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The Relative Specific Activity for Benzene Hydrogenation of Some Supported Group VIII Metals

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The specific activity for benzene hydrogenation of nickel, cobalt, and platinum supported on silica is compared over the range of 70° to 175°C at a common set of reactant partial pressures. The apparent activation energies were found to be 14.0, 5.8, and 2.3 kcal/mole for the nickel, cobalt, and platinum catalysts, respectively. The apparent activation energy increases with increasing hydrogen partial pressure. Below 90°C the relative specific activity of the metals is Pt > Co > Ni. Because of the difference in apparent activation energies, above 90°C the specific activity of nickel becomes greater than that of cobalt.

Because of the complex nature of the apparent activation energy for benzene hydrogenation, the difficulty in quantitatively relating this parameter to the stability of proposed surface π complexes is pointed out.

I. INTRODUCTION

The specific activity (i.e., the activity per unit area) is a subject of considerable interest in catalysis. In the classical work of Beeck and co-workers (*1*) the catalytic activity of various metal films was determined for ethylene hydrogenation, and it was shown how the activities could be related to the lattice spacings. Boudart (*2*), and subsequently also Beeck (*1*), showed how the activities could be equally well explained in terms of an electronic picture. Supported metals are far more typical of real catalyst systems than evaporated metal films. Consequently, a number of investigators have studied the activity of various carefully prepared supported metal catalysts of known metal surface area for a variety of reactions (*3*, *4*, *5*).

Recently a number of authors (*6*, *7*, *8*) have postulated that the hydrogenation of benzene over transition metals involves the formation of a π-bonded intermediate. Völter (*7*) and Shopov and Andreev (*8*) both proposed that the decrease in activation energy with increased alkyl substitution of the benzene reflects an increase in the strength of the ring–metal complex.

Because of severe diffusional problems in liquid-phase reaction systems, as pointed out by Bond (*9*) only vapor-phase kinetic studies need be considered. A number of studies of benzene hydrogenation with individual metals have been made, but since the reaction partial pressures and temperatures employed differed, a firm judgement concerning the relative activity of the various metals cannot be made from this data. Amano and Parravano (*10*) compared the activity of supported ruthenium, rhodium, palladium, and platinum for benzene hydrogenation at a fixed set of conditions. However, data on the dispersion of the metals was not obtained so that specific activities cannot be compared. Schuit and Van Reijen (*5*) compared the specific activity of a series of metals for benzene hydrogenation at 100°C. Activation energies were not determined, however, and as pointed out by the authors, the comparison applies only to this temperature. Clearly, there is a need for more data on the specific activity of various metals for benzene hydrogenation over a range of temperatures at a common set of reactant partial pressures.

In the present paper data on the vapor-phase hydrogenation of benzene over supported nickel, cobalt, and platinum catalysts of known surface areas are discussed. The catalysts were all prepared in the same way and contained 10 wt % metal supported on silica. The apparent activation energy of the various metals was also determined at a common set of benzene and hydrogen partial pressures, so that the specific activity of the metals can be compared over a range of temperatures.

II. EXPERIMENTAL

A. *Apparatus and Procedure*

The benzene hydrogenation data were obtained in a flow reactor system at atmospheric pressure using a vertically mounted stainless steel reactor tube 1.0 cm in diameter and 8.0 cm in length. The general features of this type of unit have been described previously (*11*). The benzene was metered to the unit by means of a calibrated Constant Rate Syringe Drive Pump obtained from the Ace Scientific Company, Linden, New Jersey. The benzene was vaporized in a preheater tube, and then mixed with the helium and hydrogen and passed downflow through the catalyst bed. The helium and hydrogen flow rates were measured in a manometer system using dibutyl phthalate as the manometer fluid, which was chosen because of its low vapor pressure (*12*). The temperature of the catalyst bed was measured by an iron-constantan thermocouple. The thermocouples were individually calibrated by their manufacturer, the Thermo-Electric Company, Saddle Brook, New Jersey. The products from the reactor were analyzed by a gas chromatographic unit coupled directly to the outlet of the reactor. The column used was 10 ft long and contained 7,8-benzoquinoline (20% on 45/60 mesh firebrick).

