NOTES

Cyclohexane Conversion on Ruthenium Catalysts of Widely Varying Dispersion

Structure-sensitive reactions at metal catalyst surfaces require sites with special structural features (1, 2). The concentration of such sites per unit surface area will in general depend on methods of catalyst preparation and variables such as the state of metal dispersion or crystallite size. Consequently, the catalytic activity per unit surface area or per surface metal atom is a function of these variables for structure-sensitive reactions. Where a given reactant may exhibit more than one reaction, there is a possibility that selectivity may be affected, since one reaction may be more structure sensitive than another. In the present communication we present data illustrating a striking example of this type, involving the conversion of cyclohexane on ruthenium catalysts of widely varying dispersion. At temperatures of about 300°C cyclohexane undergoes two reactions on ruthenium, dehydrogenation to benzene and hydrogenolysis to lower carbon number alkanes. In the latter reaction methane is the predominant product. Selectivity, defined as the ratio of the dehydrogenation rate to the hydrogenolysis rate, increases dramatically with increasing dispersion of the ruthenium. At very low dispersion the major reaction is hydrogenolysis, while at high dispersion dehydrogenation predominates.

The ruthenium catalysts investigated included an unsupported ruthenium catalyst and three catalysts in which ruthenium was supported on silica. The ruthenium–silica catalysts contained 0.1, 1.0, and 5.0 wt% ruthenium. They were prepared by impregnating silica with an aqueous solution of ruthenium trichloride and drying at approximately 110°C. The catalysts were reduced at 500°C in flowing hydrogen to the metallic form in the adsorption cell or reactor prior to making measurements. The silica employed was Cabosil HS5 with a surface area of approximately 300 m²/g, obtained from the Cabot Corporation, Boston, Mass. The unsupported ruthenium catalyst was prepared by contacting an aqueous solution of ruthenium trichloride with an ammoniacal hydrazine solution. The precipitate formed was filtered out of solution, washed with distilled water, and dried overnight at 110°C. The dried precipitate was then contacted with a stream of helium containing 5% hydrogen and heated to 150°C. After approximately 1 hr at 150°C, the temperature was increased to 400°C and maintained at this level overnight to complete the reduction. The ruthenium was purged with helium and then passivated at room temperature by controlled admission of air to the helium. After the ruthenium was charged to the adsorption cell or reactor, it was re-reduced at 400°C in flowing hydrogen.

Hydrogen chemisorption measurements were used to characterize the degree of dispersion of the ruthenium catalysts. The measurements were made at room temperature in a high vacuum apparatus which has been described in detail elsewhere (3, 4). The cyclohexane conversion runs were conducted in a flow reactor system which has
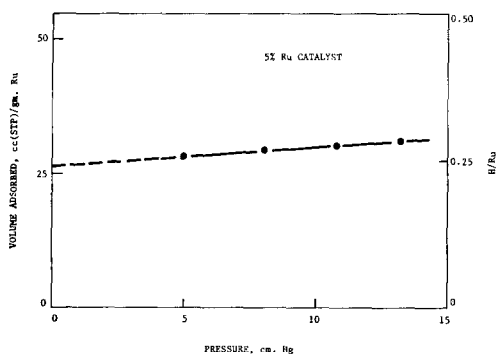
FIG. 1. Typical hydrogen chemisorption isotherm at room temperature for a catalyst containing 5 wt% ruthenium on silica. The quantity H/Ru is the number of hydrogen atoms adsorbed per atom of ruthenium in the catalyst. The catalyst was reduced in hydrogen at 500°C and evacuated at this temperature prior to determination of the isotherm at room temperature.

also been described previously (5, 6). All experiments were conducted at atmospheric pressure. The reactor was approximately 1 cm in diameter. The catalyst granules were diluted with inert alundum granules to a total volume of approximately 5 ml. Reaction products were analyzed in a gas chromatograph connected to the outlet of the reactor.

A typical hydrogen chemisorption isotherm for determining ruthenium dispersion is given in Fig. 1 for a silica-supported ruthenium catalyst containing 5 wt% ruthenium. The quantity, H/Ru, representing the number of hydrogen atoms chemisorbed per ruthenium atom in the catalyst, is given by the right hand ordinate in Fig. 1. In determining the ruthenium dispersion, defined as the fraction of ruthenium atoms present in the surface of metal crystallites, the isotherms were extrapolated to zero pressure. The value of H/Ru at zero pressure is taken as the degree of metal dispersion, the assumption being made that one hydrogen atom is adsorbed per surface ruthenium atom (3). The degree of dispersion increases markedly as the concentration of ruthenium in the catalyst decreases, increasing from 0.006 for 100% ruthenium to 0.24 for 5% ruthenium and

0.41 for 1% ruthenium. A hydrogen chemisorption measurement of dispersion was not obtained on the 0.1% ruthenium catalyst. In this case, the dispersion was assumed to be unity. The dispersion at 0.1% ruthenium concentration is certainly significantly higher than at 1%, and the assumed dispersion is not likely to be greatly in error.

