with trace water contained in the feed propylene, (b) reduction to inactive or/and less active molybdena with olefins, (c) covering of active site with carbonaceous materials (H/C < 2) produced by dehydrogenation, (d) covering of active sites with oligomers and polymers soluble in liquefied olefins, (e) covering of active sites with higher products by successive disproportionation soluble in liquefied olefins, and (f) covering of active sites by polymers insoluble or slightly soluble in liquefied olefins.

The soluble liquid hydrocarbons can be carried away from catalyst surface with liquefied olefins in liquid phase reaction, and so the catalyst is deactivated only slightly even after long time. This implies that the decrease of activity in gas phase reaction arises predominantly from factor (d). The deactivation in liquid phase reaction after a long time on the reaction stream may be due mainly to factor (f), and to a minor extent to (a), (b), and (c).

The flow system of liquid phase reaction is superior to gas phase reaction at least in the following four points: (a) activity of catalysts can be maintained for longer time, because oligomers and polymers soluble in liquefied olefins are carried away from the catalyst surface; (b) a liquid phase reaction having higher reaction rate is preferable to a gas phase reaction; that is, a higher temperature to obtain a higher rate is disadvantageous in the selectivities because the activation energy of disproportionation is generally smaller than those of isomerization and polymerization (Friedlander, 1959); (c) the oxidation state of the active site is more stable at the lower temperature; (d) the reaction apparatus can be smaller. However, the compression of propylene to the liquid state and the use of strong apparatus can be avoided in the gas phase.

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Hydrogenation of Xylose over Platinum Group Catalysts

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Xylose was hydrogenated with ruthenium, rhodium, and palladium catalysts under a wide range of temperature, pressure, catalyst concentration, and agitation rates. The reaction is pseudo-first order and is controlled by the surface reaction between atomic hydrogen and unadsorbed xylose. Kinetic surface parameters were determined for the ruthenium catalyst.

Introduction

Several products that possess a low caloric value and are of dietetic value to sufferers of diabetes have been proposed from time to time as artificial sweeteners. Saccharin, known since 1879, has a sweetening power of about 400 times than that of glucose, but leaves a bitter metallic aftertaste which makes it objectionable to some users. It occupied a very prominent place in the market for sweeteners until the introduction of cyclamates around 1950. The use of cyclamates rose very rapidly until they were ordered off the market by the FDA in 1969 after indications were shown that they may induce bladder tumors.

Saccharin, which is at present the largest selling artificial sweetener, does not have any significant pharmacological effect and is not metabolized by the organism. Nevertheless, there is conflicting evidence that, under certain conditions, it may promote cancer.

Natural and artificial sweeteners continue to be sought by people who have to restrict their sugar intake. Possible candidates are the extracts from plants such as Stevia rebaudiana and Synsepalum dulcificum, the dipeptide methylester L-aspartyl L-phenylalanine, and the pentaalcohol xylitol.

Xylitol is very soluble in water, 62.4% at 25°C. Its crystals resemble sugar and it does not caramelize at elevated temperatures. Its sweetening capacity is 20–25% greater than that of sugar (Henneke, 1970) and it has no insulin requirements, making it suitable for usage by diabetics (Lang, 1971). Xylitol can be readily prepared from xylose, a by-product of agricultural wastes such as cottonseed hulls and peanut shells.

This work was undertaken to provide kinetic information and process variable influence on the hydrogenation of xylose to xylitol using ruthenium, rhodium, and palladium catalysts. The kinetics of hydrogenation of xylose with xylitol have been the subject of several studies for the past 25 years. Tomkuljak (1949) and Leikin (1963) hydrogenated xylose with 3 to 80% Raney nickel and found that in every case the reaction was accompanied by a drop in pH. They claimed that this was caused by xylonic acid produced by a nickel-induced Cannizaro reaction. Several patents (Hoffmann-LaRoche, 1970; Kohno and Yamatsu, 1971; Steiner, 1971) deal with the high-pressure hydrogenation range, up to 50 atm, and suggest different additives to eliminate side-product formation and to facilitate crystallization.

