Tetrahedron Letters No. 26, pp 2407 - 2410.
0040-4039/79/0622-2407$02.00/0

EFFECTS OF CROWN ETHER ON HYDROGENATION OVER NICKEL AND COBALT BORIDE CATALYSTS: EFFECTS IN CATALYST PREPARATION AND EFFECTS AS ADDITIVES

Masatsugu KAJITANI*, Jun HASEGAWA, Etsuko KASAI, and Akira SUGIMORI
Department of Chemistry, Faculty of Science and Technology, Sophia University,
Kioi-cho 7, Chiyoda-ku, Tokyo 102, Japan

Abstract: The nickel and cobalt boride catalysts prepared in the presence of crown ethers show different selectivities from the ordinary boride catalysts in the reduction of cycloalkene, styrene oxide, and 4-t-butylcyclohexanone.

Crown ethers have been very extensively applied to organic syntheses. The activation of sodium borohydride by crown ethers has been reported in the reduction of ketones[1,2] and sulfoxides.[3] In contrast crown ethers are rarely used for the catalyst preparation. We report here the effects of crown ethers on the preparation of nickel and cobalt boride catalysts. The activities and selectivities of the catalysts prepared in the presence of crown ethers in the hydrogenation and hydrogenolysis are compared with those of the ordinary boride catalysts. The effects of crown ethers as additives in the hydrogenation were also investigated.

For the catalyst preparation, the standard method for the preparation of metal boride catalysts[4] was modified. Thirty cubic centimeters of an aqueous solution (A) containing 0.11 mol of $NaBH_4$ were added dropwise to 180 cm^3 of an aqueous solution (B) containing 0.017 mol of nickel or cobalt chloride under vigorous stirring. The black precipitate which formed was filtered and was washed with degassed distilled water until the washings became neutral to phenolphthalein. The catalyst thus prepared was washed several times with 2-propanol, the solvent for the hydrogenation. Catalyst preparation was modified by adding crown ethers to the solution A or B(0.011 mol). When crown ether was used as an additive, it was added to the final 2-propanol solution (C)([Substrate]/[Crown ether] = 10).

In this paper the catalysts are expressed by combining M_2B(M = Ni, Co), symbol A, B, or C indicating the step where crown ethers were used, and the ring size of the crown ether. For example, Co_2B-A-12 represents the cobalt boride catalyst prepared by the reaction of the cobalt chloride solution with the sodium borohydride solution containing 12-crown-4.

As is shown in Table 1, the addition of crown ether to $NaBH_4$ solution gave

Table 1 Hydrogenation of cyclohexene and cyclooctene over nickel boride catalysts modified with 12-crown-4

	Initial hydrogenation rate/10^{-3} mol min^{-1} g^{-1}	
Catalyst	Cyclohexene(C6)	Cyclooctene(C8)
Ni_2B	2.24	2.33
Ni_2B-A-12	3.09	2.93
Ni_2B-B-12	2.09	2.16
Ni_2B-C-12	1.62	1.58
Ni_2B-D-12*	2.11	2.22

* Ni_2B modified by treating the ordinary Ni_2B with aqueous crown ether(0.11 mol) bebore replacing water with 2-propanol.

the greatest activity to the catalyst for the hydrogenation of cyclohexene and cyclooctene(conditions for hydrogenation; substrate, 1.5 x 10^{-2} mol in 10 cm^3 of 2-propanol; temp, 30°C; H_2 pressure, 1 atm). While its effect as an additive is to deactivate the catalyst. The effects of crown ethers are also observed in the selectivities in several reactions performed over the catalysts.

Selectivity in the hydrogenation of cycloalkenes.[5] When we take the relative hydrogenation rate of cyclohexene to cyclooctene($r_{C6/C8}$) as a measure of selectivity(Fig. 1), the addition of crown ethers both in the catalyst preparation and as additives gives similar effects; when 15-crown-5 is used, the value shows a maximum.

Another measure of the selectivity is the relative adsorption coefficient, a measure of the affinity of the catalyst toward substrates. The value is obtained by means of competitive reaction.[6] The dependence of the relative adsorption coefficient(cyclohexene to cyclooctene)($K_{C6/C8}$) on the ring size of crown ethers used in the preparation of boride catalysts is different from the dependence on the ring size of these ethers used as additives (Fig. 2). This suggests that the effect of crown ether in the procedure of catalyst preparation is not due to the crown ether remaining on the catalyst surface; crown ether used in the catalyst preparation should change the character of the catalysts. In this case 15-crown-5, which forms the most stable complex with sodium ions, has a different effect from the other crown ethers.

