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Hydrogenation of Benzene on Platinum and Ruthenium Catalysts in Pulse Conditions at Very Low Contact Times

Even in the simple case of hydrogenation of benzene to cyclohexane over metallic catalysts, the facile or demanding character of the reaction is still a matter for discussion, as is the mechanism of the reaction (see, for example, Refs. (*1*) and (*2*) for Ni catalysts and Ref. (*3*) for Pt catalysts). The present contribution deals with the hydrogenation of pulses of (C_6H_6 + H_2) under 1 atmosphere pressure of H_2 gas flow at room temperature. The benzene vapor pressure was maintained constant at 8 Torr (1 Torr = 133.3 Nm^{-2}). Two platinum catalysts and one ruthenium catalyst were investigated (see Table 1).

From the data in Ref. (*6*), the turnover number for the hydrogenation of C_6H_6 on Pt at 25°C should be about 200 hr^{-1} per surface Pt atom, Pt_s. Provided that the three following hypotheses are fulfilled:

(i) all of the Pt_s atoms are active,

(ii) each C_6H_6 which chemisorbs is hydrogenated (in this regard note that the presence of hydrogen inhibits the C–H dissociative adsorption of benzene (*7*)), and

(iii) the number of Pt_s atoms per active site is equal to 2,

this would result in a residence time of each C_6H_6 molecule on the Pt surface nearly equal to 10 sec.

It follows that under conditions in which

(i) the number of C_6H_6 molecules in each pulse $n(C_6H_6)$ is greater than the number of Pt_s atoms in the sample, and

(ii) the contact time between the C_6H_6 gas molecules and the Pt surface is shorter than the residence time of each C_6H_6 molecule on the Pt surface,

one should observe a division of each C_6H_6 hydrogen diluted pulse into two parts, the first, independent of $n(C_6H_6)$ in the pulse, being converted to C_6H_{12}, and the remainder flowing directly through the catalyst as unreacted C_6H_6.

To verify the above hypothesis, a 10 to 20 liter/hr H_2 gas flow was used. Ten to twenty-five percent of this was directed to the entrance of a flame ionization detector chromatograph and the remaining 90 to 75% was evacuated. The temperature of

TABLE 1

Catalysts (Percentage Metal and Percentage Dispersion)

Catalyst[a] reduced at T_R (°C)	Percentage dispersion of Pt or Ru (from O_2 chemisorption at 25°C)	Stoichiometry assumed for the O_2 chemisorption
10% Pt/SiO_2 (Aerosil Degussa, S = 300 m^2/g) (T_R = 700)	4.8	1 O atom per Pt_s (*4*)
1.88% $Pt/\gamma\text{-}Al_2O_3$ (Al_2O_3 GFS 400 RP, S = 200 m^2/g; $\bar{r}_p$ = 76 Å) (T_R = 500)	69	1 O atom per Pt_s (*4*)
0.88% $Ru/\gamma\text{-}Al_2O_3$ (same Al_2O_3) (T_R = 500) (percentage reduction Ru = 55)	85	2 O atom per Ru_s (*5*)

[a] For the C_6H_6 hydrogenation experiments, the reactivation was carried out *in situ* at 500°C under H_2 flow.

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C_6H_6 hydrogenation was 25°C; the pulse size as well as the hydrogen flow were varied as desired. Over the two platinum catalysts investigated, a single C_6H_6 and a single C_6H_{12} peak were observed. Figure 1 shows the variation of the number of C_6H_{12} molecules ($n(C_6H_{12})$) formed in successive pulses, over Pt/SiO_2, for three different pulse sizes each of which contained a number of C_6H_6 molecules designated as $n(C_6H_6)$.

