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# The Reactivities of Polyaromatic Hydrocarbons in Catalytic Hydrogenation over Supported Noble Metals

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The reactivities of several polyaromatic hydrocarbons (pyrene: P, fluoranthene: FL, anthracene: An, fluorene: F, acridine: Ac, and carbazole: C) in the catalytic hydrogenation were studied and compared over supported noble metals (Pt, Pd, Rh, and Ru on a carbon or alumina support). The specific reactivity and selectivity were found to be strongly dependent upon the combination of the catalyst species and the substrate. The catalysts exhibited the activity order of Rh > Pd ≫ Pt > Ru for tricyclic aromatics of An, F, Ac, and C, although the catalysts provided very variable selectivities of the partially hydrogenated products which were produced via both consecutive and competitive routes, apparently according to the type of ring-skeleton and the presence of a nitrogen atom. The reactivity of the starting substrates and intermediates are compared to the quantum chemical reactivity indices, calculated based on MNDO (modified neglect of diatomic overlap). The values of the LUMO electron density, the $\pi$-bond order, and the stability of the product appear to govern the reactivity and selectivity of the hydrogenation, depending upon the combination of the catalyst species and the substrate. No hydrogenation of a substrate proceeds when its reactivity indices are less than the threshold value, which is subject to the activity of the catalyst and the reaction conditions defining product selectivity via both competitive and consecutive schemes.

The selective hydrogenation of polyaromatic hydrocarbons including heterocyclic compounds derived from coals and petroleums is one of the important steps in preparing the intermediates for functional molecules and medicines.[1–4]

The present authors have elsewhere reported the selective hydrogenation of pyrene, fluoranthene, acridine, and isoquinoline using noble metal catalysts under rather milder conditions[5–7] than those reported previously.[8–10] The former two substrates were very selectively converted into particular products of the partially-hydrogenated (especially tetrahydro) derivatives; these products could then be used as powerful hydrogen donors and synthetic intermediates.[11–13]

The selective hydrogenation of acridine was also found in a preceding paper to produce some partially hydrogenated acridines.[14] The reaction pathway of such selective hydrogenation was revealed to be competitive as well as consecutive through kinetic simulation, thermodynamic, and stereochemical comparisons of the hydrogenated products by the aid of quantum chemical calculations of the MNDO (modified neglect of diatomic overlap) method[15] and MM2 (molecular mechanics calculations).[16]

In the present study, the reactivities of several polyaromatic hydrocarbons in the catalytic hydrogenation were compared and rather comprehensively studied over typical noble metal catalysts in order to clarify the factors influencing their selective partial hydrogenation, since the specific reactivity and selectivity were found to be strongly dependent upon the combination of the catalyst species and the substrate. The reactivities of the substrates and their intermediates can be correlated to their quantum chemical indices and their stereochemical structures to explain the reaction schemes and to discuss the interaction between the substrates and the catalysts.

## Experimental

**Materials.** Commercially available polyaromatic hydrocarbons (acridine, carbazole, anthracene, fluorene, pyrene, and fluoranthene) and decalin (reaction solvent) of a guaranteed grade were used without further purification in the present study, since sulfur compounds, which are severe poisons for the noble catalysts, were not detected, the sulfur content being less than 0.1%.

Commercial noble metal catalysts of $Pd/Al_2O_3$, Pd/C, $Pt/Al_2O_3$, Pt/C, $Rh/Al_2O_3$, Rh/C, and Ru/C (Metal content: 5 wt%), supplied by the Nippon Engelhalt Co., were used without any pretreatment.

**Hydrogenation Procedures and Product Analyses.** One of the polyaromatic hydrocarbons (2 g) was placed in an autoclave (50-ml capacity) together with the solvent (10 g of decalin) and one of the catalysts (0.2 g for FL or 0.5 g for the others). The autoclave was flushed with nitrogen three times to replace the air and then filled with pure hydrogen from a cylinder. The initial pressure of hydrogen was adjusted to give a prescribed pressure of 7 MPa at the reaction temperatures. After heating the reactor to a prescribed reaction temperature (373—523 K), magnetic stirring was started when the reaction time was counted. After the prescribed reaction time, the reactor was cooled with a fan to room temperature within 10 min; the reaction mixture (liquid and solid) was then recovered with THF. The catalyst was filtered out, and the liquid product including the solvent was analyzed by a temperature programmed gas chromatograph (column: SE-30, 2 m, heating rate: 10 K min$^{-1}$ from 373 to 498 K). The hydrogenated derivatives were identified with GC-IR $^1$H and $^{13}$C NMR after the fractional distillation by reference to commercially available samples and/or the literature. The details of the product identification were described in previous papers.[5,6,14] The structures of the substrates and products are illustrated in Fig. 1.

