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Surface-mediated stereoselective hydrogenation of dienes over chromium subcarbonyls encaged in zeolite

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Tricarbonyl chromium (0) species encaged in LiX or NaX was found to be highly efficient and stereoselective for the hydrogenation of butadiene at > 230 K. The selectivity to cis-2-butene depended both on the reaction temperature and butadiene pressure. The reaction mechanism is proposed, in which cis-2-butene is formed via $(\eta^4\text{-}C_4H_6)Cr(CO)_3$, while 1-butene via $(\eta^2\text{-}C_4H_6)Cr(CO)_3$ and $(\eta^2\text{-}C_4H_6)_2Cr(CO)_3$.

Keywords: Butadiene hydrogenation; chromium carbonyl; zeolite

Catalytic properties of transition metal complexes anchored on inorganic oxide surfaces or encapsulated in porous materials have recently received extensive attention to design and exploit novel catalyst systems [1,2]. In our previous studies [3,4] it was found that $Mo(CO)_6$ encaged in alkali metal cation Y-zeolite shows high catalytic activities at 423 K for the stereoselective hydrogenation of conjugated dienes to the corresponding cis-2-olefins. The active species is suggested to be $Mo(CO)_3$ subcarbonyl species on the basis of IR study [5]. Actually, $Mo(CO)_3$ thermally stabilized in a zeolite was demonstrated to exhibit a moderate activity for butadiene hydrogenation even at 273 K [3]. The activity depended on the cation in zeolite and decreased in the order $LiY > NaY \gg KY > CsY$ [3]. In the present study, Cr-carbonyl/zeolite systems were examined for stereoselective hydrogenation of butadiene to obtain more detailed information on the catalytic behaviors of group 6 metal carbonyls encaged in zeolite.

NaX and LiX (57% ion-exchanged) zeolites used here (Si/Al atomic ratio: 1.23) have been described elsewhere [6]. After evacuation at 673 K for 60 min, zeolite (12–40 mg) in a reactor was exposed to a $Cr(CO)_6$ vapor at room temperature for 60 min. The $Cr(CO)_6$ loadings were 2.2/supercage of zeolite by means of chemical analysis.

Cr-subcarbonyl species anchored on NaX and LiX zeolites were prepared by evacuating $Cr(CO)_6$/zeolites at 373 K for 30 min and 383 K for 60 min,

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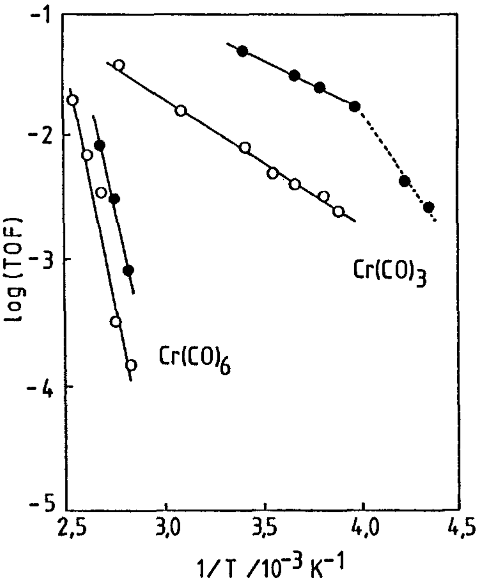


Fig. 1. Arrhenius plot for the butadiene hydrogenation over chromium carbonyl encaged in zeolite (turnover frequency: mol Cr-g-atom^{-1} s^{-1}). The initial pressures of butadiene and H_2 were 4.0 and 20 kPa, respectively. ○; NaX and ●; LiX.

respectively. The hydrogenation of butadiene was carried out using a closed circulation system (220 cm^3) [3,4] at 393–230 K. The reaction gas was analyzed by glc.

