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The Role of Support in the Catalytic Hydrogenation of Benzene over Ruthenium Catalysts

It is generally agreed that the hydrogenation of benzene over supported noble metal catalysts is a facile reaction which is independent of particle size. Previous benzene hydrogenation studies over supported Ru catalysts have been carried out using relatively noninteractive supports such as alumina and silica (*1*, *2*). Because of the possibility that more interactive supports such as magnesia or lanthana may modify the catalytic activity of supported Ru catalysts in the hydrogenation of benzene, we have extended previous studies to include magnesia, silica–alumina, and graphitic carbon as support materials.

The Ru catalysts used in this study were prepared by the incipient wetness technique. Initially, the appropriate weight of $RuCl_3 \cdot 3H_2O$ required to prepare a catalyst having a nominal weight loading of 2 wt% Ru was dissolved in an amount of doubly deionized water. The solution containing the Ru was then added to the support in a dropwise manner to give a thick slurry. The resulting slurry was dried in air at 383 K for 24 hr and then sieved to a particle size of 60–80 mesh. The catalysts were reduced in flowing H_2 at 673 K for 3 hr and stored in bottles prior to use. Each catalyst was rereduced in flowing H_2 for 2 hr before use.

All of the supports used in this study were calcined at 723 K in flowing air for 16 hr. Impregnation of the supports with $RuCl_3 \cdot H_2O$ solution was always performed following calcination of the support in air.

The MgO used in this study was prepared from the decomposition of $MgCO_3$ (Baker Chemical, research grade) as described in Ref. (*3*). The silica (Ketjen, F-2) and the silica–alumina (3.2%) were obtained from Akzo Chemie. The graphitized carbon EG was obtained from the Societe Carbonne, Lorraine, France.

Ru dispersions were obtained from H_2 chemisorption measurements at room temperature using a conventional volumetric adsorption apparatus by the static method. Because of the uncertainty associated with Ru surface area measurements using H_2 chemisorption, particle size measurements were also determined using transmission electron microscopy.

The hydrogenation of benzene was carried out in a fixed bed microreactor under differential flow conditions. Product analysis was performed using gas chromatography. The reaction was studied at 323 K at a benzene partial pressure of 56 Torr (1 Torr = 132 Pa). The partial pressure of hydrogen was 704 Torr.

Ru dispersions obtained from H_2 chemisorption measurements assuming a H/Ru(s) stoichiometry equal to unity are shown in Table 1. Because the Ru metal crystallites were always greater than 3 nm, particle size effects were assumed to have a negligible effect on catalytic reactivity and on the H/Ru(s) chemisorption stoichiometry. The Ru particle sizes obtained using transmission electron microscopy are also included in Table 1. There is good agreement between the transmission electron microscopy and the H_2 chemisorption measurements for both the supported carbon and the silica-supported catalysts. However, for magnesia, particle sizes obtained from transmission electron microscopy measurements were considerably smaller than those obtained using hydrogen chemisorption.

Catalytic activities expressed both in

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TABLE 1

Dispersion and Particle Size Measurements for Supported Ru Catalysts

Catalyst[a]	H/Ru(s)	H (nm)	TEM (nm)
Ru/MgO	0.04	24.6	10.5
Ru/C	0.27	3.6	3.3
Ru/SiO_2	0.23	4.2	4.6
Ru/SiO_2–3.2% Al_2O_3	0.07	14.2	—

[a] Metal loading was 2 wt% Ru.

terms of turnover frequencies and as moles of product per gram of catalyst are shown in Table 2. Turnover frequencies obtained over Ru/MgO were between one and two orders of magnitude greater than those obtained over the other supported catalysts studied. The very high reaction rate obtained over Ru/MgO was rather difficult to measure. For this reason, and to rule out possible heat transfer effects, the catalyst bed was diluted with the MgO support. In these experiments, the total weight of the catalyst charged to the reactor was varied from 5 to 25 mg of active catalyst. The balance of the total 30-mg charge to the reactor was pure MgO. Within experimental error, the dilution of the catalyst bed with MgO had no effect on turnover frequencies measured for the hydrogenation of benzene.

The very high turnover frequencies observed for benzene hydrogenation over Ru/MgO require an explanation. It is clear from the H_2 chemisorption measurements and from the TEM particle size measurements that there is a strong suppression of H_2 chemisorption on Ru/MgO. We suggest three possible explanations for this observation: (i) partial oxidation of Ru by the MgO support. It is well known that Ru is easily oxidized to RuO_2 in the presence of air. However, infrared and XPS studies (*4, 5*) show no evidence of higher oxidation states of Ru following reduction in H_2 at 673 K. Under the strong reducing conditions used in this study it became evident that Ru was in its zero valent oxidation state. In one run, the Ru/MgO catalyst was reduced for 12 hr at 673 K in flowing H_2. Particle sizes obtained using this pretreatment were identical to those reported in Table 1. In addition to this, turnover frequencies obtained following this pretreatment were identical to those obtained following reduction in H_2 for 3 hr.