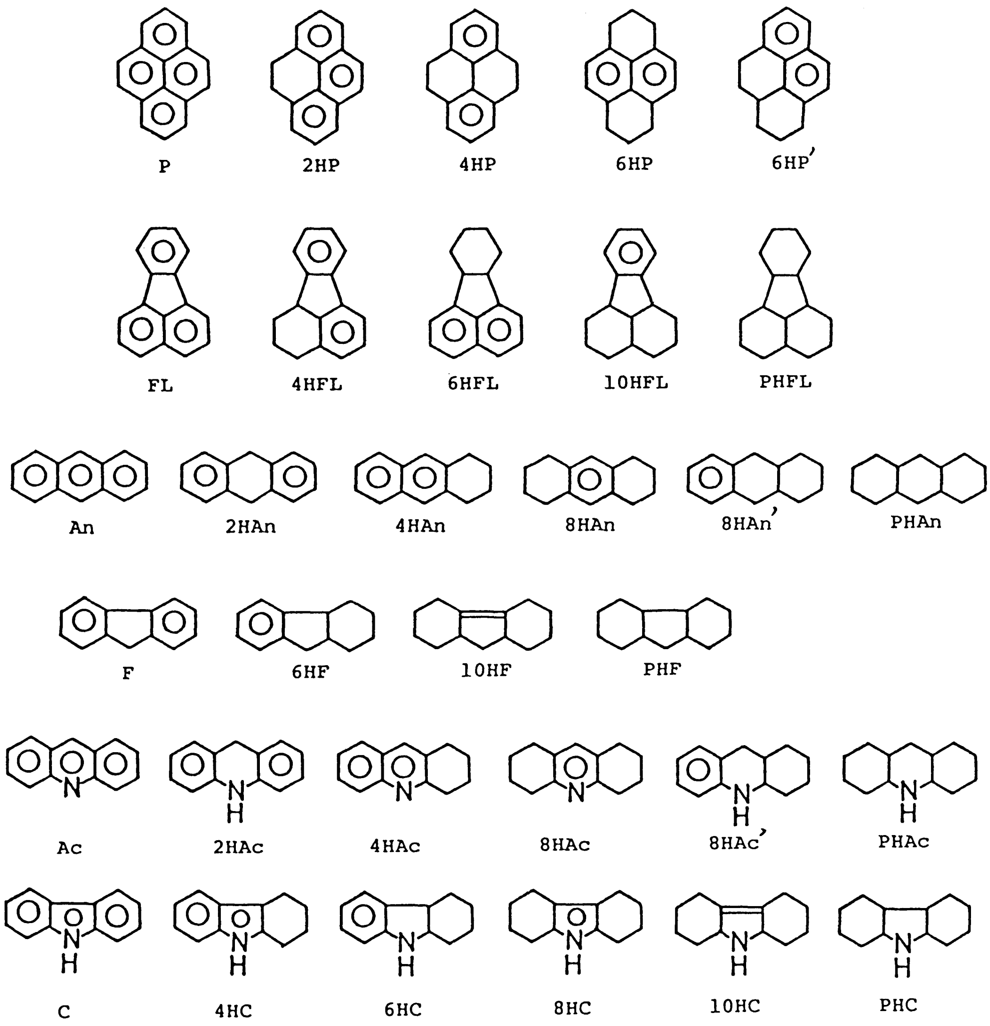

Fig. 1. Structures of the substrates and their hydrogenated products.

**Quantum Chemical Calculations.** The reactivity indices are calculated by means of the flow diagram shown in Fig. 2. According to the MM2 method,[16] the energetically optimized structures of the respective substrates and their hydrogenated products were determined. The molecular orbitals of the substrates of the determined structure were calculated according to the MNDO method[15] in order to estimate the heats of formation, the electron densities on carbon and nitrogen atoms, and the bond orders of the C-C and C-N bonds. The values thus calculated are more reasonable because the energy calculations are superior to any previously reported.[16]

## Results

**Hydrogenation Activities of Noble Metal Catalysts on Carbon.** Table 1 summarizes the conversions of polyaromatic hydrocarbons in the hydrogenation on various carbon-supporting catalysts under the reaction conditions of 423 K, 7 MPa($H_2$), and 30 min. All the catalysts except Ru, which was slightly less active, showed similar activities for pyrene (P) and fluoranthene (FL) of tetracyclic aromatics, although the latter substrate was much more reactive than the former.

The tricyclic aromatics showed very different reactivities, depending greatly on the catalyst used. The activities were in the order of $Rh > Pd \gg Pt > Ru$ in anthracene (An), fluorene (F), acridine (Ac), and carbazole (C). It should be noted, however, that the Pt and Ru catalysts exhibited much lower activities particularly for F and C, than did the other two catalysts. Figure 3 illustrates the major products in the hydrogenation of tricyclic aromatics on Rh, Pd, and Pt catalysts. The different selectivities of the catalysts were definite.

**Reactivities and Selectivities in the Hydrogenation of Tetracyclic Aromatic Hydrocarbons.** The activities and selectivities of the carbon-supported catalysts in the hydrogenations of pyrene (P) and fluoranthene (FL) are summarized in Tables 2 and 3 respectively, where severer and milder conditions than those of Table 1 were selected respectively. Except for Ru, the catalysts again exhibited similar activities under these conditions.

