-Butene, ○: *trans*-2-butene.

Table 2. Distribution of the isotopic species in the products for the coisomerization of heavy (d_8) and light (d_0) *cis*-2-butene

	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
(a) On La_2O_3 evacuated at 600 °C.									
6.5% conversion									
1-Butene	81.4	0.9	0	0	0	0	0	0.9	16.8
trans-2-Butene	60.7	0.4	0	0	0	0	0	0.1	38.8
cis-2-Butene	47.5	0.5	0	0	0	0	0	0.4	51.8
8.4% conversion									
1-Butene	68.8	0.6	0	0	0	0	0	0.7	29.1
trans-2-Butene	75.0	1.8	0	0	0	0	0	1.7	21.6
cis-2-Butene	46.0	0.4	0	0	0	0	0	0.0	53.6
16.0% conversion									
1-Butene	60.2	2.0	0	0	0	0	0	2.9	34.9
trans-2-Butene	74.3	10.0	0.8	0	0	0	0.4	3.1	11.4
cis-2-Butene	42.0	1.6	0	0	0	0	0	1.7	54.7
(b) On La_2O_3 evacuated at 700 °C.									
5.1% conversion									
1-Butene	75.3	0.2	0	0	0	0	0	0.3	24.3
trans-2-Butene	67.3	1.8	0	0	0	0	0	1.3	29.5
cis-2-Butene	43.3	0	0	0	0	0	0	0	56.7
12.1% conversion									
1-Butene	63.7	0.1	0	0	0	0	0	0.6	35.0
trans-2-Butene	69.6	4.5	0.6	0	0	0	0.7	4.1	20.5
cis-2-Butene	42.1	0.1	0	0	0	0	0	0.0	57.8
36.4% conversion									
1-Butene	29.0	1.2	0	0	0	0	0	2.8	67.0
trans-2-Butene	76.1	4.0	0	0	0	0	0	3.0	16.9
cis-2-Butene	24.9	1.7	0	0	0	0	0	2.6	70.0

involves an intramolecular H(or D) transfer. The ratio of "light molecules (d_0—d_2)" to "heavy molecules (d_6—d_8)" is plotted against the conversion in Fig. 4. The zero conversion intercept gives an isotope effect. The isotope effects for the formation of 1-butene were about 10 and 4 for La_2O_3 pretreated at 600 °C and 700 °C respectively. On the contrary, the isotope effects for the formation of *trans*-2-butene were small (≈ 1) for both catalysts. The ratio for 1-butene decreased with an increase in the conversion, while the ratio for *trans*-2-butene increased. This is attributable to a large isotope effect for the conversion of 1-butene to *trans*-2-butene.

Discussion

The catalytic actions of La_2O_3, Y_2O_3, and CeO_2 in the decomposition of 4-hydroxy-4-methyl-2-pentanone and the isomerization of butenes could be attributed to their basic property as a decisive property. The good correlation of the basicity with the activity for the decomposition of 4-hydroxy-4-methyl-2-pentanone found on La_2O_3 is similar to that found on alkaline earth oxides.[7] The order of the activities of alkaline earth oxides on a unit surface area basis followed the order of strength of the basic sites, that is, BaO>SrO>CaO>MgO. Although the basic properties of Y_2O_3 and CeO_2 were not measured, the order of the activities on a unit surface area basis, $La_2O_3>Y_2O_3>CeO_2$, suggests that the basic strength of the active sites is also $La_2O_3>Y_2O_3>CeO_2$. The activity of La_2O_3 was one order of magnitude greater than that of MgO (1.4×10^{-3} $\mathrm{min^{-1}\cdot m^{-2}}$).[7]

For the isomerization of 1-butene over La_2O_3, our results on the activity and selectivity are similar to those reported by Rosynek and Fox.[3] In their study, a maximum activity was obtained when the substance was pretreated at 650 °C, while it was obtained at 700 °C in our study. The *cis*/*trans* ratios were considerably higher than unity in both studies.

One of the criteria for the base-catalyzed isomerization of 1-butene is a high *cis*/*trans* selectivity.[8—11] The high selectivity observed for La_2O_3, combined with the existence of basic sites, seems to indicate that the isomerization is a base-catalyzed reaction, in which the initial step is an abstraction of an allylic H in the form of H^+ by a basic site to form an allyl carbanion. The *cis* form is much more stable than the *trans* form in the π-allyl carbanion. The H^+ thus abstracted transfers to the 1 carbon atom to form mainly *cis*-2-butene. In this case, an intramolecular H transfer can be observed provided that there are no H^+ around the carbanion other than the abstracted one. The observed result of an intramolecular H transfer also supports the idea that the isomerization is a base-catalyzed reaction.

There are two forms in the π-allyl carbanion, *syn* and *anti* π-allyls. Interconversion between the two allyls probably proceed by means of a σ-allyl. If the interconversion between two π-allyls is a slow step, the conversion of *cis*-2-butene to *trans*-2-butene will be slow and the isotope effect for the formation of the *trans*-2-butene will be small. These were the observed sequences. Therefore, the slow step for the direct conversion of *cis*-2-butene to *trans*-2-butene is the conversion of *anti* π-allyl to *syn* π-allyl. The increase in the ratio of "light molecules" to "heavy molecules" for *trans*-2-butene as the reaction proceeded indicates that a large part of the *trans*-2-butene was produced *via* 1-butene in the intermediate stage of the reaction. The large isotope effect for the formation of 1-butene from *cis*-2-butene suggests that an H transfer is involved in the slow step. Provided that the initiation step is common for the formations of *trans*-2-butene and 1-butene from *cis*-2-butene, a small isotope effect for the formation of *trans*-2-butene shows that the abstraction of H^+ is not a slow step. Therefore, it may be considered that the migration of the H^+ to the 3 carbon atom is the slow step for the formation of 1-butene from *cis*-2-butene.

Rosynek and Fox3) suggested, on the basis of the different activation energies for the formations of *cis*-2-butene and *trans*-2-butene, that the formations of two 2-butene isomers from the 1-butene reactant may occur on dissimilar sites. However, it does not seem necessary to postulate dissimilar sites, it is sufficient to assume different slow steps for the formations of the two 2-butene isomers.

A marked increase in the activity for the isomerizations of butenes by raising the outgassing temperature from 500 to 600 °C corresponded to an increase in the desorbed amount of carbonate groups. Therefore, it may be considered that the active sites for isomerization are generated by the removal of surface carbonate groups.

The active sites for the isomerization of butenes and for the decomposition of 4-hydroxy-4-methyl-2-pentanone may be dissimilar, because the pretreatment temperatures at which maximum activities were exhibited different for the two reactions and because basic sites generated by pretreatment at 400 °C catalyzed the decomposition, while they did not catalyze the isomerization. Perhaps, the isomerization needs stronger basic sites than the decomposition does.

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