Dehydrogeno-aromatization of Cyclohexanes with suspended Noble-metal Catalysts

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Under boiling and refluxing conditions, suspended noble-metal catalysts produced selective dehydrogenoaromatization of cyclohexanes, yielding aromatic compounds and molecular hydrogen with Pt being more active than Ru. The retardation effects caused by aromatic compounds being present in the solution were ascribed not only to active-site occupation but also to hydrogen transfer, which consumed the surface hydrogen species as the precursor of molecular hydrogen.

Alkane dehydrogenation under mild reaction conditions

$$C_n H_{2n+2} \rightarrow C_n H_{2n} + H_2 \tag{1}$$

has attracted considerable attention in catalytic chemistry,¹ since endothermic reactions are generally performed at high temperatures,² as exemplified by styrene formation³ and by various processes for petroleum reforming.⁴

The equilibrium restriction imposed for low-temperature alkane dehydrogenation can be removed under boiling and refluxing conditions, because no molecular hydrogen is allowed to remain in the reaction medium once it has evolved as a gas.⁵ Actually, heterogeneous dehydrogenoaromatization catalysts were found for a series of cyclo-hexanes under boiling and refluxing conditions:⁶

$$\bigcap R \longrightarrow \bigcap R + 3H_2 (2)$$

Homogeneous^{7,8} and heterogeneous^{9,10} active catalysts had previously been reported for cyclooctane dehydrogenation:

In the present work, dehydrogeno-aromatization of cyclohexanes is investigated with special emphasis on rate retardation due to aromatic addends using carbon-supported noble-metal catalysts.

Experimental

Cyclohexanes were treated with a mixture of concentrated sulfuric and nitric acids, then washed with water and dried over calcium chloride, aiming to remove unsaturated hydrocarbons. They were used after they had been distilled from sodium under a nitrogen atmosphere. The same noble-metal catalysts (Pt, Pd, Rh and Ru supported on carbon and alumina, 5 wt.%, N.E. Chemcat) as used for propan-2-ol dehydrogenation¹¹ were suspended in the substrate cyclohexanes. Heat treatment of the catalysts just before use in a hydrogen stream for 30 min and *in vacuo* for 10 min at 453 K was also the same as for propan-2-ol dehydrogenation except for the carbon-supported catalysts, where a drying pretreatment in a nitrogen stream for 1 h and *in vacuo* for 30 min at 453 K was necessary to eliminate water from carbon.

All manipulations were carried out under a nitrogen atmosphere. The catalyst solution (0.2 mmol metal/100 cm³) in a Schlenk tube (200 cm³) was heated to its boiling point, stirred by a magnetic stirrer (500 r.p.m.) and refluxed, keeping the temperature 30 K higher than the boiling point using an oil bath. The amount of gas evolved was measured by a gas burette (250 cm³). A prescribed amount of benzene, toluene, xylenes, and ethylbenzene or deuterium-substituted ethyl-(ethyl[${}^{2}H_{5}$]benzene and [${}^{2}H_{10}$]ethylbenzene, benzene Aldrich) was added to ethylcyclohexane (100 cm³) for the retardation experiments of aromatics. The product composition was analysed by gas chromatography, using an active carbon column or OV-1 and PEG 20M capillary columns for the gas- and liquid-phase components, respectively. Deuterium distributions were analysed with a quadrupole-type mass spectrometer (NEC Anerva, AQA 360) and a ²H NMR spectrometer (JEOL, JMN GX-400) for molecular hydrogen and the solution components, respectively.

Results and Discussion

Catalytic Dehydrogeno-aromatization of Cyclohexanes under Boiling and Refluxing Conditions

The reaction products in the gas and liquid phases after dehydrogenation for 24 h are summarized in Table 1. The stoichiometric coincidence was satisfactory. A trace amount of methane was detected, however, in all runs. Neither monoene, diene, styrene nor isomerized xylenes could be found in solution. The total turnover numbers, based on the total numbers of atoms in the system, amounted to 39.9 for ethylcyclohexane with the Pt(0.2 mmol)/carbon catalyst during 24 h of reaction under boiling and refluxing conditions. The results in Table 1 confirm that the dehydrogenoaromatization reaction proceeded catalytically. The poor activity of the Ru catalyst for this reaction is in sharp contrast to propan-2-ol dehydrogenation, for which the Ru catalyst exhibited the highest activity among similar catalysts used.¹¹ Carbon-supported catalysts were more active than the alumina-supported ones, probably because the carbon supports were dispersed better in these suspended solutions than alumina supports.