All the catalysts except for Rh/C hydrogenated 70—90% of the pyrene with a similar selectivity under the reaction conditions of 523 K, 5 MPa ($H_2$), and 6 h,

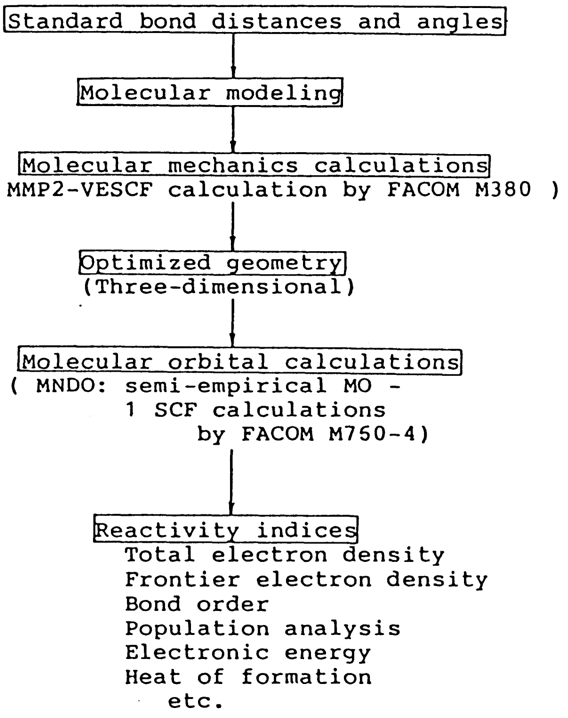

Fig. 2. Calculation diagram of reactivity indices of polyaromatic hydrocarbons.

producing preferentially the dihydro- (2HP) and tetrahydropyrene (4HP) at the selectivities of 40—60% and 30—40% respectively. The consecutive nature of the reaction is definite. The Rh/C catalyst alone produced 1,2,3,6,7,8-hexahydropyrene (6HP) by a considerable selectivity (ca. 30%) at similar conversion levels, suggesting that the competitive reaction may contribute along with the Rh/C catalyst.[5]

Fluoranthene (FL) was more easily hydrogenated than pyrene under the milder conditions of 423 K, 3 MPa ($H_2$), and 30 min with a smaller amount of the catalyst (0.2 g), as is shown in Table 3. The Pt/C and

Table 1. Hydrogenation Reactivities[a] of Various Polyaromatic Hydrocarbons on Carbon-Supported Catalysts

| Substrate | Conversion/% | | | |
|---|---|---|---|---|
| | Pt | Pd | Rh | Ru |
| Pyrene (P) | 50 | 55 | 52 | 43 |
| Fluoranthene (FL) | 100 | 100 | 100 | 95 |
| Anthracene (An) | 19 | 28 | 100 | 10 |
| Fluorene (F) | 0 | 86 | 100 | 2 |
| Acridine (Ac) | 91 | 100 | 100 | 78 |
| Carbazole (C) | 5 | 72 | 100 | 4 |

a) Reaction conditions: 423 K—7 MPa ($H_2$), 30 min. catalyst/substrate=1/4 (wt/wt).

Table 2. Screening of Various Noble Metal Catalysts in the Hydrogenation of Pyrene (P)[a]

| Catalyst | Conv. | Yield/Selectivity (%) | | | | |
|---|---|---|---|---|---|---|
| | % | 2HP | 4HP | 6HP | 6HP′ | Others[b] |
| Pt/C | 82 | 38/46 | 32/39 | 6.4/7.7 | 3.6/4.3 | 1.8/2.2 |
| Pd/C | 87 | 40/47 | 35/41 | 5.5/6.4 | 3.9/4.6 | 2.0/2.2 |
| Rh/C | 83 | 31/37 | 20/25 | 23/27 | 4.6/5.6 | 4.7/5.5 |
| Ru/C | 71 | 43/60 | 21/30 | 2.7/3.8 | 1.6/2.2 | 2.6/3.7 |

a) Reaction conditions: 523 K—5 MPa, 6 h. b) Others are more deeply hydrogenated products than the hexahydropyrenes.

Table 3. Screening of Various Noble Metal Catalysts in the Hydrogenation of Fluoranthene (FL)[a]

| Catalyst | Conv. | Yield/Selectivity (%) | | | |
|---|---|---|---|---|---|
| | % | 4HFL | 6HFL | 10HFL | PHFL |
| Pt/C | 100 | 18/18 | 2.2/2.2 | 75/75 | 4.8/4.8 |
| Pd/C | 100 | 0.2/0.2 | 0/0 | 99/99 | 0.4/0.4 |
| Rh/C | 92 | 67/73 | 5.8/6.3 | 18/20 | 0.7/0.8 |
| Ru/C | 31 | 24/78 | 2.7/8.7 | 3.7/12 | 0.4/1.3 |

a) Reaction conditions: 423 K—3 MPa, 30 min.