Recently, Wisniak, *et al.* (1974), published an extensive work on the hydrogenation of xylose using Raney nickel. Their results cover a very wide range of variables: xylose concentration, 1 to 3.5 *M;* catalyst concentration, 1 to 18% nickel; pressures, 100 to 800 psig; temperature, 80 to 140°C; and agitation rates, 300 to 1200 rpm. Under high rates of agitation, they were able to study the effect of variables in the region where the chemical resistance was dominant and thus suggest a possible kinetic mechanism. They found that the reaction followed a pseudo-first-order course with a surface-reaction controlling step between atomically absorbed hydrogen and adsorbed xylose at 100°C and unadsorbed xylose at higher temperatures. In this experimental range of conditions the reaction constant varied between 3 and 22 hr^{-1}, and at a catalyst loading of 2% and 200 psig, the activation energy was 6.5 kg/mol.

It has been known for many years that platinum and palladium are specific catalysts for the hydrogenation of unsaturated compounds in the liquid phase and that they are active enough to permit hydrogenation at ordinary temperatures and pressures. Considerably less is known about the action of ruthenium and rhodium as hydrogenation catalysts.

Breitner, *et al.* (1959), hydrogenated aliphatic, aromatic, and α,β-unsaturated ketones at atmospheric pressure and room temperature, in a solvent, with palladium, platinum, rhodium, and ruthenium deposited on high-surface carbon. Palladium was ineffective in all the solvents tested, possibly due to an exceptionally strong adsorption of the ketone. Rhodium and ruthenium catalysts hydrogenated most rapidly in neutral or basic solutions and were relatively slow in acid media. It was shown that, in a favorable environment, the latter two were exceptionally active for carbonyl reduction.

Similarly, Gilman and Cohn (1957) found that aliphatic aldehydes, such as acetaldehyde, methyl ethyl ketone, and acetone, were readily hydrogenated by a 5% ruthenium or rhodium catalyst on activated alumina or carbon powder. Ruthenium was found to be especially active for the conversion of sugars to alcohols, although it required elevated temperatures and pressures. Hydrogenation of dextrose showed that the rate increased sharply with increased pressures. Babcock, *et al.* (1957), hydrogenated α-methylstyrene with platinum, palladium, rhodium, ruthenium, and nickel catalysts. Their findings indicated that, with palladium above 3 atm, the apparent rate-controlling step was the surface reaction between dissociated hydrogen and α-methylstyrene both adsorbed on different types of active sites. Below 3 atm the reactants competed for similar active sites. Rhodium and nickel catalyzed primarily the polymerization of α-methylstyrene with a slow rate of hydrogenation. Ruthenium had a negligible catalytic activity under the experimental conditions studied.

Simultaneous hydrolysis and hydrogenation of cellulose with ruthenium catalysts has been studied by Balandin (1964) using acid solutions of the carbohydrate at 180°C and 50 to 100 atm hydrogen pressure. At lower pressures the reaction did not take place and increased pressures above 100 atm had no effect in the rate.

In a patent by Boyers (1959), details are given on the hydrogenation of a number of carbohydrates to the corresponding polyalcohols, with different ruthenium-containing catalysts. It is stated that the preferred catalysts are the ones containing elemental ruthenium on a support such as alumina or carbon, and in concentrations between 0.1 and 10% by weight of the active metal. The rate is said to increase up to hydrogen pressures of 100 to 150 atm only.

Hydrogenation of sugars at temperatures above 150°C may lead to cleavage of the carbon chain. With hexoses, rupture of the chain leads mainly to the formation of glycerol and ethylene glycols (Van Ling and Blugter, 1969).

The composition of the mixtures of xylose and xylitol can be readily determined by polarimetry, since xylitol is optically inactive, by gas-liquid chromatography (Weiss, 1972) or by direct titration of the aldehyde group with hydroxylamine hydrochloride in methanol (Patchornik, 1956).

Equipment and Procedures

Hydrogenation runs were made in a dead-end ¾-gal batch autoclave Model AF 150, manufactured by Autoclave Engineers for a working pressure of 5000 psig at 650°F. Description of the experimental setup as well as of the operating and analytical procedures have been given elsewhere (Wisniak, *et al.*, 1974).

Xylose (99% pure) was obtained from Okamura Mills, Osaka, Japan. The electrolytic hydrogen was reported by the vendor to be 99.9% pure. Platinum metal catalysts were purchased from Engelhard Industries, Newark, N. J., as 5% active metal on active carbon, and had a bulk density of 28–31 lb/ft^3 and a surface area of 1100 m^2/g. Their lot numbers were as follows: Ru (00724), Rh (M/1514/E), and Pd (M/1561). The catalysts were used as received without prior treatment. In all the following figures percentage catalyst refers to bulk catalyst per unit weight xylose.

