JOURNAL OF CATALYSIS 90, 160–164 (1984)

Transfer Hydrogenation of Conjugated Dienes over Oxide Catalysts

We have recently reported specific actions of hydrogen donor molecules in the hydrogenation of 1,3-butadiene (1,3-BD) with cyclohexadiene (CHD) over ZrO_2 catalyst (*1*): the catalyst ZrO_2 promotes hydrogenation of 1,3-BD with both CHD and H_2 gas, but the main products are distinctly different by the two hydrogen sources. The other specific feature of the transfer hydrogenation is that hydrogen donor molecules such as CHD readily hydrogenate 1,3-CHD under such a condition that neither H_2–D_2 equilibration nor hydrogenation by H_2 gas occurs (*2*). An application of hydrogen donor molecules to control the product selectivity has important potential in both applied and fundamental research. One significant area where those reactions may have an impact is the selective removal of sulfur and nitrogen from synthetic crude oil that has been derived from coal (*3*). In this article we wish to report the catalytic activities and selectivities of several metal oxide catalysts in the transfer hydrogenation of conjugated dienes by CHD; the results are compared with those obtained in direct hydrogenation with dihydrogen.

EXPERIMENTAL

The catalysts used were La_2O_3, CaO, MgO, CeO_2, ThO_2, and ZrO_2, which were activated under vacuum at a variety of temperatures. Most of the oxides were prepared from corresponding hydroxides. The hydroxides of Ca and Mg are commercially available. Hydroxides of Ce were prepared from both chloride and nitrate by hydrolysis with aqueous ammonia (*4*). CeO_2(I) and CeO_2(II) designate the oxides were prepared from nitrate and chloride, respectively.

The reactions were carried out at 20°C in a closed recirculation reactor which was equipped with a sampling manifold for gas chromatographic analysis. Typical reaction mixtures were CHD : diene = 25 : 25 (Torr) or H_2 : diene = 40 : 25 (Torr). Dehydrogenation of CHD was carried out separately by a pulse microreactor with He as a carrier gas at 20°C. Each pulse contained 3.1 μmol of reactant. Lower hydrocarbons such as butenes were analyzed by a 5-m column of VZ-7 (Gasukuro Kogyo KK.) at 0°C; cyclic compounds such as CHD were separated at 40°C by a 2-m column packed with PEG 200. Samples separated by gas chromatography were subjected to mass spectrometric (Hitachi M-52) or ^{1}H NMR spectroscopic analysis.

Purifications of reactants were reported in our previous paper (*1b*).

RESULTS AND DISCUSSION

1. General Observations of Transfer Hydrogenation of 1,3-Butadiene with Cyclohexadiene over Various Oxide Catalysts

Table 1 summarizes the catalytic activities of various oxides in the hydrogenation of 1,3-BD with CHD and H_2. In general, the rates of hydrogenation by CHD are faster by one or two orders of magnitude than those of hydrogenation by H_2 molecules. Though the rates of hydrogenation by H_2 over CeO_2(II)–H-600 and ZrO_2-800 are especially low, CHD effectively hydrogenates dienes. No apparent coke formation was observed. Thus a hydrogen donor molecules is quite useful as an alternative hydrogen source.

One of the characteristics of the hydrogenation of 1,3-BD by H_2 over oxide catalysts

0021-9517/84 $3.00

TABLE 1

Hydrogenation of 1,3-BD with 1,3-CHD or H_2

Catalyst[a]	Surface area (m^2/g)	CHD				H_2			
		Rate[b] (10^{-5} mol/g·min)	Composition (%)[d] 1-B	*trans*	*cis*	Rate[b] (10^{-5} mol/g·min)	Composition (%)[d] 1-B	*trans*	*cis*
La_2O_3-600	39	246	8	62	30	14.1	2	84	14
CaO-700	52	250	4	71	25	56.2	2	75	23
MgO-600	135	128	8	63	29	0.57	2	75	23
MgO-1000	76	26.9	13	13	74	12.2	12	11	77
CeO_2(I)-600	13	1.4	13	72	15	0.04		—	
CeO_2(I)–H-600	13	79.0	15	50	35	1.2	15	50	35
CeO_2(II)–H-600	13	7.5	6	92	2	0.01		—	
ThO_2-700	59	43.3	11	60	29	—		—	
ZrO_2-500	65	1.9[c]	67	12	21	3.9[c]	15	80	5
ZrO_2-800	11	2.5[c]	65	15	20	0		—	

[a] La_2O_3-600, etc. denote that catalyst was evacuated at 600°C and so on.

[b] Initial rate at 20°C.

[c] Initial rate at 50°C.