The thermodynamic restriction imposed for the formation of benzene and hydrogen from cyclohexane at temperatures as low as 355 K was avoided under the reaction conditions used with accompanying product separation. Dehydrogenoaromatization of cyclohexane at low temperatures is especially important from the viewpoint of thermal energy conversion, because a fuel cell can be constructed using its reverse reaction, *i.e.* hydrogenation of benzene.¹²

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Table 1	Dehydrogenation of o	cyclohexanes with sus	pended noble-metal cat	alysts under boiling as	nd refluxing conditions
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catalyst	substrate	T/K	H ₂ /mmol	aromatics/mmol
Pt/carbon	ethylcyclohexane	405	23.93	7.75 (ethylbenzene)
Pt/alumina	ethylcyclohexane	405	13.04	4.15 (ethylbenzene)
Pd/carbon	ethylcyclohexane	405	9.22	3.18 (ethylbenzene)
Pd/alumina	ethylcyclohexane	405	3.67	1.25 (ethylbenzene)
Rh/carbon	ethylcyclohexane	405	2.59	0.98 (ethylbenzene)
Rh/alumina	ethylcyclohexane	405	1.96	0.78 (ethylbenzene)
Ru/carbon	ethylcyclohexane	405	0.15	0.06 (ethylbenzene)
Ru/alumina	ethylcyclohexane	405	0.04	0.02 (ethylbenzene)
Pt/carbon	1.2-dimethylcyclohexane	400	13.20	4.20 (o-rylene)
Pt/carbon	1.3-dimethylcyclohexane	395	13.12	3 79 (<i>m</i> -xylene)
Pt/carbon	1.4-dimethylcyclohexane	395	12.78	3.78 (<i>p</i> -xylene)
Pt/carbon	methylcyclohexane	373	4 59	1 42 (toluene)
Pt/carbon	cyclohexane	355	1.89	0.48 (benzene)

Catalyst concentration, 0.2 mmol metal per 100 cm³; Reaction time, 24 h.

 Table 2
 Effect of aromatic additive on catalytic dehydrogeno-aromatization of ethylcyclohexane: rate retardation of hydrogen evolution and hydrogen transfer to aromatics

	reaction product/mmol			
aromatic additive	ethylbenzene	hydrogen	hydrogenated species	
ethylbenzene	1.31	3.77		
benzene	1.54	3.47	0.32 (cyclohexane)	
toluene	1.99	4.27	0.56 (methylcyclohexane)	
o-xylene	4.13	11.26	0.05 (1,2-dimethylcyclohexane)	
<i>m</i> -xylene	4.13	11.18	0.16 (1,3-dimethylcyclohexane)	
p-xylene	2.45	6.50	0.14 (1,4-dimethylcyclohexane)	

Solution, ethylcyclohexane (100 cm³) with additive (2.0 cm³); catalyst, Pt/carbon (0.2 mmol metal, 5 wt.%), 0.78 g; reaction conditions, boiling and refluxing (405 K) for 5 h.

Rate Retardation due to Aromatic Compounds

The rates of hydrogen evolution were suppressed by aromatic compounds added to the ethylcyclohexane solution of the carbon-supported platinum catalyst, as shown in Fig. 1. The large retardation effects of ethylbenzene, toluene and benzene are noteworthy.

It was found that a fraction of added benzene, toluene or xylene was changed into cyclohexane, methylcyclohexane or corresponding dimethylcyclohexanes (Table 2). Intermolecular hydrogen transfer from ethylcyclohexane to aromatic compounds proceeds simultaneously during catalytic hydrogen evolution. Ethylbenzene formation was well correlated stoichiometrically with the sum of hydrogen transfer from ethylcyclohexane to the aromatic additive and hydrogen evolution. The site-blocking ability of aromatics, indicated by the decrease in the rate of ethylbenzene formation, was apparently larger for ethylbenzene, benzene and toluene than the others. Adsorption of aromatic additives must cause the rate decrease of ethylcyclohexane dehydrogeno-aromatization not only through active-site occupation but also by hydrogen transfer, with the surface hydrogen species consumed.