(ii) The electronic structure of Ru is modified through an interaction with the support. Aika *et al.* (*6*) have reported electron transfer from the support to the metal for Ru/alkaline earth supports such as MgO. Because of the Ru crystallite sizes used in this study (10 nm) we feel that this would be rather unlikely. Joyner *et al.* (*7*) have pointed out that metal–support electron transfers affect only the metal atoms in intimate contact with the support. Over large

TABLE 2

The Hydrogenation of Benzene over Supported Ru. Catalytic Activity and Catalyst Deactivation

Catalyst	$k_h \times 10^6$[a] (mol g^{-1} s^{-1})	TOF $\times 10^2$ (molec $site^{-1}$ s^{-1})	$k_e \times 10^3$[b] (min^{-1})	$k'_d \times 10^{10}$[c]
Ru/MgO	70.5	800	0.07	1.1
Ru/C	13.4	24	1.0	3.7
Ru/SiO_2	6.6	16	2.0	3.0
Ru/SiO_2–Al_2O_3	2.9	17	2.0	3.2

[a] Initial activity extrapolated to zero time, from Fig. 1.

[b] From Ref. (*11*).

[c] From Ref. (*12*, Eq. (2)).

supported metal crystallites, this electronic interaction is expected to be small.

(iii) The Ru metal particles are partially decorated by the magnesia support. MgO can readily react with surface hydroxyl groups to give $Mg(OH)_2$ (*8*). Poels *et al.* (*9*) have shown that over Rh/MgO, this reaction occurs readily to create a partial blockage of the metal surface. Shastri and Schwank (*10*) have reported that for a series of Ru–Au/MgO catalysts, a number of the particles were trapped below the surface by the MgO support. This decoration or entrainment of the metal by the support would undoubtedly lead to a depression in H_2 chemisorption by the metal. Particle size measurements using TEM, on the other hand, would not be affected by decoration of the metal by the support.

The very high turnover frequency observed for the hydrogenation of benzene over Ru/MgO cannot be explained by invoking dispersion effects. Ru crystallite sizes for all of the catalysts studied were greater than 3.0 nm. However, decoration of the Ru by MgO might possibly decrease the extent to which the surface is poisoned as the result of carbon formation. Coke formation on the surface of a metal is a demanding reaction and is promoted by the presence of the adsorbed aromatic ring together with Ru surface ensembles. Decoration of Ru by MgO might possibly reduce the size of the Ru surface ensembles on which carbon polymerization can occur. This would inhibit self-poisoning of the reaction by carbon and lead to an enhanced catalytic activity. In order to pursue this possibility, the time dependence of the deactivation process was studied. The results of this deactivation study are shown in Fig. 1. The deactivation follows the hyperbolic relationship proposed by Germain and Maurel (*11*). The slopes of the resulting straight lines are shown in Table 2. According to the deactivation model proposed by Levenspiel (*12*) for a self-poisoning process, the slopes of the lines may be expressed as

$$k_e = (\text{constant})(kd/k_h)W, \qquad (1)$$

where k_e is the experimentally determined slope, k_h is the rate constant for the reaction, and W is the mass of the catalyst sample. Equation (1) is based on a zero-order rate of reaction. The constant term includes the partial pressure of the reactants and the flow rate. Using this equation, the deactivation constant can be calculated as

$$k'_d = k_d(\text{constant}) = k_e \frac{k_h}{W}. \qquad (2)$$

The deactivation constants shown in Table 2 clearly show that the rate of deactivation is considerably lower for the Ru/MgO catalyst.

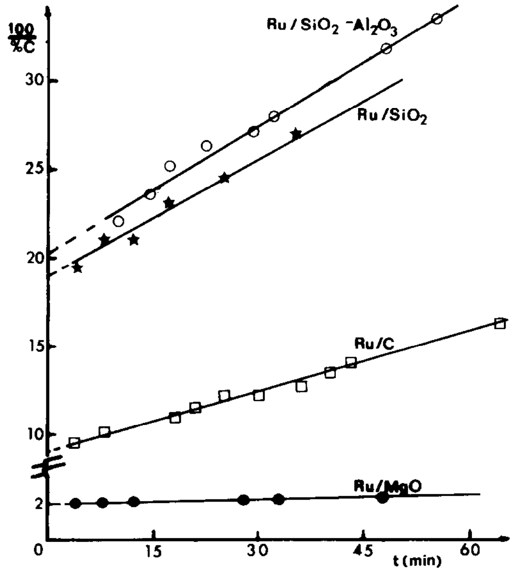

FIG. 1. Catalyst deactivation as a function of time. Reaction conditions; T = 323 K, total pressure = 1 atm, $PH_2/P_{\text{benzene}} = 13$. The deactivation is expressed as 100% conversion.

CONCLUSIONS

The following important conclusions emerge from this study.

(i) The inhibition of hydrogen chemisorption on Ru/MgO is due to the partial decoration of the Ru by MgO.

(ii) The higher rate of benzene hydrogenation over Ru/MgO can be explained by invoking a decrease in the rate at which coke formation inhibits the self-poisoning of the Ru surface.

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