Dehydrogeno-aromatization of Cyclohexanes with Suspended Noble Metal Catalysts

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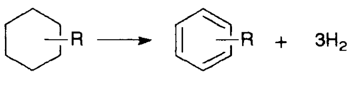
Selective dehydrogeno-aromatization of cyclohexanes to produce aromatic compounds and dihydrogen proceeds catalytically with suspended noble metal catalysts under boiling and refluxing conditions.

The equilibrium restriction imposed at low temperatures for alkane dehydrogenation to generate the alkene and dihydrogen [eqn. (1)][1] can be avoided under boiling and refluxing

$$\text{Alkane} \rightarrow \text{Alkene} + H_2 \qquad (1)$$

conditions, because the dihydrogen generated does not remain in the reaction medium, once it is evolved as a gas. The Wilkinson catalyst, $RhClL_3$, was in fact shown to exhibit dehydrogenation activity for cyclooctane.[2] Not only homogeneous organometallic compounds but also suspended noble metal catalysts are active for alkane dehydrogenation, since cyclooctane was catalytically dehydrogenated, yielding cyclooctene and dihydrogen by using carbon- and alumina-supported Pd, Rh and Ru catalysts.[3] With suspended Pt-on-alumina catalyst (Pt/Al_2O_3), however, ethylcyclohexane and ethylbenzene were obtained from cyclooctane, in addition to cyclooctene.[3] In the present work, the dehydrogenation activities of suspended noble metal catalysts for cyclohexanes, yielding aromatic compounds and dihydrogen [eqn. (2)], have been studied under boiling and refluxing conditions.



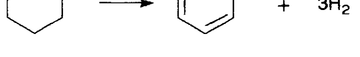
(2)

Supported metal catalysts (Pt, Pd, Rh and Ru on carbon and alumina; 5 wt%; N. E. Chemcat.), preheated in H_2 and *in vacuo* at 180 °C, were dispersed in purified cyclohexanes (ethylcyclohexane, dimethylcyclohexanes, methylcyclohexane and cyclohexane; 0.2 mmol metal per 100 ml) under nitrogen atmosphere in a Schlenk tube (200 ml). Immediately after the suspended solution began boiling and refluxing (cooled by running water), the amount of evolved gas was measured by a gas burette (250 ml), and its composition analysed gas chromatographically with an active-carbon column. The liquid-phase components were determined with OV-1 and PEG-20M capillary columns after the reaction.

Formation of dihydrogen and ethylbenzene, with no accompanying formation of the monoene, diene or styrene, was found for ethylcyclohexane over the Pt, Pd and Rh catalysts. The Ru catalyst exhibited no catalytic activities. The time dependence of H_2 evolution is shown in Fig. 1, with total turnovers of evolved H_2 within 24 h per supported Pt atoms amounting to 119 (Pt/C). The catalytic dehydrogeno-aromatization of ethylcyclohexane has thus been accomplished under thermal conditions as mild as 132 °C. The activity order (Pt > Pd > Rh) and the preference for carbon rather than alumina as catalyst supports are summarized in Table 1.

The dehydrogenation rates of cyclohexanes were compared using the most active Pt/C catalyst. As shown in Fig. 2 and Table 2, higher rates were observed for the less volatile substrates as expected from the reaction temperatures. No isomerized xylenes were found.

In comparison with the conventional reforming processes,[4] catalytic formation of benzene from cyclohexane [eqn. (3)] at low temperature (81.7 °C) saves energy.



(3)

Table 1 Dehydrogenation of ethylcyclohexane with suspended noble metal catalysts under boiling and refluxing conditions[a]

Catalyst	H_2/mmol	Ethylbenzene/mmol
Pt/C	23.93	7.75
Pt/Al_2O_3	13.04	4.15
Pd/C	9.22	3.18
Pd/Al_2O_3	3.67	1.25
Rh/C	2.59	0.98
Rh/Al_2O_3	1.96	0.78
Ru/C	0.15	0.06
Ru/Al_2O_3	0.04	0.02

[a] Catalyst concentration: 0.2 mmol metal per 100 ml; reaction temperature: 132 °C; reaction time: 24 h.

Table 2 Dehydrogenation of cyclohexanes with the suspended Pt/C catalyst under boiling and refluxing conditions[a]

Substrate (b.p.)	H_2/mmol	Liquid phase product (mmol)
Ethylcyclohexane (132 °C)	23.93	Ethylbenzene (7.75)
1,2-Dimethylcylcohexane (127 °C)	13.20	*o*-Xylene (4.20)
1,3-Dimethylcyclohexane (122 °C)	13.12	*m*-Xylene (3.79)
1,4-Dimethylcyclohexane (122 °C)	12.78	*p*-Xylene (3.78)
Methylcyclohexane (100 °C)	4.59	Toluene (1.42)
Cyclohexane (82 °C)	1.89	Benzene (0.48)

[a] Catalyst concentration: 0.2 mmol metal per 100 ml; reaction temperature: boiling point; reaction time: 24 h.

