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Dehydrogenation of Cycloalkanes by Suspended Platinum Catalysts

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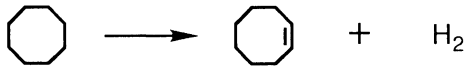
Heterogenized cluster complex $[Pt_3(CO)_6]_5^{2-}$ and reduced platinum metal have catalyzed cyclooctane dehydrogenation at comparable rates, whereas dehydrogenoaromatization of ethylcyclohexane proceeded predominantly with the latter. Active-site ensembles for the formation of cyclooctene, bicyclooctane and aromatics were discussed on reference to the appropriate stretch of platinum metal atoms.

The reaction of alkane dehydrogenation yielding alkene and molecular hydrogen under mild conditions has been one of the most challenging targets in catalytic chemistry.[1)]

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2 \quad (1)$$

The equilibrium restriction imposed at low temperatures for this reaction can be avoided under boiling and refluxing conditions, because molecular hydrogen does not remain in the reaction medium, once evolved as gas.[2)] Actually, homogeneous[3)] and heterogeneous dehydrogenation catalysts active for cyclooctane(Eq. 2)[4)] and even cyclohexane(Eq. 3)[5)] were found.



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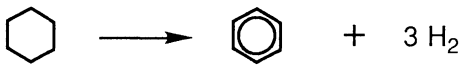
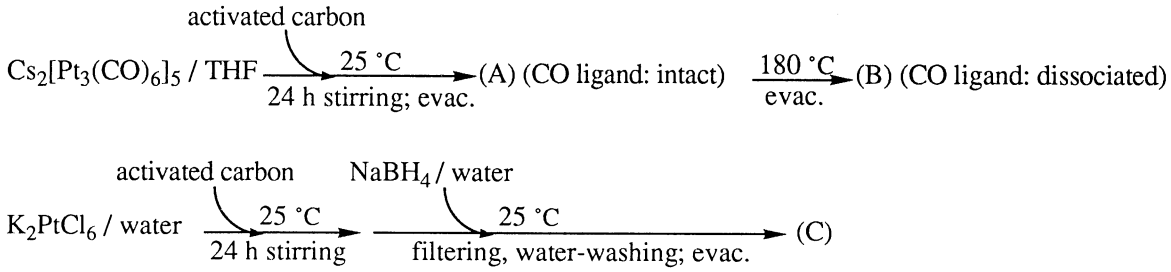


(3)

In the present work, thermocatalysis of heterogenized platinum cluster complex $[Pt_3(CO)_6]_5^{2-}$ and reduced platinum metal from $PtCl_6^{2-}$ with $NaBH_4$ has been investigated for dehydrogenation of cyclooctane and ethylcyclohexane in order to elucidate the role of metal atom stretch as active-site ensemble.

Unsaturated hydrocarbons in cyclooctane and ethylcyclohexane were removed with conc. HNO_3 and H_2SO_4, followed by water-washing/$CaCl_2$-drying and distillation in the presence of Na under N_2 atmosphere. A KOH-activated carbon[6)](BET specific surface area : 3100 $m^2\ g^{-1}$, Kansai Netsukagaku Co.), preheated under H_2 for 2 h and evacuated for 20 minutes, was used as the catalyst support. Three types of Pt(5 wt%)/carbon catalysts were prepared as described in Scheme I. The gaseous and liquid-phase components were analyzed gas-chromatographically, using an active carbon column and PEG-20M and OV-1 capillary columns, respectively.

Time-course plots of H_2 evolution from cyclooctane using the three kinds of carbon-supported platinum catalysts(A, B,and C) indicate that the dehydrogenation activities per platinum atom are similar with each other, as

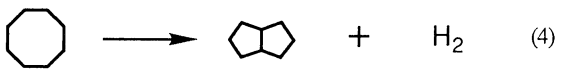


Scheme 1. Preparation of carbon-supported platinum(5 wt%) catalyst.

shown in Fig. 1. The activity of the commercial catalyst (D) was also alike.

With regard to the carbon-supported $Cs_2[Pt_3(CO)_6]_5$ (A), the extent of CO desorption from the complex under reaction conditions was observed to be 49%; another half of the CO ligands of this heterogenized cluster was therefore retained without dissociation. When the carbon-supported cluster was pretreated severely, all the CO ligands were eliminated from the Pt_{15} segment (B) before the use for reaction. Presence of CO on the platinum moiety was thus ascertained to exert little influence upon the rates of H_2 evolution from cyclooctane.

As far as the reaction products in the solution were concerned, a distinct difference was found between (A) and (B). The heterogenized cluster preserving CO (A) yielded cyclooctene exclusively, whereas the one without CO (B) gave not only cyclooctene but also bicyclooctane (Eq. 4). The carbon-supported platinum metal catalysts (C and D) gave also both cyclooctene and bicyclooctane (Table 1).



