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Hydrogenation of Propylene over Group VIII Metals

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The reaction between propylene and hydrogen over pumice-supported metals of the eighth group has been investigated in a constant volume reactor for a wide range of temperature and reactant ratios. The orders of hydrogenation reaction are first, or slightly lower, and zero or slightly negative with respect to hydrogen and propylene respectively. The apparent activation energies for Ni, Fe, Co, Pt, Pd, Rh, Ir, Ru, and Os are 13.0, 10.0, 8.1, 16.0, 11.0, 13.0, 15.0, 6.5, and 7.4 kcal/mole respectively. The catalytic activity of the metals are in the sequence: Rh > Ir > Ru > Pt > Pd > Ni > Fe > Co > Os.

INTRODUCTION

Though several papers have appeared in the last thirty years, describing the kinetics of catalytic hydrogenation of ethylene over metals, very little has been reported about the kinetics of propylene hydrogenation over metal catalysts.

Hydrogenation of propylene has been studied by Toyama (*1*), Schuster (*2*), Baker and Bernstein (*3*), and Fair (*4*) on nickel, by Farkas and Farkas (*5*) and Rogers on platinum (*6*), by Kayser and Hoelcher (*7*) on palladium, by Pease (*8*) on copper and on iron by Emmett and Gray (*9*). Bond and Wells (*10*) have recently reviewed the existing literature on hydrogenation of propylene briefly.

However, no single study has been made by anyone comparing the catalytic activites and kinetics of propylene hydrogenation over the metals of the eighth group. This paper describes a detailed study of the kinetics of propylene hydrogenation over pumice supported metals of the eighth group between 25 and 250°C, and discusses the results in terms of electronic and geometric structures.

APPARATUS

The apparatus, materials and experimental technique were the same as reported earlier by Mann and Naik (*11*) for methylacetylene hydrogen. All catalysts, except osmium were prepared by impregnating and evaporating solutions containing the calculated weight of Analar grade chemicals, in presence of pumice. While iron, cobalt, and nickel catalysts were prepared from their nitrates, ruthenium, rhodium, palladium, and platinum were prepared from their chlorides. Iridium catalyst was prepared from iridic ammonium chloride. Osmium catalyst was prepared by adding the required amount of aqueous solution of ammonium chlorosmate to the pumice granules, and the mixture kept in a warm water bath, while being dried in a stream of nitrogen.

The reaction was followed by measuring the pressure fall using a mercury manometer. Quantitative analysis for the hydrogenation reactions over various metals was made by means of a Perkin-Elmer Vapor Fractometer Model 154 D, using a 12 ft column of 2.5-hexadione on 60–80 mesh fire brick. Products other than propane were less than 0.01% indicating virtually an absence of any side reactions or pyrolysis of propylene or propane.

RESULTS

(a) *Catalytic Activity*

The catalytic activity of all the catalysts, except palladium remained nearly constant

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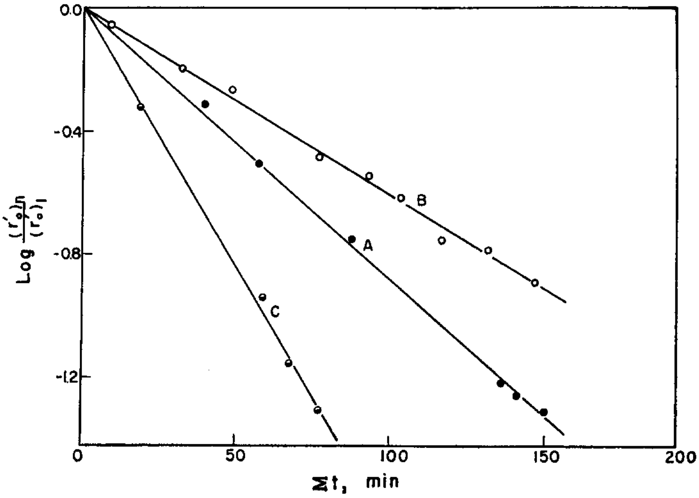

FIG. 1. Decrease in the activity of Pd catalyst with time. A—0.2004 g 0.5% Pd at 30°C. mercury vapor gained access to the catalyst. B—0.2002 g of 0.5% Pd at 30°C very limited access of mercury to the catalyst. C—0.2003 g 0.5% Pd at 118°C limited access of mercury $(r'_0)_1$, $(r'_0)_n$, initial reaction rates, mm Hg/min for first and *n*th reaction.

during the hydrogenation of propylene for several days, and no regeneration and reactivation of the catalyst in between the series of runs was required. The palladium catalyst quickly lost its ability to hydrogenate propylene and suffered a rapid deactivation. Figure 1 shows the poisoning curve for palladium catalyst. This phenomenon is similar to the one observed by Bond and Wells (*12*) in the hydrogenation of acetylene and ethylene over palladium-alumina catalyst.