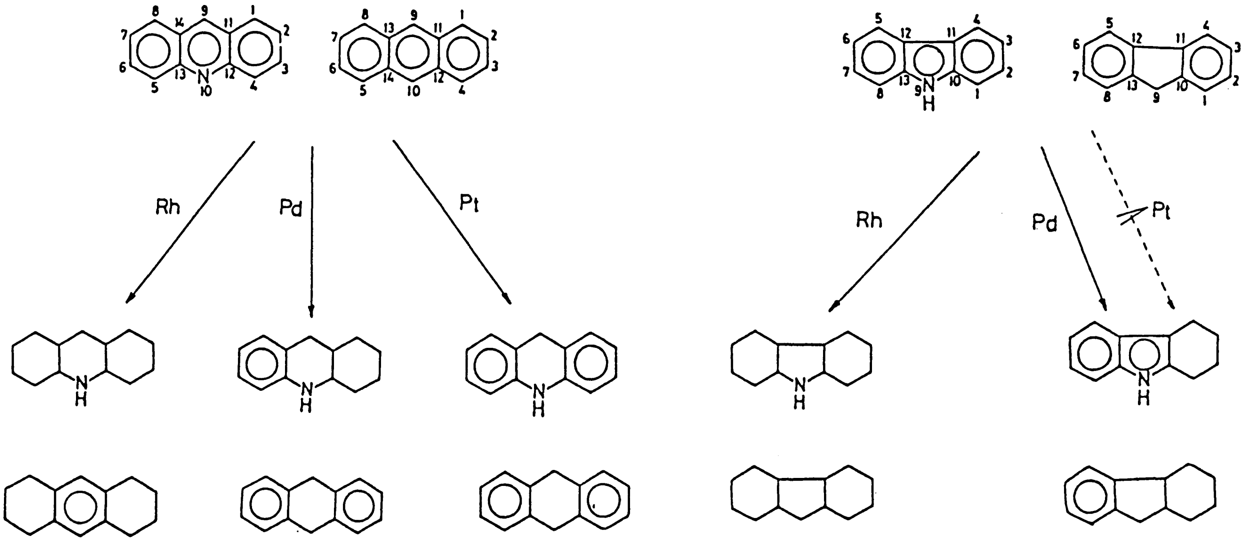

Fig. 3. Main routes in the hydrogenation of tricyclic aromatics on Rh, Pd, and Pt catalysts.

Pd/C catalysts exhibited the highest activity (conversion: 100%), producing 1,2,3,4,5,6,11,12,15,16-decahydrofluoranthene (10HFL) as the major product (selectivity: 75 and 99% respectively). The Rh/C catalyst hydrogenated 92% of the FL, exhibiting the highest selectivity (73%) for tetrahydro FL (4HFL). In marked contrast, the Ru/C catalyst converted only 31% of the FL, mainly into 4HFL (78% selectivity).

**Reactivities and Selectivities in the Hydrogenation of Tricyclic Aromatic Hydrocarbons.** The reactivities of anthracene (An) and fluorene (F) on alumina-supporting catalysts under some conditions are summarized in Tables 4 and 5 respectively. The Rh catalyst hydrogenated An much faster than the other two catalysts to achieve a 100% conversion within 5 min at 423 K and 7 MPa of $H_2$, producing principally 1,2,3,4,5,6,7,8-octahydroanthracene (8HAn, 73% selectivity). A minor production of 1,2,3,4,4a,9,9a,10-octahydroanthracene (8HAn′) and perhydroanthracene (PHAn) was also observed. The consecutive path of An→4HAn→8HAn→PHAn appears predominant. Dihydro and tetrahydro derivatives were rapidly hydrogenated into octahydro derivatives, which are rather unreactive under these conditions. In contrast, Pd and Pt catalysts produced principally 9,10-dihydroanthracene (2HAn) at a selectivity of 60—70% at the reaction time of 180 min. Tetrahydro derivative (20—30%) was the second major product, the selectivities for the other products being very low.

The Pd and Rh catalysts converted 100% of the fluorene (F) under the conditions of 473 K, 7 MPa ($H_2$), and 5 min, principally into hexahydrofluorene (6HF, 71% selectivity) and perhydrofluorene (PHF, 72% selectivity). The other products found suggest a consecutive path on both catalysts, although the reaction stopped at their respective products of partial hydrogenation. In contrast, the Pt catalyst exhibited a much lower activity for F under the same conditions, converting only 2.7% of the F into 6HF.

**Reactivities and Selectivities in the Hydrogenation of Nitrogen-Containing Aromatics.** Tables 6 and 7 summarize the hydrogenation reactivities of acridine (Ac) and carbazole (C) on carbon- and alumina-supporting catalysts respectively. All the catalysts, examined under the conditions of 423 K, 7 MPa, and 10 min, exhibited very high activities against Ac, allowing the conversions of 90—100%. However their selectivities were very different, depending on the metal species, as is shown in Table 6.