Platinum surface atoms have various extents of stretch, which acts as the catalytic active site. Heterogenized platinum cluster retaining a half of its CO ligands would activate only a pair of adjacent C-H bonds, with cyclooctene yielded. On the contrary, splitting of two distant C-H bonds would form bicyclooctane (*vide infra*).

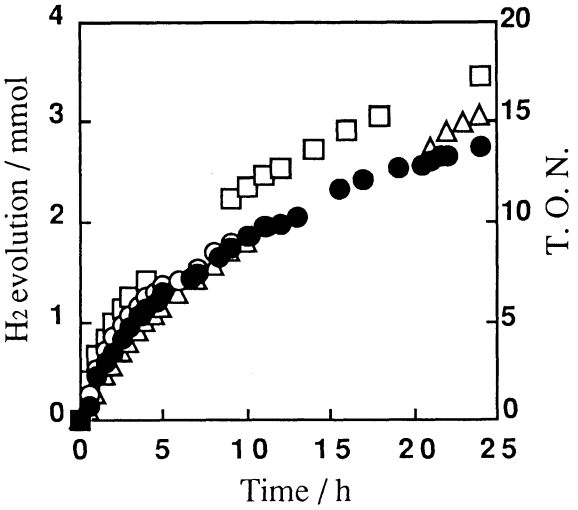


Fig. 1. H_2 evolution from cyclooctane using $Cs_2[Pt_3(CO)_6]_5$ / C(A, △), $Cs_2[Pt_3(CO)_6]_5$ / C(B, ●), K_2PtCl_6 / C(C, ○), and commercial Pt / C catalyst(D, □) in suspended solutions (0.2 mmol metal per 100 ml) under boiling and refluxing conditions (151 °C).

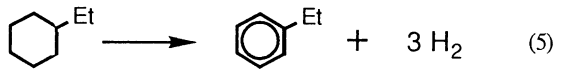
Table 1. Dehydrogenation of cyclooctane with carbon-supported platinum catalysts[a)]

Catalyst	Time / h	Products / mmol		
		H_2		
A	24	3.05	3.02	0.0
B	24	2.75	1.60	1.1
C	12	1.95	1.32	0.6
D	24	3.42	1.70	1.7

a) Catalyst solution: 0.2 mmol / 100 ml substrate. Reaction conditions: Boiling and refluxing (151 °C)

Time-course plots of catalytic hydrogen evolution from ethylcyclohexane under boiling and refluxing

conditions are depicted in Fig. 2. In contrast to cyclooctane dehydrogenation, the platinum metal catalysts (C and D) were distinctly more active than the one originated from the platinum cluster (B), whereas inactive was the heterogenized cluster preserving CO (A). The reaction product in the solution was exclusively ethylbenzene (Eq. 5).



(5)

Products of ethylcyclohexane dehydrogenation with the four kinds of carbon-supported platinum catalysts under boiling and refluxing conditions are summarized in Table 2. Stoichiometric correlation with respect to hydrogen seems to be satisfactory, since the amounts of hydrogen yielded were nearly three times of ethylbenzene. No byproducts of styrene, cyclohexene and cyclohexadiene were recognized for each catalyst.

Turnover numbers within 5 h were obtained as 1.7, 19.4 and 12.6 for (B), (C) and (D), respectively. The initial mixture of product ethylbenzene to ethylcyclohexane (0.99 vol%) revealed us a contrast between small decrement in (B: 1.6) and significant reduction in (C: 6.9) and (D: 5.2).

The analysis of a Langmuir-type rate equation, $v = k / (1 + K[\text{ethylbenzene}])$, gave the retardation constant K(mmol h^{-1} g^{-1}) for the cluster-originated catalyst (B: 0.010) and the reduced metal catalyst (C: 0.045), respectively.

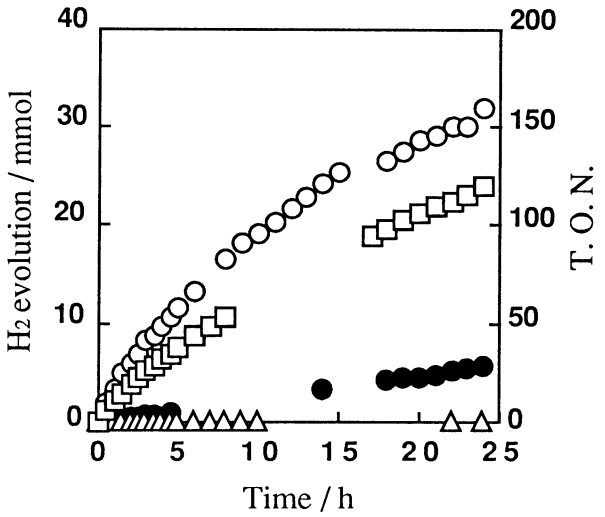


Fig. 2. H_2 evolution from ethylcyclohexane using $Cs_2[Pt_3(CO)_6]_5$ / C(A, △), $Cs_2[Pt_3(CO)_6]_5$ / C(B, ●), K_2PtCl_6 / C(C, ○), and Commercial Pt / C catalyst(D, □) in suspended solutions (0.2 mmol metal per 100 ml) under boiling and refluxing conditions (132 °C).