Results and Discussion

About 150 runs were made in the variable range described in Table I. The course of the reaction was followed in each case by plotting the logarithm of xylose concentration *vs.* the time of the reaction. In every run the plot yielded a straight line so that the overall rate could be represented by a pseudo-first-order reaction.

$$r = -\frac{dC}{dt} = kC \qquad (1)$$

Figure 1 shows typical results for each catalyst. The first-order reaction could thus be used to characterize a particular set of variables. In all runs, it was found that the initial pH of 6.5 dropped to 4.5 within 20 to 40 min and remained constant afterward. The points indicated in every figure are usually the average of two runs under similar conditions.

Homogeneous Reaction. Runs made in the absence of a catalyst under varied conditions showed no xylose conver-

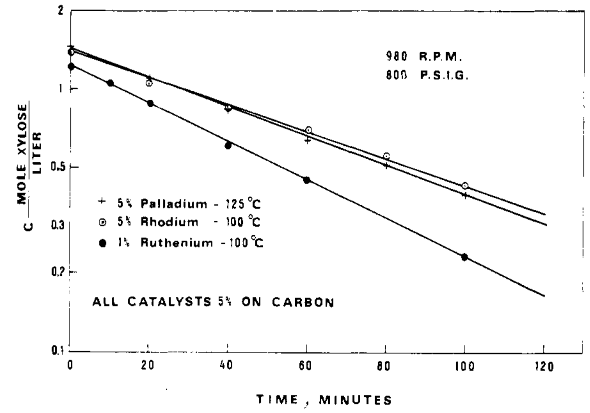

Figure 1. Typical hydrogenation runs.

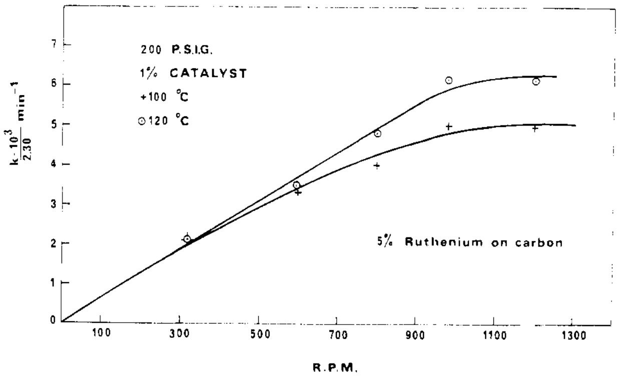

Figure 2. Influence of agitation rate.

Table I. Range of Operating Variables

	Concn, %^{a}	Pressure, psig	Temp, °C	Agitation, rpm
Ruthenium	1-10	200-800	100-125	300-1300
Rhodium	5	300-800	100-125	980
Palladium	5-25	400-800	100-125	980

[a] Catalyst as is, weight of xylose.

sion. Thus, it can be concluded that, within experimental conditions, the homogeneous reaction was negligible and there were no catalytic effects by the metal walls of the system.

Mass Transfer Effects. Hydrogenation runs made in variable agitation regimes at various temperatures showed that the rate was independent of the impeller speed above 980 rpm (Figure 2). These results, together with those obtained at different catalyst loadings, indicate that the reacting system was probably controlled by the chemical resistance.

Temperature. The behavior of the catalysts with temperature is strikingly different. Figures 3 and 7 indicate some of these differences. For ruthenium at 1% catalyst load and 200 psig, the Arrhenius equation is satisfied in the range 80 to 125°C with an activation energy of about 5 kcal/mol. Wisniak, *et al.* (1974), showed that for Raney nickel at 2% concentration the activation energy was 6.5 kcal/mol so that ruthenium is substantially more active than Raney nickel under similar conditions. From Figures 1 and 7, it can be inferred that temperature has a much lesser influence on reactions catalyzed by rhodium, and that palladium is by far the poorest catalyst among the three considered here.

Higher temperatures could not be explored because of xylose decomposition. At temperatures below 80°C hydrogenation rates with ruthenium dropped substantially because of a probable strong adsorption of xylitol. This behavior is similar to that observed with Raney nickel (Wisniak, *et al.*, 1974).