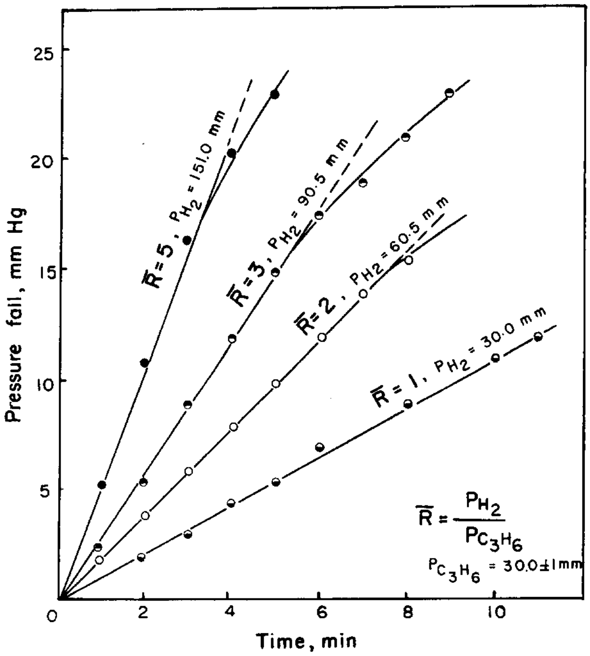

FIG. 2. Effect of hydrogen/propylene ratios ($\bar{R}$), on the slopes of pressure-time curves for nickel at 80°C.

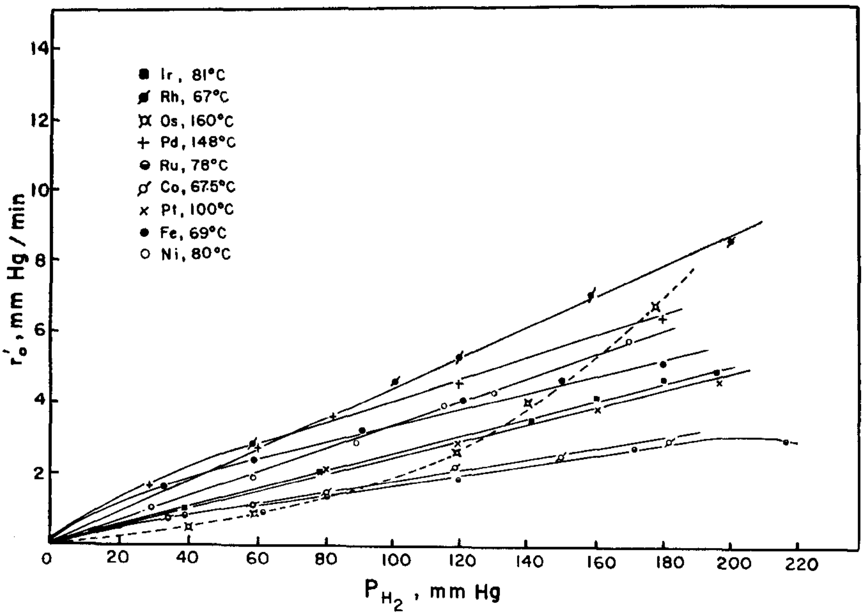

FIG. 3. Dependence of initial rates upon initial pressures of hydrogen over pumice supported catalyst.

Two traps 3 in. long and about ½ in. i.d. were subsequently provided in the system to reduce the exposure of the catalyst to the mercury vapor. The traps were maintained at 0°C. The results discussed in the discussion section are the ones that were obtained with palladium catalyst with minimum possible exposure to mercury vapor.