Figure 1 shows (i) a slow decrease of $n(C_6H_{12})$ as the number of pulses increased, due to some self-poisoning; and (ii) the absence of variation of $n(C_6H_{12})$ per pulse, when $n(C_6H_6)$ per pulse was varied in a 1 to 8 ratio. When $n(C_6H_6)$ per pulse was increased above 3×10^{-6} mole, $n(C_6H_{12})$ per pulse was also observed to increase. On the left-hand side of Fig. 1, $n(C_6H_{12})$ for the fresh catalyst is approximately 0.6 C_6H_{12} molecule per Pt_s. Similar results were obtained over Pt/Al_2O_3, with an $n(C_6H_{12})$ to $n(Pt_s)$ ratio of 0.45.

Over Ru/Al_2O_3 the results were more complicated, as indicated below:

(i) Figure 2 shows a continual increase in $n(C_6H_{12})$ as $n(C_6H_6)$ increased in a 1 to 5 ratio (measurements performed at room temperature over a sample prestabilized by injection of 15 pulses of hydrogen-diluted C_6H_6). The different behavior of the Ru and of the Pt catalysts should be related to the greater turnover number of Ru compared to Pt in the hydrogenation of C_6H_6 (*8*). Some C_6H_{12} molecules were then desorbed from the Ru metal surface before the excess of C_6H_6 had flowed quantitatively out of the catalyst bed. Consequently further C_6H_{12} was formed from the residual C_6H_6. It was not found experimentally possible to attain with Ru the regime where $n(C_6H_{12})$ was independent of $n(C_6H_6)$.

(ii) Over the fresh Ru catalyst, some coking possibly together with nonreactive chemisorption, occurred first. Neither C_6H_6 nor any C_6H_{12} was detected in fact in the first pulse. Some C_6H_6 together with C_6H_{12} was detected in the subsequent pulses. (See Figure 3.) The increase in $n(C_6H_6)$ as the number of pulses increased up to 5 may be ascribed to an increase in the selectivity for hydrogenation compared to coking plus nonreactive chemisorption. The decrease in $n(C_6H_{12})$ as the number of pulses increased from 6–7 up to 15

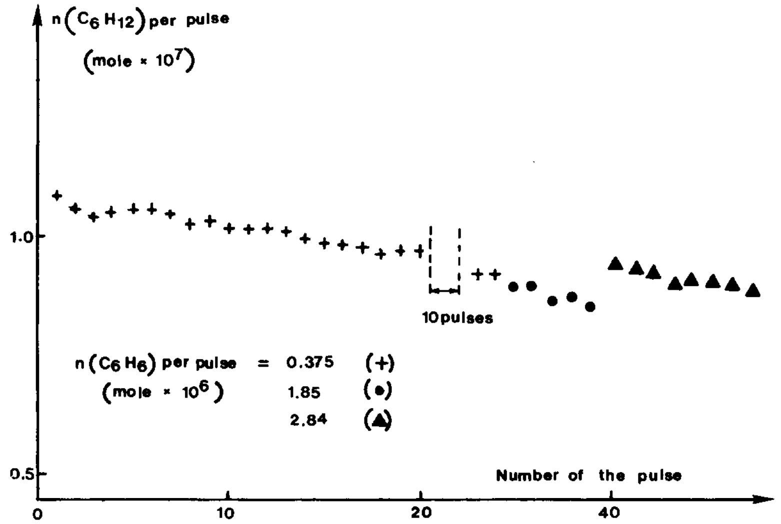

FIG. 1. Hydrogenation of C_6H_6 over Pt/SiO_2 (m = 6 mg; $D(H_2)$ = 18 liters/hr); $n(C_6H_{12})$ as a function on the number of pulses.