Table 2. Dehydrogenation of ethylcyclohexane with carbon-supported platinum catalysts[a)]

Catalyst	Time / h	Products / mmol	
		H_2	Ethylbenzene
A	24	0.13	0.00
B	24	5.62	2.05
C	24	32.1	10.9
D	24	23.9	7.75

a) Catalyst solution: 0.2 mmol / 100 ml substrate. Reaction conditions: Boiling and refluxing (132 °C)

As for the platinum metal catalyst (D), the rates of H_2 evolution from ethylcyclohexane (100 ml) were decreased from the beginning in the presence of various aromatic addends (0.5 ml), where the extents of retardation were larger for ethylbenzene, toluene or benzene than for xylenes (Fig. 3). Partial transformations of benzene, toluene and xylenes into cyclohexane (2.81 mmol), methylcyclohexane (2.61 mmol) and dimethylcyclohexanes (1,2-: 0.66 mmol, 1,3-: 0.59 mmol and 1,4-: 1.25 mmol, respectively) during the 5-h reaction were observed, which indicates the possible simultaneous process of hydrogen transfer from ethylcyclohexane to ethylbenzene during dehydrogeno-aromatization.

A certain stretch of surface platinum atoms would be required for alkane dehydrogenation.[7)] With regard to cyclooctane, the required active-site ensemble is smaller for cyclooctene than for bicyclooctane. The reduced metal catalysts (C and D) should have more spacious stretch of surface platinum atoms than the heterogenized Pt_{15} cluster catalyst (A and B). Size requirement on the active-site ensemble for dehydrogeno-aromatization of ethylcyclohexane will be larger than that for dehydrogenation of cyclooctane, since more distinct activities for the

former reaction (Eq. 5) were attained with (C) and (D) than (A) and (B), being in contrast to the catalytic activities for the latter (Eqs. 2 and 4). The metal atom stretches as active-site ensembles are depicted in Fig. 4 so as to discriminate these three kinds of alkane dehydrogenation.

As deduced from retardation analysis for ethylcyclohexane dehydrogeno-aromatization, the small-sized platinum catalyst (B) exhibits a smaller capability of ethylbenzene adsorption than the large-sized one (C). Provided that the stretch of surface platinum atoms be too extensive, some of surface hydrogen species originated from ethylcyclohexane would not be used for the formation of molecular hydrogen but be consumed to hydrogen transfer toward adsorbed ethylbenzene.

The appropriate size of platinum metal particles as the catalyst for dehydrogeno-aromatization of cyclohexanes may be intermediate between those prepared from the heterogenized $[Pt_3(CO)_6]_5^{2-}$ cluster and the $NaBH_4$-reduced $PtCl_6^{2-}$ adsorbate.

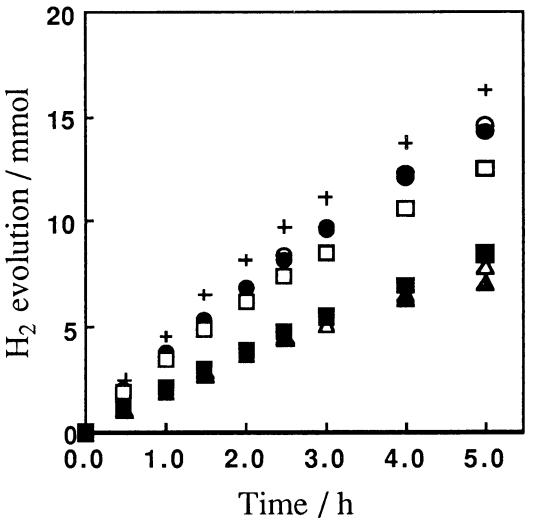
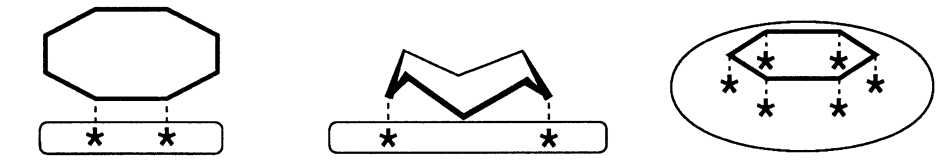


Fig. 3. H_2 evolution from ethylcyclohexane(+) with the addends of m-xylene(○), o-xylene(●), p-xylene(□), toluene(■), benzene(△) and ethylbenzene(▲) using commercial Pt/C catalyst in suspended solution (0.2 mmol metal per 100 ml) under boiling and refluxing conditions(132 °C).



Cyclooctene formation from cyclooctane | Bicyclooctane formation from cyclooctane | Aromatics formation from cyclohexanes

Fig. 4. Schematic metal stretch as active-site ensemble on the platinum catalyst surface.

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