(b) *Order of Reaction with Respect to Hydrogen and Proylene*

Using a fixed propylene pressure of 30 mm and a wide range of hydrogen pressures (30–200 mm) orders in hydrogen were determined at several temperatures. Similarly, the order of reaction with respect to propylene was obtained by using 60 mm of hydrogen and varying the propylene

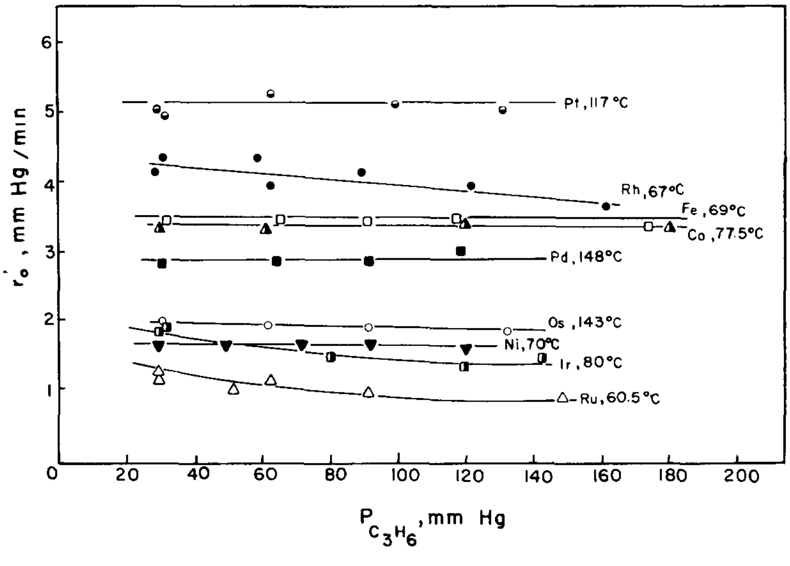

FIG. 4. Dependence of initial rates upon initial pressure of propylene over pumice supported catalysts.

TABLE 1
ORDER OF REACTION AND ACTIVATION ENERGIES

Catalyst	Weight of metal (g)	Temperature (°C)	Average order[a] m	Average order[a] n	Activation energy at 80°C kcal/mole	log r_{os}[b]
Ni	0.0448	40–100	1.0 ± 0.01	0	13.0 ± 0.2	2.04
Fe	0.1450	50–110	0.65 ± 0.01	0	10.0 ± 0.2	1.72
Co	0.0876	52–125	0.95 ± 0.01	0	8.1 ± 0.2	1.59
Pt	0.0020	89–129	0.80 ± 0.01	0	16.0 ± 0.2	2.71
Pd	0.0025	120–161	0.80 ± 0.01	0	11.0 ± 0.2	2.07
Rh	0.0020	40–100	0.75 ± 0.01	−0.05 ± 0.01	13.0 ± 0.2	3.77
Ir	0.0025	60–115	1.0 ± 0.01	−0.05 ± 0.01	15.0 ± 0.2	3.06
Ru	0.0025	50–130	0.75 ± 0.01	−0.05 ± 0.01	6.5 ± 0.2	3.03
Os	0.0100	110–188	1.6 ± 0.01	0	7.4 ± 0.2	1.50

[a] Rate = $kP_{H_2}^{m}P_{C_3H_6}$.
[b] r_{os} = Initial rate, mm Hg/min/g of metal.

pressures. Initial rates were obtained from the slopes of the pressure-time curves. Figure 2 shows the effect of hydrogen/propylene ratios ($\bar{R}$) on the slopes of the pressure-time curves for nickel at 80°C. The dependence of initial rates determined from the slopes of the pressure-time curves upon the initial pressures of hydrogen and propylene over various catalysts is shown in Figs. 3 and 4, respectively.

The orders of reaction with respect to hydrogen (n) and propylene (m) were obtained by plotting log r_0^1 against log P_{H_2} at constant propylene pressure, and log r_0^1 against log $P_{C_3H_6}$ at constant hydrogen pressure at a particular temperatures. Orders of reaction thus derived are given in Table 1 for the metal catalysts. The orders with respect to propylene were zero and independent of temperature for all the catalysts, except for rhodium, iridium and ruthenium and iridium, which were slightly negative (0 to —0.05). The reaction order with respect to initial hydrogen pressure ranged from 0.6 to 1.0 for all the catalysts except for osmium for which it was nearly 1.6.

(c) *Activation Energy*

The activation energies for various catalysts were calculated from initial rate measurements. The activation energy thus calculated for each catalyst is given in Table 1.

DISCUSSIONS

The activities of silica supported metals for ethylene hydrogenation were studied by Schuit and van Reijen (*13*) in an effort to determine whether the earlier findings of Beek and co-workers (*14*) with evaporated metal films applied to supported metals as well. They concluded that the results were generally in agreement with the results obtained by Beeck over metal films.