The Pd catalyst hydrogenated Ac successively, producing mainly one of 1,2,3,4,4a,9,9a,10-octahydro-Ac (8HAc′) via 9,10-dihydro-Ac (2HAc), although the selectivity depended upon the support. The Rh catalysts exhibited the highest activity among the catalysts examined, converting most of the Ac into perhydro-Ac (PHAc) via 1,2,3,4,5,6,7,8-octahydro-Ac (8HAc), regardless of the support.

In contrast, the Pt catalysts exhibited the highest selectivity for 2HAc (59% on Pt/C and 80% on Pt/$Al_2O_3$), producing very little of the more deeply hydro-

Table 5. Screening of Various Noble Metal Catalysts in the Hydrogenation of Fluorene (F)[a]

| Catalyst | Conv. | Yield/% | | | |
|---|---|---|---|---|---|
| | % | 6HF | 10HF | PHF | Others[b] |
| Pd/$Al_2O_3$ | 100 | 71 | 9.5 | 16 | 3.6 |
| Rh/$Al_2O_3$ | 100 | 0.7 | 26 | 72 | 1.4 |
| Pt/$Al_2O_3$ | 2.7 | 1.4 | 0.1 | 0.1 | 1.1 |

a) Reaction conditions: 473 K—7 MPa, 5 min.
b) Others are unidentified products.

Table 4. Screening of Various Noble Metal Catalysts in the Hydrogenation of Anthracene (An)[a]

| Catalyst | Conv. | Yield/Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | % | 2HAn | 4HAn | 8HAn | 8HAn′ | PHAn | Others[b] |
| Pd/$Al_2O_3$ | 85 | 57/67 | 24/28 | 1.2/1.4 | 0.7/0.8 | 1.5/1.8 | 1.5/1.8 |
| Rh/$Al_2O_3$ | 100 | 1.1/1.1 | 0.7/0.7 | 72/73 | 12/12 | 13/13 | 0.8/0.8 |
| Pt/$Al_2O_3$ | 58 | 37/63 | 17/30 | 1.0/1.7 | 0.3/0.5 | 0.9/1.5 | 2.2/3.8 |

a) Reaction conditions: 423 K—7 MPa, 180 min (Pd and Pt); 423 K—7 MPa, 5 min (Rh).
b) Others are unidentified products.

Table 6. Screening of Various Noble Metal Catalysts in the Hydrogenation of Acridine (Ac)[a]

| Catalyst | Conv. | Yield/Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | % | 2HAc | 4HAc | 8HAc | 8HAc′ | PHAc | Others[b] |
| Pd/C | 95 | 16/17 | 1.8/1.9 | 11/11 | 44/47 | 16/16 | 5.9/6.2 |
| Pd/$Al_2O_3$ | 95 | 44/47 | 1.6/1.7 | 4.6/4.9 | 36/38 | 2.8/3.0 | 5.9/6.2 |
| Rh/C | 98 | 0.1/0.1 | 0.6/0.6 | 5.2/5.3 | 0.9/0.9 | 90/92 | 1.3/1.3 |
| Rh/$Al_2O_3$ | 99 | 0/0 | 0.1/0.1 | 0.9/0.9 | 0.1/0.1 | 98/99 | 0.1/0.1 |
| Pt/C | 85 | 50/59 | 1.1/1.3 | 2.8/3.3 | 12/14 | 5.8/6.9 | 13/16 |
| Pt/$Al_2O_3$ | 96 | 77/80 | 0.5/0.5 | 1.1/1.2 | 6.0/6.3 | 1.9/2.0 | 9.2/9.6 |

a) Reaction conditions: 423 K—7 MPa, 10 min. b) Others are unidentified products.

Table 7. Screening of Various Noble Metal Catalysts in the Hydrogenation of Carbazole (C)[a]

| Catalyst | Conv. | Yield/Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | % | 4HC | 6HC | 8HC | 10HC | PHC | Others[b] |
| Pd/C | 82 | 39/48 | 3.9/4.7 | 3.7/4.5 | 3.8/4.6 | 25/31 | 6.3/7.6 |
| Pd/$Al_2O_3$ | 71 | 40/57 | 4.5/6.4 | 14/20 | 1.4/2.0 | 1.3/1.8 | 8.7/12 |
| Rh/C | 99 | 0.2/0.2 | 1.2/1.2 | 4.1/4.2 | 0.8/0.8 | 85/87 | 6.9/7.0 |
| Rh/$Al_2O_3$ | 98 | 3.1/3.2 | 2.0/2.0 | 21/22 | 6.0/6.1 | 56/57 | 10/11 |
| Pt/C | 19 | 7.7/40 | 2.1/11 | 4.0/21 | 0.1/0.5 | 0.9/4.7 | 4.4/23 |
| Pt/$Al_2O_3$ | 9.2 | 1.7/19 | 1.6/17 | 1.6/17 | 0.2/2.2 | 0.7/7.6 | 3.4/37 |

a) Reaction conditions: 473 K—7 MPa, 15 min. b) Others are unidentified products.