The reactants, benzene and hydrogen, were passed over the catalyst in the presence of helium diluent. A total gas flow rate of 1 liter/min was used through out. The run procedure consisted of passing the reactants over the catalyst for a period of 5 min, at which time a sample of the product was taken for chromatographic analysis. The benzene flow was then shut off and the hydrogen and helium flow continued for a period of 15 min at the reaction temperature prior to another run. In this way, it was possible to minimize variation in catalyst activity from period to period. In each run the catalyst was diluted with 0.5 g of ground Vycor beads of the same particle size as the catalyst. The catalyst charge varied from 55 to 105 mg, and quartz wool was packed on top of the catalyst to hold it in place. A preliminary experiment indicated that the ground Vycor and quartz wool was inactive for benzene hydrogenation over the range of conditions encountered in this work. The catalyst was reduced overnight at 370°C with flowing H_2 using a procedure previously described (*3*).

B. *Materials*

The gases employed in this work were ultra-high-purity helium (ionization grade) and ultra-high-purity hydrogen obtained from the Matheson Company, East Rutherford, New Jersey. The hydrogen was further purified by passing it through a Deoxo unit containing palladium catalyst to remove traces of oxygen as water prior to passage through a molecular sieve drier. The benzene employed was high-purity chromatoquality benzene obtained from Matheson Coleman and Bell, East Rutherford, New Jersey. Chromatographic analyses indicated it to be 99.9% benzene. An analyses for sulfur indicated it to contain 1.2 parts per million. The benzene was dried before use with 13 × molecular sieve.

The supported metal catalysts investigated in this work all contained 10% by weight of metal based on the combined weight of metal and support. The catalysts were prepared by impregnating silica with solutions of salts of the metals in deionized water. Aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$, were used for impregnating the nickel and cobalt catalysts, respectively. The platinum catalyst was prepared by impregnating the silica with $Pt(NH_3)_2(NO_2)_2$, obtained from the Baker Division of Englehard Industries, Newark, New Jersey. The silica used as a support was Cabosil HS 5 (300 m^2/g surface area), obtained from the Cabot Corp., Boston, Mass. After impregnation, the catalysts were all dried overnight at 105°. The dried catalysts were pressed at 8000 psi into wafers which were subsequently crushed and screened to a size between 45 and 50 mesh.

III. RESULTS

The reaction of benzene with hydrogen to form cyclohexane was studied over the various catalysts at temperatures from 70° to 175°C at low conversion levels. The degree of conversion ranged from about 0.1% to 2.0%, most of the data having been obtained at conversion levels below 1%. Consequently, the partial pressures of the reactants (benzene and hydrogen) do not vary much through the reaction zone, and the system approaches that of a differential reactor. The reaction rates per gram of catalyst were determined from the relation