Schuit and van Reijen (*13*) reported the fractional orders of pressure dependence. The range of fractional orders with respect to hydrogen pressure for the propylene hydrogenation in the present study is in good agreement with those of Schuit and van Reijen obtained for ethylene hydrogenation over silica supported metal catalysts. However, the order of reaction with respect to propylene was mostly zero to slightly negative (—0.05) as compared to —0.5 obtained for rhodium and ruthenium with respect to ethylene. The slight differences in the results may be due to the method of preparation of the catalysts, and its subsequent activation, support material and to the reactant hydrocarbon. We did not subject the catalyst used in the present investigation to any regeneration, since they showed fairly constnat activity after they were sufficiently aged. Schuit and van Reijen found that olefins greatly inhibited the activity for hydrogenation and that poisoning of the catalyst was proportional to the ratio of olefin/hydrogen pressures, and inversely to reaction temperature. They also used fresh catalyst as compared to the aged ones used by us.

Beeck (*15–17*) and Schuit and van Reijen (*13*) found that the activation energy for the hydrogenation of ethylene was independent of the metals. Contrary to their results, we have found that the activation energy for the hydrogenation of propylene varied between 6.5 and 16.0 kcal/mole for various metals. The order of activation energies were lowest in the Fe, Ru, and Os group, and highest in the nickel, palladium, and platinum group. Beeck suggested that the apparent activation energy is equal to the sum of the energy of surface reaction and the heat of adsorption of the reactants. The apparent activation energies may vary due to variations in either the heats of adsorption or energies of surface reaction.

Many factors such as the nature of the chemical bonds in the metal, the configuration of crystal lattice, the physical forms of the metals, the method of the preparation and activation of the catalyst, the nature of the reactants, and the fraction of the surface covered by the reactants can affect both the energy of surface reaction and heats of adsorption of reactants, and thus the apparent activation energy. The apparent activation energies for propylene hydrogenation have been determined as 2.0 (*18*), 4.8 (*2*), and 8.6 (*4*) kcal/mole with nickel catalyst, 15.0 (*6*) kcal/mole with a platinum catalyst, 11.7 kcal/mole with a palladium catalyst (*7*) and 10.5 kcal/mole with a copper catalyst (*19*). These variation in the activation energies, as determined by various investigators may be due to the above mentioned factors.

The order of relative activities of the various metals (Table 1) for the hydrogenation of propylene in the present investigation was

$$\text{Rh} > \text{Ir} > \text{Ru} > \text{Pt} > \text{Pd} > \text{Ni} > \text{Fe} > \text{Co} > \text{Os}$$

as compared to the following order

$$\text{Rh} > \text{Pd} > \text{Pt} > \text{Ni} > \text{W} > \text{Cr} > \text{Fe}$$

obtained by Beeck on metal films, and

$$\text{Rh} > \text{Ru} > \text{Pd} > \text{Ni} > \text{Pt} > \text{Ir} > \text{Co} > \text{Fe}$$

obtained by Schuit and van Reijen for ethylene hydrogenation. Since no studies have been made of the catalytic activity of various metals for propylene hydrogenation by any single investigator, no direct comparison of this work can be made with any published work. However, the results of this work show substantial similarity in the catalytic activities of metals with the work of Schuit and van Reijen. Rh has been found to be the most active catalyst for propylene hydrogenation as well. It is surprising that iridium which was found to be very little active for ethylene hydrogenation has a very high order of activity in propylene hydrogenation. The similarities in the order of activities of the metals for ethylene and propylene hydrogenation suggest that certain characteristics of the catalyst may affect the rates of hydrogenation similarly.

Beeck (*15*) stressed the importance of the geometric factor on catalysis, and showed that the activity of various metal films for ethylene hydrogenation was a function of the lattice distance.

The activation energies for the metals with a face-centered cubic structures have been found to be greater than the activation energy for iron which has a body centered cubic structure. The metals with a close-packed hexagonal structure were found to have the lowest activation energies. A plot of activation energies against the lattice distance gives a straight line (Fig. 5) for all the metals except palladium. This could be due somewhat to the poisoning of palladium by mercury vapor inspite of our taking the data with minimum possible exposure of the catalyst to mercury vapor. The results show that the larger the lattice distance, the greater the activation energy. Nevertheless, the variation in catalytic activity could not be explained in terms of lattice spacing only.