Data on the rates and selectivity of conversion of cyclohexane are shown as a function of ruthenium dispersion in Fig. 2. The rates are expressed as molecules of cyclohexane converted per second per surface site, the number of surface sites per ruthenium atom in a given catalyst corresponding simply to the quantity H/Ru determined from the hydrogen chemisorption isotherm. The rates were determined at low conversion levels, lower than about
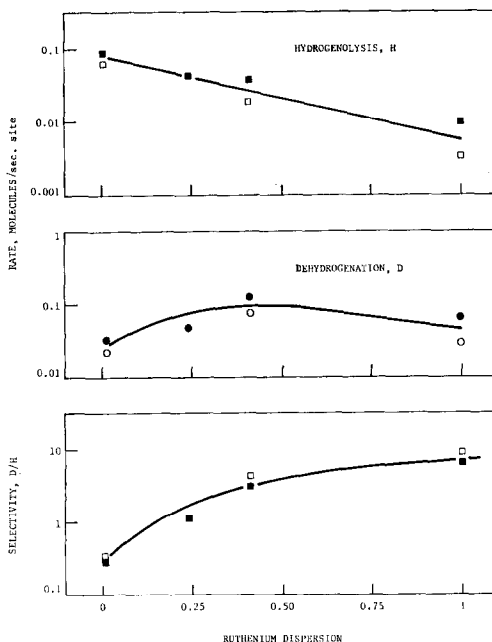

FIG. 2. The effect of ruthenium dispersion on the rates of hydrogenolysis and dehydrogenation of cyclohexane and on the selectivity. The rates are shown for a temperature of 316°C and cyclohexane and hydrogen pressures of 0.17 and 0.83 atm, respectively. The selectivity is the ratio D/H of dehydrogenation rate to hydrogenolysis rate. The solid points represent initial rates and selectivities after about 10–20 min of exposure of the catalysts to reactants, while the open points represent data obtained after about 2 hr.

5% throughout. The closed points in Fig. 2 represent initial rates and selectivities determined after the catalyst had been contacted with the reactants for 10–20 min, while the open points represent data obtained after about 2 hr. While rates declined with time for all the catalysts, this did not affect the conclusions. The rate of hydrogenolysis, H, decreased by an order of magnitude when the dispersion was increased from 0.006 to unity. The rate of dehydrogenation, D, was less sensitive to dispersion, and actually increased initially with increasing dispersion. The selectivity D/H increased by more than one order of magnitude when ruthenium dispersion was increased from 0.006 to unity.

The major feature of the present work is the demonstration of the striking effect of ruthenium dispersion on the selectivity of conversion of cyclohexane. The result could have been anticipated from previous work in which the effect of metal dispersion on hydrogenolysis and dehydrogenation reactions was investigated individually. Thus, studies of the effect of metal dispersion on the activity of rhodium for ethane hydrogenolysis (4) and of platinum for neopentane hydrogenolysis (7) have shown that hydrogenolysis reactions of hydrocarbons on metals are structure sensitive, while studies of the dehydrogenation of cyclohexane to benzene on platinum have shown this reaction to be structure insensitive (8, 9). Nonetheless, the direct demonstration of the effect of metal dispersion on the selectivity of cyclohexane conversion provides important confirmation of the relative structure sensitivities of the two types of reactions. A clear observation of the effect of metal dispersion on selectivity of cyclohexane conversion dictates the choice of a metal exhibiting comparable rates of hydrogenolysis and dehydrogenation. Platinum is not a good candidate, since the hydrogenolysis rate is negligible compared to the dehydrogenation rate. By contrast, ruthenium is ideal for such a study because it possesses hydrogenolysis and dehydro-

genation activities of the same order of magnitude.

The effect of metal dispersion on the selectivity of conversion of cyclohexane to benzene is probably rationalized most readily on the basis of differences in the nature of the chemisorbed intermediates involved in the hydrogenolysis and dehydrogenation reactions. The chemisorbed intermediate in hydrogenolysis, by analogy with conclusions drawn in ethane hydrogenolysis (10), is probably a dehydrogenated surface species which forms a number of bonds with surface metal atoms. The probability of finding a suitable array of surface atoms to accommodate such a chemisorbed intermediate is high on a large metal crystal where most of the surface atoms are present in plane faces of the crystal. On very small crystallites a large fraction of the total surface atoms exists at corners and edges, and geometric constraints become more pronounced. By contrast, the chemisorbed intermediate in dehydrogenation presumably does not require a site consisting of a number of metal atoms arranged in a special way and, hence, is less sensitive to geometric constraints.

ACKNOWLEDGMENTS

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