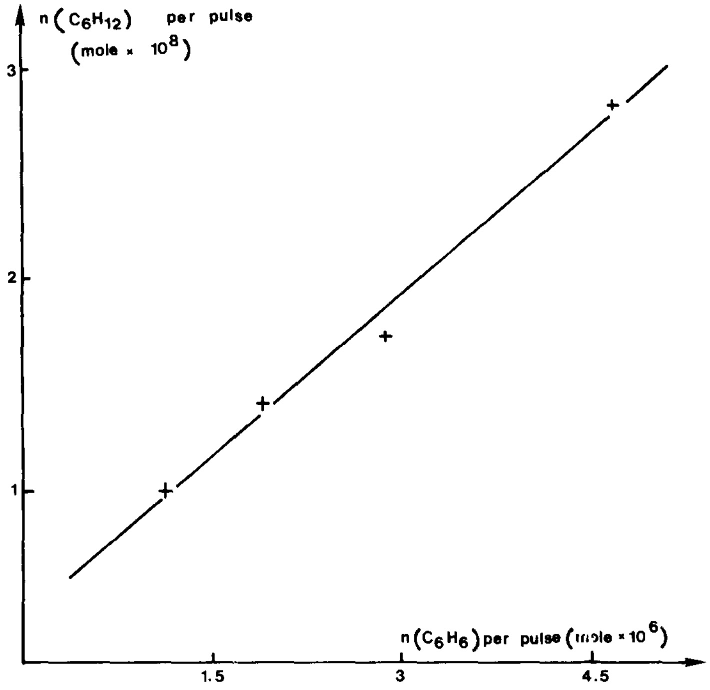

FIG. 2. Hydrogenation of C_6H_6 over prestabilized Ru/Al_2O_3 (m = 60 mg of a 2% catalyst + 98% quartz mixture; $D(H_2)$ = 18 liters/hr); $n(C_6H_{12})$ as a function of $n(C_6H_6)$.

most probably arises from the inhibiting effect of the carbon deposits on the hydrogenation of C_6H_6 to C_6H_{12}.

The difference in behavior for the Ru and for the Pt catalysts confirms that the discovery that the $n(C_6H_{12})$ to $n(Pt_s)$ ratio is approximately equal to 0.5 was not fortuitous. Hence it may be thought that:

(i) Almost all of the Pt_s atoms are working during the catalytic hydrogenation of C_6H_6. Otherwise, a much smaller value for the $n(C_6H_{12})$ to $n(C_6H_6)$ ratio would have been expected.

(ii) The Pt surface in the two catalysts investigated behaves rather homogeneously. Assuming that the metallic surface is

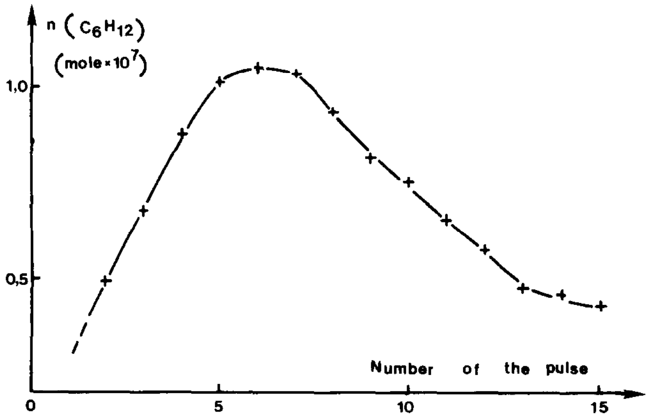

FIG. 3. Hydrogenation of C_6H_6 over fresh Ru/Al_2O_3 (m and D as in Fig. 2); $n(C_6H_{12})$ as a function of the number of the pulse (2.8×10^{-6} mole C_6H_6 per pulse).

composed of sites with turnover numbers varying in ratio from 1 to 10, we should have observed either a strong broadening of the single C_6H_{12} peak or even several C_6H_{12} peaks, but this was not the case.

(iii) The conclusions of other workers who stated that the number of surface atoms involved in the hydrogenation of one C_6H_6 molecule over metals is very low are corroborated (for example Ref. (*9*) for nickel catalysts and Ref. (*10*) for platinum catalysts).

Finally, the present approach should be of further interest in the study of the hydrogenation of C_6H_6 (or the conversion of other hydrocarbons) over catalysts where there is deviation from "facile" character or which are contaminated by various poisons, and also over bimetallic catalysts.

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