[d] Extrapolated to zero conversion.

is the high selectivity for partial hydrogenation. So long as 1,3-BD molecules remain in the gas phase, no complete hydrogenation takes place even though the catalysts have an ability to hydrogenate monoenes under the same reaction conditions. Hydrogen donor molecules are highly effective for hydrogenation, but the partial hydrogenation takes place exclusively. A successive hydrogenation to butane may be retarded by a strong adsorption of CHD and 1,3-BD.

Another specificity of oxide catalysts is the conservation of the molecular identity of the hydrogen during the hydrogenation. Except on MgO-600 and CaO, a mixture of 1,3-BD, D_2, and CHD gave butene-d_0 and -d_2, the contents of the former species being higher. No exchange between 1,3-BD or CHD and D_2 was found. This means that not only the molecular identity of hydrogen is conserved, but deuterium from D_2 and hydrogen from CHD are discriminated during the hydrogenation in such a way that the rate of hydrogenation by CHD is faster than the hydrogenation by molecular hydrogen. Since most of the catalysts except MgO-1000 are active for H_2–D_2 equilibration in the absence of diene molecules, the conservation of molecular identity during the hydrogenation indicates that not only the adsorption of H_2 molecules but the surface migration and recombination of dissociated hydrogen atoms are retarded by organic molecules adsorbed. Organic hydrogen donors such as CHD, a cyclic conjugated diene, may have a similar adsorption capability to linear conjugated dienes and have lower dissociation energy (C–H bond rupture) than H_2 (H–H bond rupture). Hence the concentration of hydrogen atoms derived from CHD is expected to be higher than that from H_2 gas. This may result in the high efficiency of hydrogenating butadienes when CHD is used as a hydrogen source.

Though a pronounced change in the composition of butene isomers produced was found on ZrO_2 when CHD was used (*1*), no such a change was observed over other oxide catalysts.

2. *Transfer Hydrogenation over MgO Catalyst*

Characteristics of MgO in the transfer

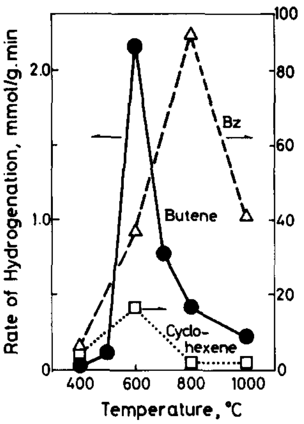

FIG. 1. Variation of catalytic activity in hydrogenation of 1,3-BD with 1,3-CHD and dehydrogenation of 1,3-CHD on MgO with evacuation temperature.

hydrogenation were examined in some detail by changing evacuation temperatures. The temperature dependencies of the hydrogenation of 1,3-BD and the dehydrogenation of CHD are shown in Fig. 1. An activity optimum for the transfer hydrogenation was found at 600°C. For hydrogenation by molecular hydrogen, it is necessary to activate MgO at temperatures over 1000°C, though H_2–D_2 equilibration takes place quite rapidly on the 600°C-evacuated MgO (*5*). Surface area goes through a maximum at 300°C. Optimum pretreatment temperatures for both the transfer hydrogenation and the dehydrogenation of CHD over ZrO_2 were the same, while MgO has different optimum temperatures. It has been reported that the rate of 1-butene isomerization over MgO also goes through a maximum at 800°C (*6*). Coincidence of the optimum temperature of evacuation for both isomerization and dehydrogenation indicates the importance of the abstraction of proton from both 1-butene and CHD molecules.

Rapid dehydrogenation compared with hydrogenation on the 800°C-evacuated catalyst lead to formation of a large amount of gaseous hydrogen, while the amount of hydrogen formed was not so large on the 600°C-evacuated sample (Fig. 2). Even though gaseous dihydrogen was liberated, it did not participate in hydrogenation. This was revealed by a reaction of a mixture of 1,3-BD, CHD, and D_2 (40 : 40 : 40 Torr). Almost exclusive formation of butene-d_0 and a lack of butene-d_n ($n \geq 1$) species indicated that the H atoms from CHD should be transferred to a 1,3-BD molecule before they desorbed; D molecules and the hydrogens liberated from CHD should be equivalent in the gas phase. In the presence of hydrocarbon molecules, H_2 seems not to adsorb on a catalyst surface; this might be one of the reasons why hydrogenation by gaseous hydrogen does not take place in the course of transfer hydrogenation even though the catalyst may be active for H_2–D_2 equilibration.

3. Hydrogenation on CeO_2 Catalyst

Catalytic activity of CeO_2 depends markedly on the starting materials and pretreatment. CeO_2 from chloride (CeO_2(II)) was almost inactive for the isomerization of butene, H_2–D_2 equilibration (*4*), and hydrogenation of 1,3-BD by molecular hydrogen, while CeO_2 from its nitrate (CeO_2(I)) was active for all these reactions. Treatment with 10 Torr of H_2 for 2 h before reaction enhanced the catalytic activity by one to two orders of magnitude in the isomerization of 1-butene (*4*) and the hydrogenation (see Table 1).