On the basis of the temperature programmed decomposition profiles of various $Cr(CO)_6$/zeolite systems, a thermally stable Cr-subcarbonyl species was found to be prepared in X-type zeolites on evacuation at 373–383 K. The IR spectra of the Cr-subcarbonyl species/NaX (1917 and 1767 cm^{-1}) indicated the formation of $Cr(CO)_3$ species [7,8]. Analogous $Mo(CO)_3$ species have been reported to be thermally stabilized in Y- [8–11] and X-zeolites [11]. The preparation of $Cr(CO)_3$/LiX required a higher evacuation temperature (383 K) than $Cr(CO)_3$/NaX, probably, due to weaker $Cr(CO)_6$-zeolite interactions.

The hydrogenation rates are presented in fig. 1 for Cr-carbonyl/X-type zeolite catalysts. The reaction was first order with H_2 pressure (< 56 kPa). The reaction products were predominantly cis-2-butene ($> 95\%$) accompanying a small amount of 1-butene. No formations of trans-2-butene and butane were observed. In contrast to Mo-carbonyl anchored in alkali metal cation zeolite Y [3], no isomerization of butene was observed over Cr-carbonyl systems even after a complete consumption of butadiene. It is demonstrated in fig. 1 that $Cr(CO)_3$/LiX is highly active and selective for the hydrogenation and that it shows a substantial activity (TOF: 3.6×10^{-3} s^{-1} or 13 h^{-1}) even at 230 K. The apparent activation energies were 36.5 and 30.8 kcal mol^{-1} for $Cr(CO)_6$/NaX and LiX and 5.2 and 3.9 kcal mol^{-1} for $Cr(CO)_3$/NaX and LiX, respectively. A

Table 1
Turnover frequencies [a] of butadiene hydrogenation over Cr- and Mo-carbonyl catalysts at 273 K

Catalyst	TOF/s^{-1}
$Cr(CO)_3$/LiX	0.27 (0.61 [b])
$Cr(CO)_3$/NaX	0.031 (0.11 [b])
$Cr(CO)_6$/LiX [c]	1.4×10^{-8}
$Mo(CO)_3$/LiY [d]	0.0012
$Mo(CO)_6$/LiY [c,d]	3.1×10^{-10}
$Cr(CO)_3(CH_3CN)_3$ [e]	0.13 [b]
$Cr(CO)_6$/h [e]	0.0009 [f]

[a] Adjusted to 1 atm of H_2 assuming a first order with respect to H_2 pressure.
[b] At 313 K.
[c] Extrapolated values.
[d] Ref. [3].
[e] Calculated from the tables in ref. [12]. 2-methyl-1,3-butadiene was used instead of 1,3-butadiene.
[f] At 283 K.

precipitous activity drop for $Cr(CO)_3$/LiX at very low temperatures is ascribed to butadiene condensation in the zeolite cages.

The turnover frequencies (TOF) of the butadiene hydrogenation at 273 K and 1 atm of H_2 are summarized in table 1 for the present Cr-carbonyl catalysts and compared with those for other catalyst systems including a homogeneous $Cr(CO)_6$ photocatalyst and $Cr(CO)_3(CH_3CN)_3$ [12] (the most active catalyst in a homogeneous system cited in ref. [12]). It is demonstrated that $Cr(CO)_3$/LiX is about 230 times more active than $Mo(CO)_3$/LiY, which has been reported to be most active in Mo-carbonyl/zeolite systems for the stereoselective hydrogenation of butadiene [3]. Although a strict comparison is not possible because of the difference in the reactant, it seems that $Cr(CO)_3$/LiX is as active as or more active than $Cr(CO)_3(CH_3CN)_3$ for the diene hydrogenation. $Cr(CO)_3$/LiX is two orders of magnitude more active than the photo-catalytic reaction system. The low activities of $Cr(CO)_6$ in both thermal- and photo-catalytic systems are undoubtedly ascribed to low fractions of active species during the reaction.

Zeolite framework oxygens are considered to play important roles in the $Cr(CO)_x$/zeolite catalyst systems as solid ligands. The higher activity of $Cr(CO)_3$/LiX than that of $Cr(CO)_3$/NaX is attributed to weaker interactions of $Cr(CO)_6$ with zeolite framework oxygens, since LiX shows lower basicity than NaX [6].