$$r = (F/W)X \qquad (1)$$

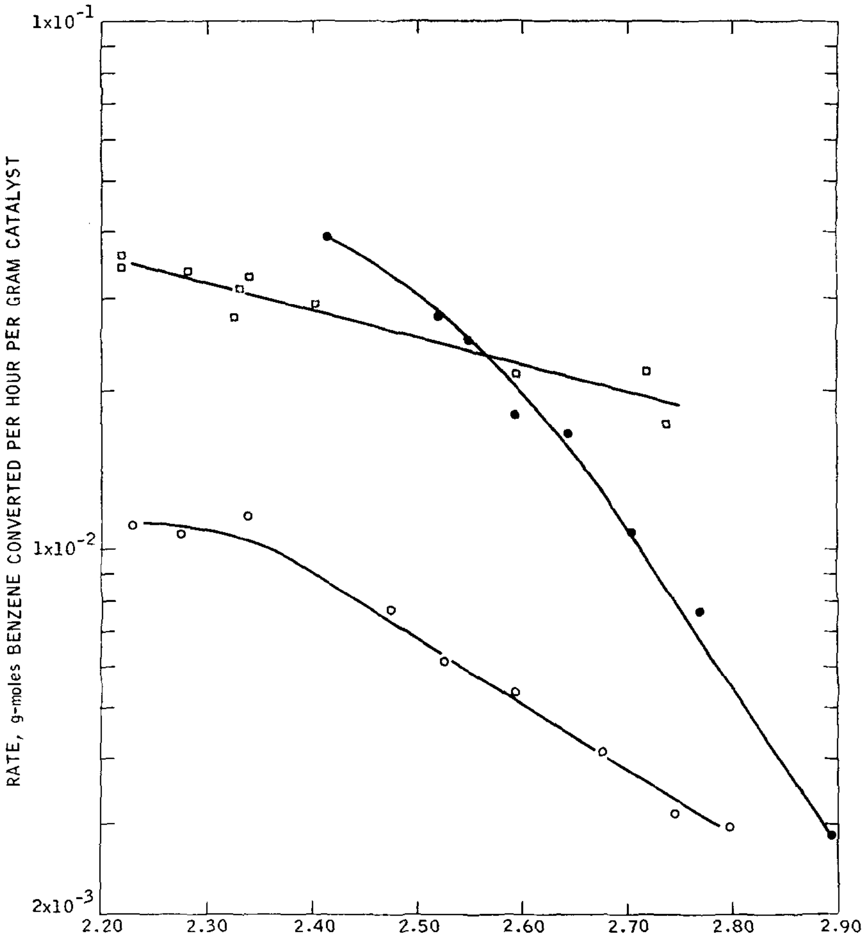

FIG. 1. The effect of temperature on the rate of benzene hydrogenation on supported metal catalysts at $P_B = 0.040$ atm and $P_H = 0.500$ atm: □, Pt/SiO_2; ●, Ni/SiO_2; ○, Co/SiO_2.

where F represents the feed rate of benzene to the reactor in g-moles per hour, W represents the weight in grams of the catalyst charged to the reactor, and X represents the fraction of benzene converted to cyclohexane.

In an actual run to determine reaction rates, the catalyst was first prereduced with flowing hydrogen, after which the reactor was cooled in flowing hydrogen to a convenient reaction temperature. At a standard set of conditions of hydrogen and benzene partial pressures, P_{H} and P_{B} respectively, the activity of the freshly reduced catalyst was determined. Following this, reaction rates were measured at a series of temperatures. The data are shown in the Arrhenius plots in Fig. 1. Apparent activation energies were derived from the linear, low-temperature portion of the Arrhenius plots in Fig. 1, and are listed in Table 1.

TABLE 1

Summary of Specific Activities and Apparent Activation Energies

	Pt/SiO_2	Ni/SiO_2	Co/SiO_2
Rate at 100°C, (g-mole conv. per hr per g catalyst)[a]	2.05×10^{-2}	1.25×10^{-2}	3.93×10^{-3}
Metal surface area (m^2/g)[b]	4.4	13.6	5.6
Specific rate at 100°C (g-mole conv. per hr per m^2 metal surface)[a]	4.67×10^{-3}	9.20×10^{-4}	7.02×10^{-4}
Apparent activation energy (kcal/mole)	2.3[a]	14.0[a] 9.7[c]	5.8[a]
Pre-exponential factor, r' [d], (g-moles conv. per hr per m^2 of metal)	1.04×10^{-1}	1.45×10^{5}	1.73

[a] Other conditions, $P_{\mathrm{B}} = 0.040$ atm, $P_{\mathrm{H}} = 0.500$ atm.

[b] From ref. (*3*).