Table 8. Hydrogenation of Acridine(Ac) on Pt/$Al_2O_3$ under Variable Conditions

| Reaction conditions (K/MPa/min) | Conv. | Yield/% | | | | | |
|---|---|---|---|---|---|---|---|
| | % | 2HAc | 4HAc | 8HAc | HAc′ | PHAc | Others[a] |
| 423/7/10 | 96 | 77 | 0.5 | 1.1 | 6.0 | 1.9 | 9.2 |
| 423/7/30 | 96 | 79 | 0.6 | 1.0 | 6.5 | 1.7 | 7.4 |
| 423/7/120 | 96 | 68 | 0.5 | 0.8 | 7.1 | 1.7 | 18 |
| 423/7/240 | 96 | 69 | 0.4 | 0.6 | 7.9 | 1.9 | 16 |
| 473/7/60 | 96 | 54 | 0.5 | 1.1 | 17 | 9.1 | 15 |
| 473/7/180 | 96 | 46 | 0.6 | 0.7 | 18 | 13 | 19 |
| 473/7/300 | 96 | 9.5 | 0.7 | 1.1 | 16 | 55 | 13 |
| 523/7/30 | 98 | 8.2 | 0.8 | 3.2 | 17 | 62 | 4.9 |

a) Others are unidentified products.

genated products. It should be noted that the selectivity on the Pt catalysts did not significantly change upon much longer reaction times of 120—240 min at 423 K or even at a higher temperature of 473 K until 180 min, as is shown in Table 8. PHAc became the major product at 473 K and 300 min or at 523 K and 30 min; this suggests that the 2HAc was converted directly to a fully hydrogenated product (PHAc). 2HAc, prepared separately, which was alone converted very slowly into more deeply hydrogenated products at 423 K, as is shown in Table 9, the major product being 8HAc′. Its low reactivity and weak adsorption may stop the reaction at this substrate.

Although alumina- and carbon-supporting catalysts showed much the same activities in the hydrogenation of Ac, as is shown in Table 6, less-hydrogenated 2HAc was more selectively produced on the alumina-supporting Pt and Pd catalysts, much less production of deeply hydrogenated products being observed. PHAc was the principal product on the Rh catalysts.

Tetrahydro-C (4HC) was the principal product with Pd on both supports, although a considerable amount of PHC was also produced with the carbon-supporting one. Both Rh catalysts provided PHC as the major product; however, a considerable amount of 8HC was also produced on the alumina-supporting catalyst. The Pt catalysts a exhibited much lower activity (conversion: 10—20%). No marked selectivity was observed. Thus, carbon-supporting catalysts tend to give more deeply hydrogenated products from nitrogen-containing compounds than do alumina-supporting ones, although the extent of hydrogenation varies with the catalyst species. In contrast, supports exhibited a negligible influence on the hydrogenations of such hydrocarbons as P, FL, An, and F which carry no heteroatom.

Table 9. Hydrogenation of 2HAc on Pt/$Al_2O_3$ at 423 K and 7 MPa of $H_2$

| Reaction time/min | Composition/% | | | | | | |
|---|---|---|---|---|---|---|---|
| | Ac | 2HAc | 4HAc | 8HAc | 8HAc′ | PHAc | Others[a] |
| 0 | 5.0 | 77 | 0.3 | 0.7 | 1.2 | 0.5 | 15 |
| 30 | 4.9 | 54 | 1.0 | 3.8 | 13 | 4.6 | 18 |
| 240 | 5.2 | 39 | 1.3 | 4.8 | 18 | 6.4 | 25 |

a) Others are unidentified products.

## Discussion

The present study has revealed that the specific reactivity and selectivity in the hydrogenation on supported noble metals were both strongly dependent upon the combination of the catalyst and the substrate.

The catalytic hydrogenation of polyaromatic hydrocarbons follows competitive-consecutive reaction paths. Hence, the selectivity is governed by both the reaction positions of the first hydrogenation and the extent of successive hydrogenation. Thus, the reactivity of the respective positions of the substrate, the hydrogen reactivity activated by the catalyst, and allowed forms of the adsorbed substrate on the catalyst may define the rate and selectivity of the reaction.

The initial reactivity of the respective position in the substrate may be described appropriately by such quantum chemical indices as the LUMO electron density and the π-bond order.[17] Such indices may reflect the reactivity with hydride or the coordination force to the metal for the adsorption. The higher reactivity of hydrogen may lead to the larger rate of the reaction, but it may be less sensitive to the reactivity differences in the reactive positions. In the consecutive reactions, the hydrogenation may progress or cease, depending upon the stability, reactivity, and adsorbed form of the intermediate product, and also the reactivity of hydrogen, the last two factors being strongly influenced by the catalyst species and the reaction conditions. Based on such considerations, the rate and selectivity of the present study can be discussed.

Rh catalysts always exhibited the highest activity for the hydrogenation of the tricyclic aromatic hydrocarbons examined in the present study, although the selectivity for a specific product was always lower than in the other catalysts. The Rh catalysts may most activate molecular hydrogens, failing to distinguish the specific position of the substrate. Hence, the Rh catalysts are not suitable for a selective hydrogenation, but they can provide a considerable amount of a product which is very minor compared with the other catalysts. The nitrogen atom in the substrates is not so influential in the selectivity on the Rh catalysts, no difference in selectivity between anthracene and acridine being observed.