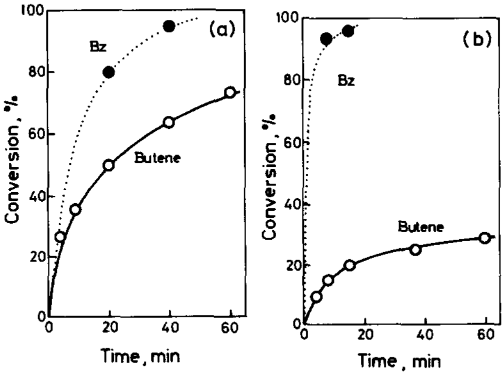

FIG. 2. Hydrogenation and dehydrogenation during reaction of 1,3-BD with 1,3-CHD and D_2 on MgO-600 (a) and -800 (b).

Though the hydrogenating activity of CeO$_2$(I)-600 and CeO$_2$(II)–H-600 was quite low when H$_2$ was used as a hydrogen source, a large increase in reaction rate was found by using CHD as a hydrogen donor. One unique character of the transfer hydrogenation reaction on CeO$_2$ is that the rate of hydrogenation strongly depends on the kind of CHD : 1,3-CHD or 1,4-CHD. Typical examples are listed in Table 2 which includes the hydrogenation of 1,3-BD, 2-M-1,3-BD, and 1,3-PD. For all of these reactions, 1,4-CHD was a more effective hydrogen donor than 1,3-CHD.

A large difference in hydrogenating ability in 1,3- and 1,4-CHD may be understood if one considers that the simultaneous abstraction of two hydrogen atoms from 1,4-CHD is an allowed process, while that from 1,3-CHD is a forbidden process by the Woodward–Hoffmann rules (*7*). In fact, 1,4-CHD dehydrogenates to yield benzene and dihydrogen in a homogeneous gas-phase reaction at temperatures over 300°C, whereas 1,3-CHD does not (*8*). On CeO$_2$, a removal of hydrogen atoms from 1,4-CHD may proceed via a simultaneous abstraction process. The relative rate of the hydrogenation by two donor molecules was high in 1,3-BD hydrogenation and somewhat lower for methyl-substituted 1,3-BD. This difference may result from the relative strengths of adsorption of donor and acceptor molecules.

A high yield of the *trans* isomer was found on CeO$_2$; about 90 to 95% of products was the *trans* isomer, whatever the hydrogen sources were. Since CeO$_2$(II) does not have an ability to isomerize butene even in the absence of dienes, the high yield of *trans* isomer could not be the result of the isomerization of butenes produced. To con-

TABLE 2

Hydrogenation of Conjugated Dienes over CeO$_2$(II)–H-600 with Cyclohexadienes at 20°C

Reactant	Rate (10^{-5} mol/g·min)	Composition (%)		
		1-B	*trans*[c]	*cis*[d]
1,3-BD + 1,4-CHD	239	8.0	86.5	5.5
+ 1,3-CHD	7.5	4.5	94.0	1.5
+ D$_2$	0.01	tr	95	tr
		2-M-1-B[e]	2-M-2-B[f]	3-M-1-B[g]
2-M-1,3-BD[a] + 1,4-CHD	72.0	9.5	89.5	1.0
+ 1,3-CHD	10.8	8.5	91.5	—
		1-P[h]	*trans*[i]	*cis*[j]
1,3-PD[b] + 1,4-CHD	2.26	4.5	92.0	3.0
+ 1,3-CHD	0.37	7.0	90.5	2.5

[a] 2-Methyl-1,3-butadiene.
[b] 1,3-Pentadiene.
[c] *trans*-2-Butene.
[d] *cis*-2-Butene.
[e] 2-Methyl-1-butene.
[f] 2-Methyl-2-butene.
[g] 3-Methyl-1-butene.
[h] 1-Pentene.
[i] *trans*-2-Pentene.
[j] *cis*-2-Pentene.

firm this, both mass spectral and ^1H NMR analysis of the deuterated compounds were performed on the products of both 1,3-BD-d_6 + 1,3-CHD and 1,3-BD-d_6 + 1,4-CHD. One-hundred percent of the *trans* isomer molecules were doubly labeled with H, and all the H atoms were located in the terminal methyl groups. We thus concluded that the *trans* isomer produced is not a secondary product by isomerization, but is the primary product, which reflects the course of hydrogen addition to 1,3-BD molecules.

ACKNOWLEDGMENT

Support of this work by Grant-in-Aid 464135 for scientific research of the Ministry of Education, Japan, is gratefully acknowledged.

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Received October 6, 1983

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