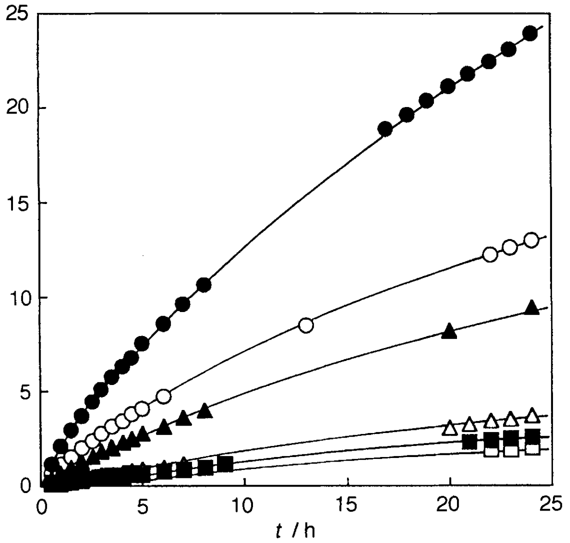


Fig. 1 Time dependence of H_2 evolution from ethylcyclohexane using Pt/C (●), Pt/Al_2O_3 (○), Pd/C (▲), Pd/Al_2O_3 (△), Rh/C (■) and Rh/Al_2O_3 (□) catalysts in suspended solutions (0.2 mmol metal per 100 ml) under boiling and refluxing conditions (132 °C)

We suggest two reasons for the rate decrease depicted in Figs. 1 and 2. One is an irreversible fouling of the carbon,[5] as ascertained by the investigation of spent catalysts. The other is a reversible retardation due to adsorption of the aromatic products. The effects of ethylbenzene on the initial reaction rates for ethylcyclohexane dehydrogenation using the suspended Pt/C catalyst could be analysed well using a Langmuir-type rate equation [eqn. (4)], where values of the rate constant, k, and the equilibrium constant of ethylbenzene adsorption, K, of 53.0 mmol h^{-1} g^{-1} and 0.010 dm^3 $mmol^{-1}$, respectively, were obtained.

$$v = k/(1 + K[\text{ethylbenzene}]) \qquad (4)$$

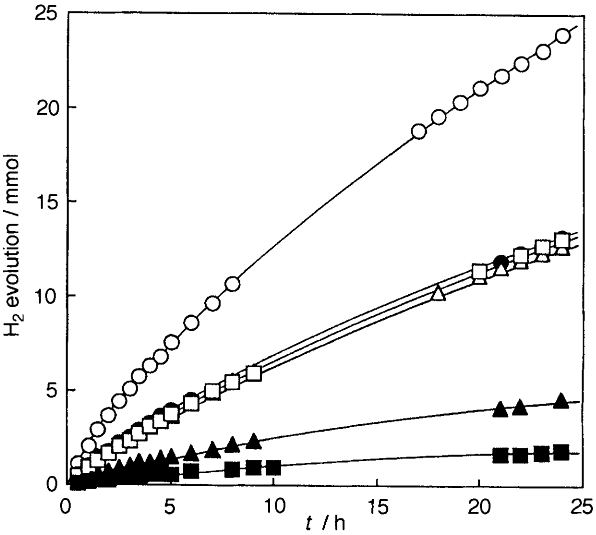


Fig. 2 Time dependence of H_2 evolution from ethylcyclohexane (○), 1,2-dimethylcyclohexane (●), 1,3-dimethylcyclohexane (▲), 1,4-dimethylcyclohexane (□), methylcyclohexane (■) and cyclohexane (△) under boiling and refluxing conditions using the suspended Pt/C catalyst (0.2 mmol metal per 100 ml)

Catalytic liquid-phase dehydrogenation of propan-2-ol is one of the key reactions in a chemical heat pump system recently proposed.[6] Abundant quantitites of heat of low quality (temp. *ca.* 80 °C) are readily available and may be supplied to the system for both the endothermic reaction and the fractional distillation, in which acetone and hydrogen are separated from propan-2-ol in conjunction with a cooling procedure (*ca.* 30 °C). Since the hydrogenation of acetone is exothermic and proceeds at higher temperatures (*ca.* 200 °C), more available thermal energy can be recovered from low-quality heat through partial heat removal at ambient temepratures. Carbon-supported Ru[7] and Ru-Pt composite[8] catalysts exhibited sufficient activity for dehydrogenation of propan-2-ol.

The present work provides another possibility for a chemical heat pump system, by use of the pair of reversible reactions: endothermic dehydrogenation of cyclohexanes at the boiling points (cyclohexane, 81.7 °C, to ethylcyclohexane 132 °C) and exothermic hydrogenation of aromatic compounds at high temperatures (so-called 'turning temperatures', where $\Delta G° = 0$). Low quality heat (*ca.* 80 °C) can be upgraded to utilizable thermal energy (even 300 °C), provided that output heat (*ca.* 200 °C) is adopted as the input heat for a cyclohexane–benzene–hydrogen system, operated at elevated pressure.

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