Shown in fig. 2 is the fraction of cis-2-butene as a function of reaction temperature for Cr-carbonyl/NaX. A similar correlation was obtained for Cr-carbonyl/LiX. It is evident that the selectivity depends on the reaction temperature: the fraction of cis-2-butene exhibits a maximum at 330–350 K (98.5%). $Cr(CO)_6$ and $Cr(CO)_3$/zeolite showed the identical selectivity, indicating that the active species are common in both reaction systems and are,

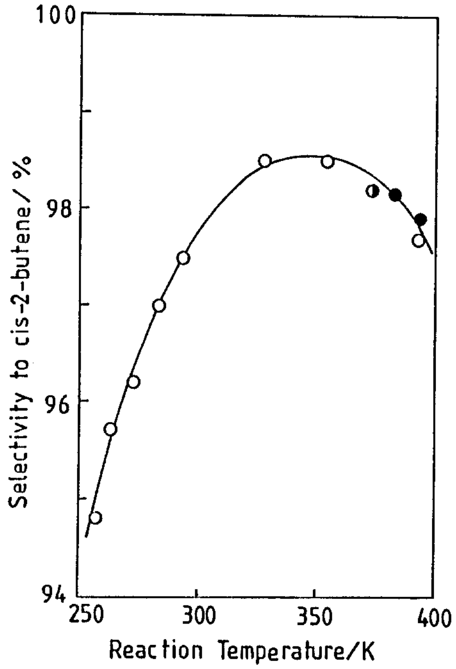
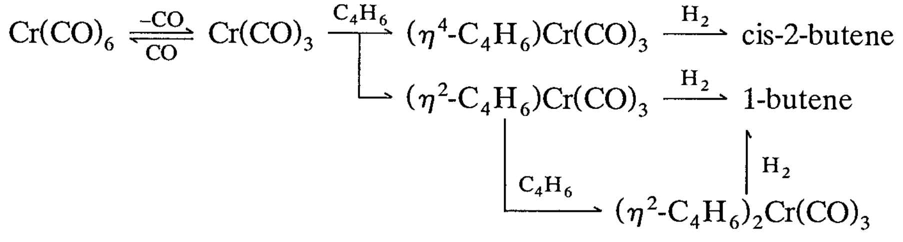


Fig. 2. Selectivity to cis-2-butene as a function of reaction temperature in the hydrogenation of butadiene over chromium carbonyl encaged in NaX. Reaction conditions are shown in fig. 1. ○; $Cr(CO)_3$ and ●; $Cr(CO)_6$.

probably, $Cr(CO)_3$ [7]. It was also found with Cr-carbonyl/NaX that the selectivity to cis-2-butene decreased with increasing butadiene pressure. Since 1-butene is not a secondary product due to the isomerization of cis-2-butene, these findings indicate that the relative rates of 1,2- and 1,4-H_2 additions to butadiene depend on the reaction temperature and butadiene pressure. It is considered that $(\eta^4\text{-}C_4H_6)Cr(CO)_3$ is thermally more stable than $(\eta^2\text{-}C_4H_6)Cr(CO)_3$ or $(\eta^2\text{-}C_4H_6)_2Cr(CO)_3$ and that the proportion of $(\eta^2\text{-}C_4H_6)_2Cr(CO)_3$ increases at a low temperature or at a high butadiene pressure as a consequence of the increase in the amount of C_4H_6 adsorption in the supercage of zeolite. Accordingly, the selectivity dependences on reaction temperature and butadiene pressure can be explained by invoking a reaction mechanism in which $(\eta^4\text{-}C_4H_6)Cr(CO)_3$ is responsible for the cis-2-butene production, while $(\eta^2\text{-}C_4H_6)Cr(CO)_3$ and $(\eta^2\text{-}C_4H_6)_2Cr(CO)_3$ complexes are responsible for the 1-butene formation.



The above reaction network is supported by a precise kinetic analysis and will be presented elsewhere.

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