The Pd catalysts exhibited a moderate activity for the selective hydrogenation of polyaromatic hydrocarbons if the optimum reaction conditions were selected in terms of the reaction temperature and the time. The carbon-supported Pd catalyst selectively hydrogenated pyrene and acridine into tetrahydro and octahydro products respectively at very high yields.[5,6] It should be noted that the Pd catalysts exhibited much different selectivities for acridine and anthracene of the same skeleton, whether or not the nitrogen atom is contained. The Pd catalysts produced 8HAc′ at a rather high yield, although they failed to produce 8HAn′ of the same structure as 8HAc′, indicating that the nitrogen atom is influential on the Pd catalysts.

The Pt catalysts exhibited a very limited activity for the hydrogenations of Ac and An, producing principally 2HAc and 2HAn respectively. Their activity for the hydrogenations of C and F was also very low, producing principally tetra- and hexahydrogenated products respectively. The Pt catalysts hydrogenated preferentially or even exclusively the 9,10-positions of An and Ac. Further hydrogenation proceeded only under severer conditions to give deeply hydrogenated products.

The Ru/C catalyst exhibited the lowest activity of all the substrates examined in the present study, reflecting its smallest ability of molecular hydrogen activation among the four noble metals examined.

In contrast to tricyclic aromatic hydrocarbons, tetracyclic hydrocarbons exhibited much less sensitivity to the catalyst species.

The reactivity and selectivity for the hydrogenation of polyaromatic substrates may be supposed to be controlled by the interactions among the LUMOs and/or all π-orbitals of the substrate and the catalyst, and the HOMO (highest occupied molecular orbital) Frontier electron density of adsorbed hydrogen on the catalyst, which may have a form of hydride to interact with the substrate.[17]

The π-bond order as well as the LUMO electron density, summarized in Table 10, are influential on the hydrogenation reactivity of the tetracyclic aromatics, such as pyrene and fluoranthene. The intermediate product, such as pyrene, hydrogenated initially at the 1 position of the highest LUMO electron density is too unstable under the present conditions to survive as the final product. The hydrogenation of pyrene proceeds initially at the pair of positions 4 and 5, where the LUMO electron density is second highest, but the π-bond order is the largest, as is shown in Fig. 4, thus producing 4HP via 2HP as the major products in the consecutive manner in all case of the present study. Only the Rh/C catalyst provided a considerable amount of 6HP. The active catalyst may rapidly hydrogenate the rather unreactive position 2 as well as

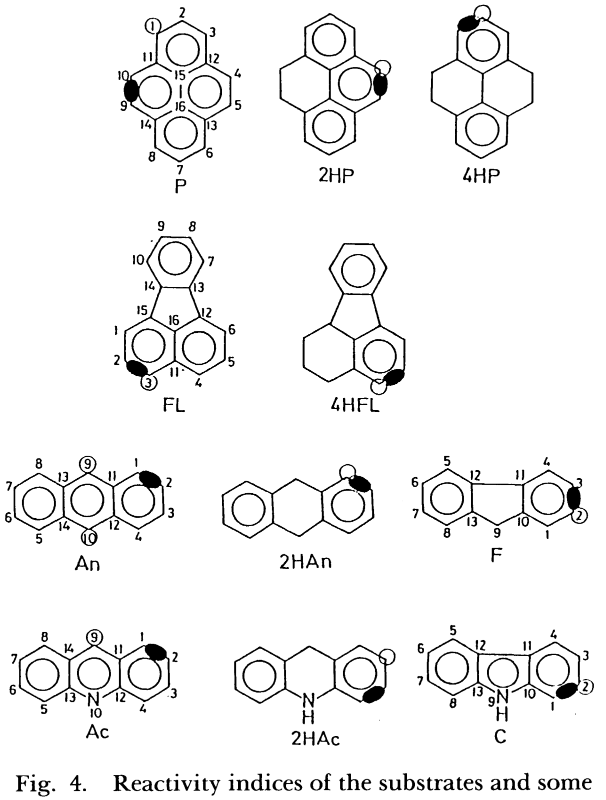

Fig. 4. Reactivity indices of the substrates and some hydrogenated products.
○: Largest LUMO electron density position. ●: Largest π-bond order bond.