[c] Other conditions $P_{\mathrm{B}} = 0.040$ atm, $P_{\mathrm{H}} = 0.300$ atm.

[d] Determined from the relationship $r = r' \exp(-E/RT)$ where r is the specific rate shown above and E is the apparent activation energy measured at the same conditions.

A number of investigators have reported that the order of reaction with respect to benzene and hydrogen increases with increasing temperature with metal catalysts (*9, 13, 14*); with nickel the order has also been shown to decrease with increasing hydrogen partial pressure (*13*). These changes in reaction order reflect the effect of a change in reactant partial pressure or temperature on the surface coverage. From this it follows that the apparent activation energy must also vary with changes in reactant partial pressures. To demonstrate this, the apparent activation energy over the nickel catalyst was also measured at a different hydrogen partial pressure than that used for the comparison of the three metals. This value is also listed in Table 1. It can be seen that increasing the hydrogen partial pressure for a fixed benzene partial pressure increased the apparent activation energy.

A comparison of the specific activities of the various metals at 100°C was made by dividing the observed rate of benzene conversion per gram of catalyst by the known metal surface areas per gram of catalyst (*3*). Preexponential factors were also calculated from the specific rates and the known apparent activation energies. All these data are listed in Table 1.

IV. Discussion

At 100°C the relative specific activity of the metals for benzene hydrogenation was found to be Pt > Ni > Co. At the same temperature, but at different reactant partial pressures ($P_{\mathrm{B}} = 0.130$ atm, $P_{\mathrm{H}} = 0.92$ atm) Schuit and Van Reijen reported a relative order of Pt > Co > Ni. In both cases the difference in specific activity between cobalt and nickel was relatively small (and may simply reflect an effect of the difference in reactant partial pressures), so that it is concluded that the rankings at 100°C are in essential agreement. At temperatures below 100°C, because of the difference in apparent activation energies, the activity advantage of platinum relative to nickel and cobalt will widen, but the relative position of cobalt and nickel will shift. Thus, below approximately 90°C the relative specific activity is $Pt \gg Co > Ni$. The relative specific activity of the metals above 100°C did not change over the range of temperature studied. Because the effect of a change in reactant partial pressures on the apparent activation energy may differ from metal to metal, the temperature at which the specific activity of nickel and cobalt cross may vary.

A comparison of pre-exponential factors derived from specific activities and apparent activation energies indicates a ranking of $Ni \gg Co > Pt$. Thus, the relatively high specific activity of platinum results from its low apparent activation energy.

The effect of alkyl substitution on the rate of hydrogenation of benzene has been studied over both nickel and platinum (*9*). Increased alkyl substitution reduces the relative rate of hydrogenation, and as pointed out by Bond (*9*), this decrease in rate could be interpreted in terms of an increase in the strength of adsorption of the reactants through the electron-releasing effects of the alkyl groups. Recent interpretations of the variation in apparent activation energy when hydrogenating a series of alkyl-substituted benzenes, led to a similar conclusion (*7*, *8*). Völter (*7*) pointed out that the apparent activation energy for the hydrogenation of various alkyl-substituted benzenes over a nickel catalyst varied inversely with the stability of some π complexes of these alkylbenzenes; and assuming the formation of a π-bonded intermediate, related this to the change in the donor properties of the benzene ring on substitution. Similarly, Shopov and Andreev (*8*) correlated the apparent activation energy for the hydrogenation of various methyl-substituted benzenes with the stability of the proposed surface π complex, which was estimated via calculations. An interpretation in this framework of the variation in apparent activation energies between the various metals would predict that the stability of the benzene-metal complex formed varies in the order: $Pt > Co > Ni$. However, because of the complex nature of the apparent activation energy, such a prediction would seem to be tenuous. In this respect, Teichner (*15*) has pointed out the problems of interpreting apparent activation energies because of possible variations in surface coverage by the reactants.

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