The activity of the transition metals has been attributed to the existence of partly filled *d*-bands which are available for bonding. Baker and Jenkins (*20*) have suggested

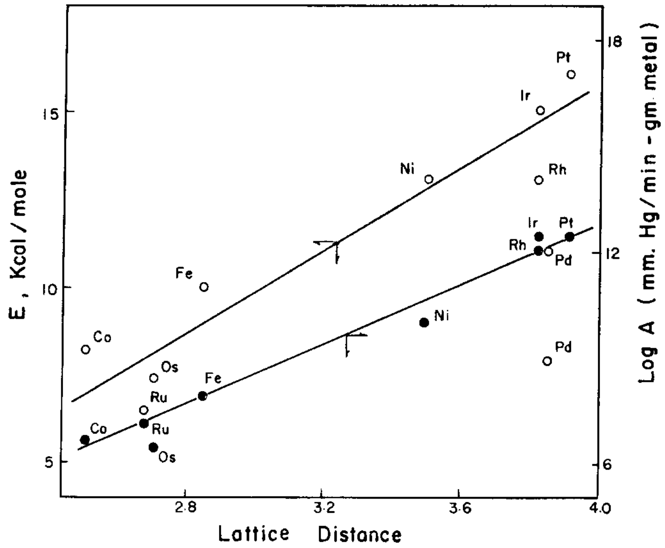

FIG. 5. Activation energy (*E*), and Arrhenius parameter (*A*) as a function of lattice distance, ○ *E*, ● log *A*.

that the lattice spacings are less important in comparison to Pauling's percentage δ-character (*21*, *22*) in catalysis by metals. The correlation of the relative activity with the δ-percentage character of metals is shown in Fig. 6. The results obtained by Beeck (*14–17*) and Schuit and van Reijen (*13*) for the hydrogenation of ethylene are

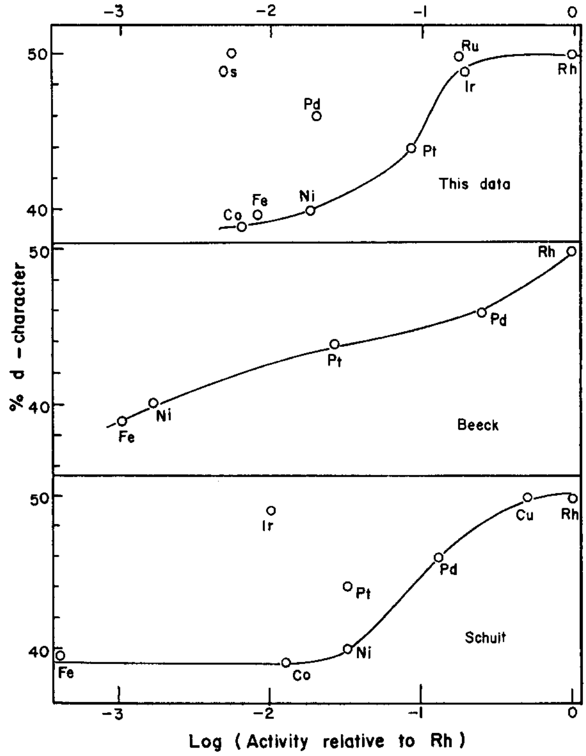

FIG. 6. Catalystic activity as a function of % δ-character for hydrogenation of propylene.

also plotted for comparison. In comparing the results of Beeck and Schuit and van Reijen for ethylene hydrogenation with those obtained in propylene hydrogenation in this investigation, it must be pointed out that while Beeck studied the hydrogenation over only five evaporated metals of the eighth groups, Schuit studied the reaction over silica supported metals. None of these investigators studied the activity of osmium. While the results of Schuit and van Reijen show considerable scattering for platinum and iridium in ethylene hydrogenation, osmium (a very inactive catalyst) and palladium show considerably scattering in propylene hydrogenation. Considering, that the catalysts used by us were supported on pumice and could not be completely impurity free like evaporated films, and that palladium was much more susceptible to poisoning by mercury vapor during propylene hydrogenation than ethylene hydrogenation, and osmium had practically no activity for olefin hydrogenation, it appears that a reasonable correlation holds between the percentage δ-character, and catalytic activity. Though the electron theory of catalysis explains fairly the catalytic activity of the transition metals, yet it cannot be considered as completely satisfactory, and percentage δ-character by itself is not sufficient to correlate all the data. Both electronic and geometric factors play a role in determining the catalytic activities of metals for propylene hydrogenation. Any correlation of activity must therefore take into account both factors.

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