Selectivity in the reduction of styrene oxide.[7] In the reduction of styrene oxide (conditions for reduction; over nickel catalysts; substrate, 0.05 mol in 10 cm^3 of 2-propanol; temp, 30°C; H_2 pressure, 1 atm; over cobalt catalyst; substrate, 0.05 mol in 40 cm^3 of 2-propanol; temp, 30°C; H_2 pressure, 40 atm), a significant effect due to crown ether is observed in the catalysis of cobalt boride. As is seen in Fig. 3, the reduction over Co_2B-A (prepared by using the mixture of sodium borohydride and crown ether) gave more dehydrogenated products than over ordinary Co_2B in both the presence and the absence of

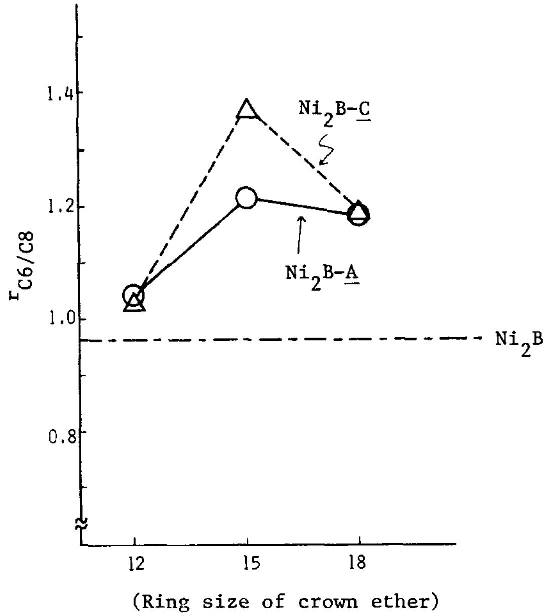

Fig. 1. Relative hydrogenation rate of cyclohexene to cyclooctene

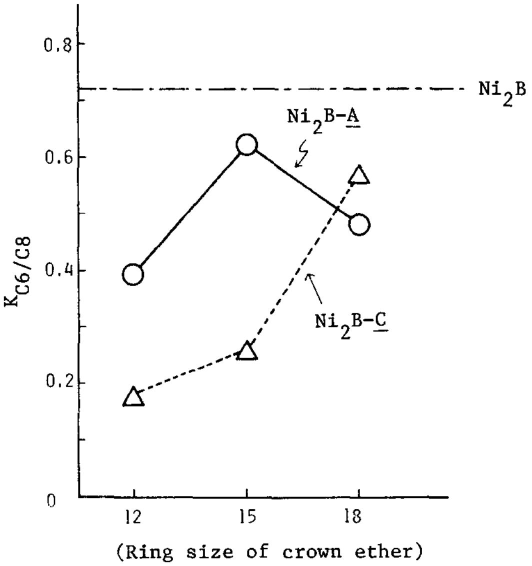

Fig. 2. Relative adsorption coefficient of cyclohexene to cyclooctene

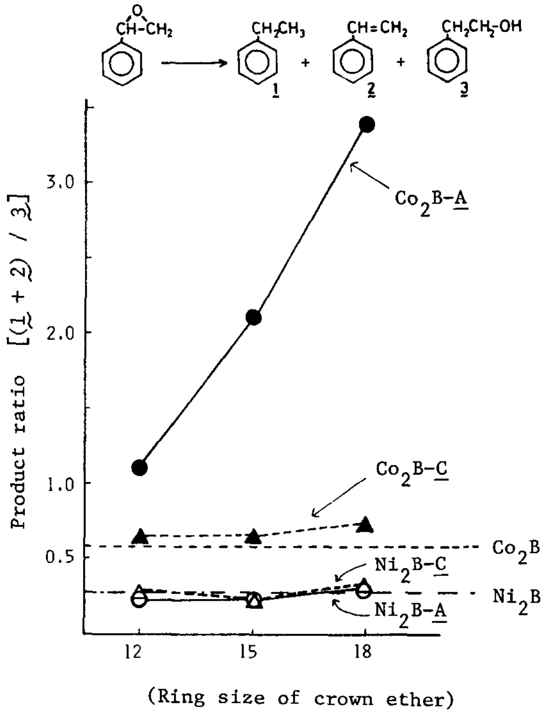

Fig. 3. Selecticity in the hydrogenation of styrene oxide

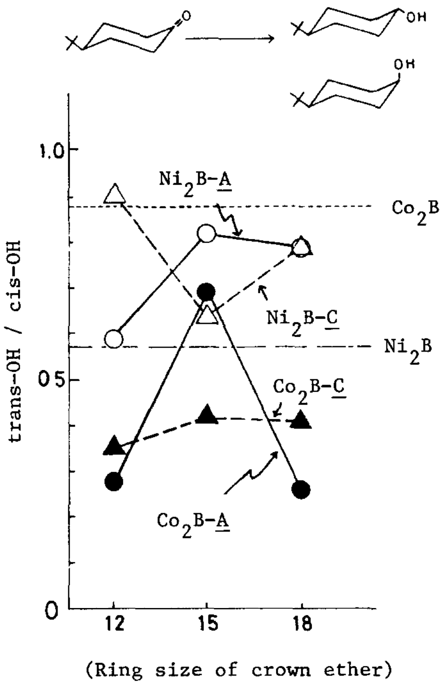

Fig. 4. Stereoselectivity in the hydrogenation of 4-t-butylcyclohexanone

crown ethers. This also indicates that the role of crown ethers in the catalyst preparation is to change the character of the catalyst.

Stereoselectivity in the hydrogenation of 4-t-butylcyclohexanone.[8] The modification of nickel and cobalt boride catalysts with crown ethers changes the stereoselectivity in the hydrogenation of 4-t-butylcyclohexanone. In the hydrogenation over A type catalysts (conditions for hydrogenation; substrate, 0.025 mol in 40 cm^3 of 2-propanol; temp, 20 - 70°C; H_2 pressure, 50 atm), the dependence of the stereoselectivity on the ring size of crown ether is different from that in the hydrogenation over C type catalysts. As in the hydrogenation of cycloalkenes, the effect of 15-crown-5 is different from that of 12-crown-4 and 18-crown-6. The hydrogenation over Co_2B-A-12 and Co_2B-A-18 gave the highest selectivity for the less stable cis-isomer.