Note that adsorption equilibrium is not established between the catalyst surface and the solution for hydrogen under boiling and refluxing conditions in contrast to aromatic additives. The concentration of hydrogen species on the surface is determined from the relative rate of ethylcyclohexane dehydrogenation on the surface, desorption of molecular hydrogen and hydrogen transfer to adsorbed aromatics, because no molecular hydrogen is allowed to dissolve in the solution under boiling and refluxing conditions.



Fig. 1 Catalytic H₂ evolution from ethylcyclohexane added with 0.5 cm³ (a) and 2.0 cm³ (b) *m*-xylene (\bigcirc), *p*-xylene (\square), *p*-xylene (\square), *b*enzene (\triangle) and ethylbenzene (\blacktriangle), or no additive (\bigstar) in the suspended Pt/carbon solution (0.2 mmol metal per 100 cm³) under boiling and refluxing conditions (405 K)



Fig. 2 Effect of *m*-xylene (\bigcirc) , *o*-xylene (\bigcirc) , *p*-xylene (\bigcirc) , toluene (\boxdot) , benzene (\triangle) , and ethylbenzene (\blacktriangle) on the rate of catalytic hydrogen evolution from ethylcyclohexane

The initial rate of hydrogen evolution (v) and the concentrations of aromatic compounds ([Add]) were well correlated by a Langmuir-type rate equation

$$v = k/(1 + K[Add]) \tag{4}$$

since 1/v as a function of [Add] gave straight lines, as shown in Fig. 2.

The retardation constants (K) for ethylbenzene, toluene and benzene additives and the rate constants of hydrogen transfer $(k_{\rm HT})$ [eqn. (5)] for both benzene and toluene were larger in magnitude than those for xylenes (Table 3).

$$v_{\rm HT} = k_{\rm HT} [\rm Add] \tag{5}$$

Ethylcyclohexane Dehydrogenation in the Presence of Deuterium-substituted Ethylbenzene

The rate retardation induced by deuterium-substituted ethylbenzene for catalytic ethylcyclohexane dehydrogenation increased in the order of $[{}^{2}H_{0}]$ ethylbenzene < ethyl $[{}^{2}H_{5}]$ benzene < $[{}^{2}H_{10}]$ ethylbenzene, indicating the operation of kinetic deuterium isotope effects with respect to hydrogen evolution (Fig. 3).

Molecular hydrogen included deuterium, the H : D ratios of which are depicted as a function of reaction periods in Fig. 4. H : D ratios as large as 6–11 for the ethylcyclohexane-ethyl[${}^{2}H_{s}$]benzene solution indicate the predominant surface coverage with H species.

From the observed linear correlations, initial H : D ratios of 5.9 and 0.79 were obtained by extrapolation for the ethylcyclohexane solutions containing $ethyl[^{2}H_{5}]$ benzene and $[^{2}H_{10}]$ ethylbenzene, respectively. The initial H : D ratio of 0.79 and the concentration of $[^{2}H_{10}]$ ethylbenzene in the catalyst solution suggested to us that the supply of D atoms from ethylbenzene to the surface proceeded 250 times faster than that of H atoms from ethylcyclohexane. As for the relative rates of deuterium supply from the two kinds of groups

 Table 3
 Catalytic dehydrogeno-aromatization of ethylcyclohexane

 retarded by additives and accompanying hydrogen transfer

aromatic additive	$K/10^{-3} \text{ mmol}^{-1} \text{ dm}^3$	$k_{\rm HT}/10^{-2} \rm h^{-1} g^{-1}$	
ethylbenzene	33.7		
benzene	22.9	27.4	
toluene	21.8	46.2	
o-xylene	5.34	1.39	
m-xylene	3.34	6.67	
p-xylene	10.6	3.33	

Solution, ethylcyclohexane (100 cm³) with additives $(0.5-2.0 \text{ cm}^3)$; catalyst, Pt/C (0.2 mmol metal, 5 wt.%) 0.78 g; reaction conditions, boiling and refluxing (405 K) for 5 h.