Table 10. Largest LUMO Electron Density and $\pi$-Bond Order of the Substrates and Some Hydrogenated Products

| | Largest LUMO | | Largest $\pi$-bond order | |
|---|---|---|---|---|
| | Position | Value | Position | Value |
| P | $C_1$ | 0.25 | $C_9$–$C_{10}$ | 0.89 |
| 2HP | $C_4$ | 0.29 | $C_4$–$C_5$ | 0.87 |
| 4HP | $C_2$ | 0.29 | $C_1$–$C_2$ | 0.66 |
| FL | $C_3$ | 0.25 | $C_2$–$C_3$ | 0.79 |
| 4HFL | $C_4$ | 0.30 | $C_4$–$C_5$ | 0.66 |
| An | $C_{9,10}$ | 0.39 | $C_1$–$C_2$ | 0.84 |
| 2HAn | $C_1$ | 0.17 | $C_1$–$C_2$ | 0.68 |
| F | $C_2$ | 0.31 | $C_2$–$C_3$ | 0.67 |
| Ac | $C_9$ | 0.48 | $C_1$–$C_2$ | 0.85 |
| 2HAc | $C_2$ | 0.28 | $C_3$–$C_4$ | 0.68 |
| C | $C_1$ | 0.35 | $C_1$–$C_2$ | 0.72 |

the most reactive positions, 1 and 3. Hydrogenation around room temperature is reported to provide 1,6-dihydropyrene (2HP′), which is produced via the hydrogenation of the most reactive positions, 1 and 6, since the product is stable under these conditions.[12]

The large difference in hydrogenation reactivity between pyrene and fluoranthene can be explained by a combination of the effects of the $\pi$-bond order and the LUMO electron density. Fluoranthene has the highest $\pi$-bond order and LUMO electron density at the same positions of $C_2$–$C_3$, while pyrene has those at the different positions, as has been described above. It is the same reason that tetrahydrofluoranthene (4HFL) is more easily and selectively produced from fluoranthene under milder conditions regardless of the catalyst species. 1,2,3,4,5,6,11,12,15,16-decahydrofluoranthene (10HFL) is the major consecutive product, as is to be expected from the reactivity indices of 4HFL. It should be noted that the less active Pt and Pd catalysts provided more of the consecutive product from this particular substrate than did the active Rh. The high reactivity of the substrate may not discriminate the activity of the catalysts.

The reactivity and selectivity in the hydrogenation of tricyclic substrates are very different from those of tetracyclic systems. Anthracene and acridine have a pair of the most reactive 9,10-positions of the highest LUMO electron densities, yielding very selectively the 9,10-dihydro derivatives as the rather stable initial products on the Pt and Pd catalysts, although their $\pi$-bond order is never the largest. The hydrogenation of the positions of the largest $\pi$-bond order provide the product with the second largest $\pi$-bond order. MNDO suggests a large difference in the stability of 2HP′ and 2HAn, the former of which cannot be a stable product. The further hydrogenation of dihydro products is very slow in the consecutive steps, because the maximum LUMO electron density and $\pi$-bond order are much reduced to levels which are not large enough to be consecutively hydrogenated at 423 K on Pd or, more especially, Pt catalysts. The successive reaction at a higher temperature overcomes the barrier to produce 8HAn and 8HAc′ selectively.

Although the Rh catalyst provided deeply-hydrogenated products through consecutive reactions, considerable amounts of 8HAn and 8HAc were also produced, indicating that their largest $\pi$-bond order positions may be comparatively reactive on Rh catalysts. However, the higher reactivity of Ac than that of An may reflect its larger LUMO electron density, since their largest $\pi$-bond order values were much the same.

Fluorene and carbazole have values of the highest $\pi$-bond orders (ca. 0.70) at the $C_2$–$C_3$ and $C_1$–$C_2$ bonds respectively similar to that of the 9,10-dihydro products of anthracene and acridine, as is shown in Table 10 and Fig. 4. It should be noted that such substrates are hardly hydrogenated at all on the Pt catalysts. The $\pi$-bond order (ca. 0.70) of these substrates may be a threshold to restrict the hydrogenation on the Pt catalysts under the present conditions.

Pd catalysts could hydrogenate rather selectively one of phenyl groups in these substrates. The $C_2$–$C_3$ and $C_1$–$C_2$ positions in fluorene and carbazole, where the LUMO electron density and the $\pi$-bond order are at their maximum, are hydrogenated first to complete the hydrogenation of the ring. The second phenyl group resists being hydrogenated because of the reduced reactivity caused by the hydrogenation of the pair. The Rh catalyst is very active in hydrogenating every position in an unselective manner. It is interesting that certain amounts of 10HC and 10HF with a double bond between two rings are produced. Highly hindered olefin of the partially hydrogenated products can survive the hydrogenation.

Nitrogen-containing carbazole is again more reactive than fluorene. Nitrogen increases the reactivity indices.

In conclusion, the first hydrogenation of polyaromatic hydrocarbons is found to be principally governed by the LUMO and/or the $\pi$-bond order. Such reactivity indices determine the rate and selectivity of the hydrogenation, reflecting the activity of the catalyst. The active catalyst can hydrogenate the positions of a lower reactivity, performing the consecutive reaction to the more deeply hydrogenated product for a substrate and the competitive reactions to lower the selectivity for another substrate.

Hence, selective hydrogenation can be designed by selecting the catalyst and the reaction conditions to match the reactivity of the reaction position in the particular substrate, as predicted on the basis of quantum chemical calculations.

Noble metals' activation ability against molecular hydrogen and their adsorption ability against an aromatic bond are the origins of their catalytic activity; however, no theoretical explanation is available at present. Their empirical classification may, therefore, practical use at present.

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