Crown ethers may change the composition and the surface character of the boride catalysts by complexing the metal ions in the catalyst preparation.

---

1) T.Matsuda and K.Koida, Bull. Chem. Soc. Jpn., 46, 2259 (1976).

2) D.Landini, F.Montanari, and F.M.Piris, J. Chem. Soc., Chem. Commun., 1974, 879.

3) H.D.Durst,J.W.Zubrick, and G.R.Kieczykowski, Tetrahedron Lett, 1974, 1777.

4) a) R.Paul, P.Buisson, and N.Joseph, Ind. Eng. Chem., 44, 1006 (1952); b) C.A.Brown, J. Org. Chem., 35, 1900 (1970).

5) a) M.Kajitani, Y.Sasaki, J.Okada, K.Ohmura, A.Sugimori, and Y.Urushibara, Bull. Chem. Soc. Jpn., 47, 1203 (1974); b) Y.Nitta, T.Imanaka, and S.Teranishi, Nippon Kagaku Kaishi, 1976, 1362.

6) When the adsorption follows the Langmuir isotherm and the rate of hydrogenation is proportional to the amount of adsorbed M_1 and M_2, the product ratio($[P_1]/[P_2]$) at the initial stage of the competitive reaction starting from 1 : 1 mixture of M_1 and M_2 is expressed as
$[P_1]/[P_2] = (K_1/K_2)\cdot(k_1/k_2)$
where K_1/K_2 is the relative adsorption coefficient of M_1 with respect to M_2, and k_1/k_2 is the ratio of the rates in the individual reaction. From k_1/k_2 and $[P_1]/[P_2]$ obtained experimentally, we can obtain K_1/K_2. See a detailed kinetic treatment: T.Chihara and K.Tanaka, Chem. Lett., 1977, 843.

7) a) M.S.Newman, G.Underwood, and M.Renold, J. Am. Chem. Soc., 71, 3362 (1949); b) G.J.Park and R.J.Fuchs, J. Org. Chem., 22, 93 (1957).

8) S.Mitsui, H.Saito, Y.Yamashita, M.Kaminaga, and Y.Senda, Tetrahedron, 29, 1531 (1973).

(Received in Japan 28 March 1979)