Fig. 3 Catalytic hydrogen evolution from ethylcyclohexane with 0.5 cm³ of $[^{2}H_{0}]$ ethylbenzene (\bigcirc), ethyl $[^{2}H_{5}]$ benzene (\triangle) and $[^{2}H_{10}]$ ethylbenzene (\square) in the suspended Pt/carbon solution (0.2 mmol metal per 100 cm³) under boiling and refluxing conditions (405 K)

in ethylbenzene, it was deduced that the ethyl group supplied D atoms 6.4 times faster than the phenyl group.

The H-D exchanges between the components in solution were examined by means of ¹H, ²H and ¹³C NMR. The ¹H NMR spectrum of ethylcyclohexane exhibited three superimposed peaks at 0.8-1.75 ppm, which were correlated with its ¹³C NMR spectrum by the ¹H-¹³C two-dimensional method (Fig. 5). The highest-field ¹H NMR peaks (0.8-0.9 ppm) of ethylcyclohexane were assigned to the superimposition of hydrogen atoms at the methyl group of the ethyl substituent and the meta position of the cyclohexyl ring. The middle peaks (1.1-1.3 ppm) were composed of the methylene group of the ethyl substituent and the ortho, para and ipso positions of the cyclohexyl ring. The lowest-field peaks (1.6-1.75 ppm) were ascribed to the cyclohexyl protons in the ortho, meta and para positions. With regard to the ²H NMR spectra, the methylene group of ethylbenzene gave a broad peak around 2.65 ppm, which did not overlap with either ethylcyclohexane or with the other groups of ethylbenzene as a consequence of the inductive effect caused by the phenyl moiety.

Fig. 6 shows the ²H NMR spectra of a catalytic solution of the ethyl[${}^{2}H_{5}$]benzene-ethylcyclohexane mixture before (a) and after 24 h reaction (b). Dissociative adsorption of ethylbenzene at the ethyl group was confirmed, since a new ²H peak appeared around 2.65 ppm, belonging to the methylene group of ethylbenzene. Deuterium substitution of the cyclo-



Fig. 4 H:D ratios in molecular hydrogen evolved from ethylcyclohexane added with 0.5 cm³ of ethyl[²H₅]benzene (\Box) and [²H₁₀]ethylbenzene (Δ) in the suspended Pt/carbon solution (0.2 mmol metal per 100 cm³) under boiling and refluxing conditions (405 K)

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Fig. 5 2D ¹H-¹³C correlated NMR spectrum of ethylcyclohexane, with the ¹³C NMR spectrum projected horizontally and the ¹H NMR vertically

hexyl group was also confirmed, since ethylbenzene gave no contribution to the region around 1.70 ppm.

The rate of hydrogen transfer from ethylcyclohexane to ethylbenzene was estimated to be at least $15 \times 10^{-2} h^{-1} g^{-1}$ from the total amount of D atoms remaining in the solution, and was comparable to the rates obtained for benzene and toluene (Table 3). Not only was H-D exchange between the adsorbed ethylbenzene and the surface hydrogen species demonstrated but also hydrogen transfer from ethylcyclohexane to ethylbenzene.

Conclusions

1. The rate of ethylcyclohexane dehydrogeno-aromatization, yielding ethylbenzene and molecular hydrogen, was retarded by the adsorption of aromatic compounds.



Fig. 6 ²H NMR spectra of the mixture of ethyl[²H₅]benzene (0.5 cm³) and ethylcyclohexane (100 cm³) for suspending the Pt-carbon catalyst (0.2 mmol metal) before (a) and after 24 h reaction (b) under boiling and refluxing conditions (405 K)

2. The adsorption of aromatics on the catalyst caused not only blocking of the active sites but also consumption of the surface hydrogen species through hydrogen transfer, sacrificing the precursor of molecular hydrogen.

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