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HYDROGENATION OF 1,3-BUTADIENE WITH CYCLOHEXADIENES OVER CERIUM OXIDE

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Cerium oxide, which is not active for H_2-D_2 equilibration, catalyzes the hydrogenation of 1,3-butadiene using cyclohexadiene as a hydrogen source and gives trans-2-butene almost exclusively. Marked difference in hydrogenating activity was found on cerium oxide between 1,4- and 1,3-cyclohexadienes, the former being much more active than the latter, while there was no difference over MgO.

Activation of H_2 molecule is the most important process in hydrogenation of unsaturated hydrocarbons. The necessity of the dissociation of H_2 molecules has typically been shown in the hydrogenation of cyclohexene on a Au-Pd/Ag catalyst[1). In fact, many metal and metal oxide catalysts which catalyze the hydrogenation reaction are also active for H_2-D_2 equilibration.

In this article we wish to show an alternative process which includes the application of hydrogen donor molecules to the hydrogenation of 1,3-butadiene (1,3-BD)[2) over such a catalyst that catalyzes neither H_2-D_2 equilibration nor the hydrogenation with H_2 molecules.

Cerium oxide was prepared from the hydrolysis of cerium chloride with aqueous ammonia to form an insoluble hydroxide which was then evacuated and treated with hydrogen at 873°K *in situ* prior to use. Magnesium hydroxide was evacuated *in situ* at 1273°K to give MgO catalyst. Typical reaction mixtures contained 33.3×10^2 Pa of 1,3-BD and cyclohexadiene (CHD). The reaction was carried out in a closed recirculation reactor at 293°K.

Table 1 and 2 show the comparisons of the four sets of reactions on cerium oxide and MgO using different hydrogen sources. The products were n-butenes, hydrogen, benzene, isomeric CHD, and a trace amount of cyclohexene. No butane and cyclohexane was obtained.

Table 1. Reactions over cerium oxide at 293°K

Reaction	Rate ($mol \cdot g^{-1} \cdot min^{-1}$)	Relative rate	Product % 1-B[a)	t-2-B[a)	c-2-B[a)
1,3-BD + 1,4-CHD	1.72×10^{-3}	16400	8.0	86.5	5.5
1,3-BD + 1,3-CHD	7.29×10^{-5}	694	4.5	94.0	1.5
1,3-BD + H_2	1.05×10^{-7}	1	trace	95	trace
H_2 + D_2	no	—	—	—	—

a) 1-B: 1-butene, t-2-B: trans-2-butene, c-2-B: cis-2-butene

From these Tables, we can see some important results. First of all, though the cerium oxide catalyst has very low activity to the hydrogenation by H_2 (or D_2) molecules and to H_2-D_2 equilibration, it shows a high activity for hydrogenation of 1,3-BD when CHD is used as a hydrogen source. Secondly, 1,4-cyclohexadiene (1,4-CHD) is the more effective hydrogen source than 1,3-CHD on the cerium oxide catalyst, while there is no difference in both the dienes on MgO. A marked difference in the hydrogen donating ability of two CHDs over cerium oxide suggests that the two hydrogen atoms are abstracted or transferred to the catalyst or to the diolefin molecule simultaneously. Iridium complexes have also been reported to catalyze the disproportionation of 1,4-CHD to benzene and cyclohexene while 1,3-CHD was completely inert3). This is not the case on MgO; one hydrogen atom is liberated from CHD (probably as a proton) and a common intermediate is formed, which gives one benzene molecule by dropping another hydrogen atom or could be an intermediate of the interconversion between 1,3-and 1,4-CHD. In fact, the isomerization between 1,3-and 1,4-CHD on cerium oxide hardly took place, while it was very rapid on MgO. Thirdly, almost exclusive formation of trans-2-butene was found on the cerium oxide catalyst. The selectivity of olefin isomers did not change by changing the hydrogen sources, unlike the case of $ZrO_2$2), though an intrinsic selectivity was completely different over those two catalysts. The predominance of 2-olefin may suggests that the π-allyl intermediate is important, as Kwiatek has postulated.4). The exclusive formation of trans isomer on cerium oxide may reflect the gas phase composition of 1,3-BD, anti form being much more favorable than the syn form. On the other hand, syn-π-allyl-system was proposed on MgO which is known as a typical base catalyst5).

Table 2. Reactions over MgO at 293°K

Reaction	Rate	Relative	Product %		
	$(mol\cdot g^{-1}\cdot min^{-1})$	rate	1-B a)	t-2-B a)	c-2-B a)
1,3-BD + 1,4-CHD	7.56×10^{-4}	5.3	12.0	11.5	77.0
1,3-BD + 1,3-CHD	7.78×10^{-4}	5.4	12.5	17.5	73.0
1,3-BD + H_2	1.43×10^{-4}	1	12.5	12.5	76.0
H_2 + D_2	no	—	—	—	—

a) See the footnote of Table 1.

Proton NMR analysis revealed that the two H atoms are located almost exclusively on the 1 and 4 carbon atoms of trans-$C_4H_2D_6$ which was formed from the reaction of 1,4-CHD and 1,3-C_4D_6 on the cerium oxide catalyst. This clearly shows that trans-2-butene is the primary product and not an isomerized product.

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