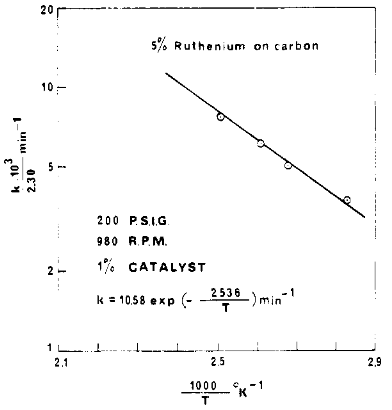

Figure 3. Temperature influence on reaction rate constant.

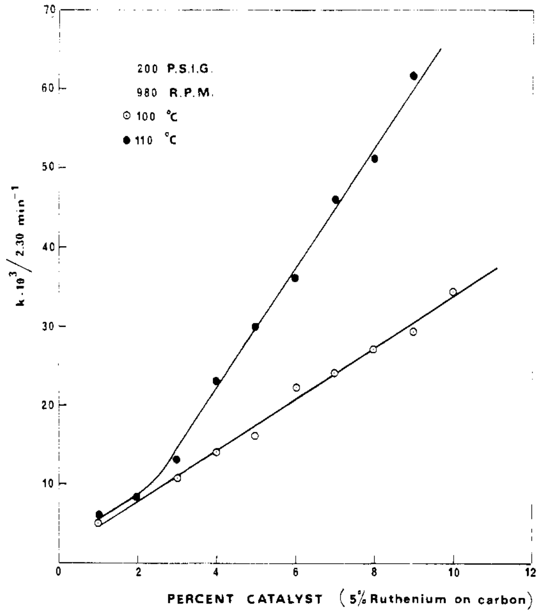

Figure 4. Effect of ruthenium catalyst concentration.

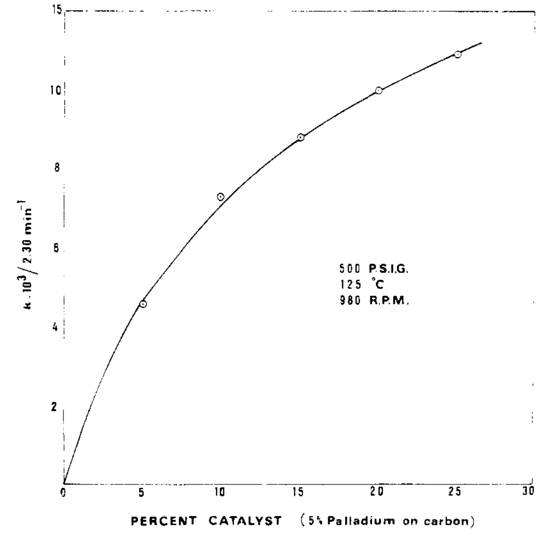

Figure 5. Effect of palladium catalyst concentration.

Xylose Concentration. Runs made under various initial concentrations of xylose showed that the rate was independent of this variable.

Catalyst Concentration. Figures 4 and 5 show the in-

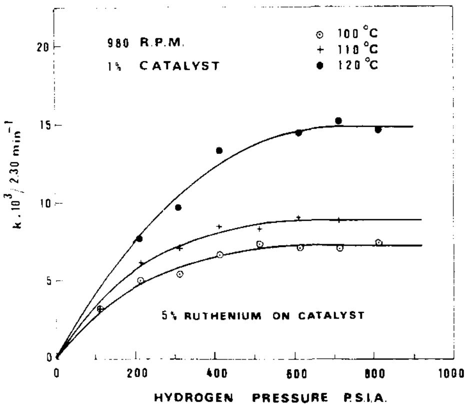

Figure 6. Pressure dependence, ruthenium catalyst.

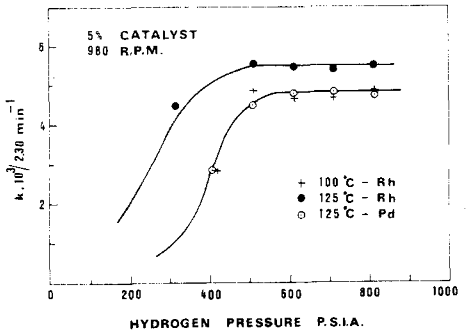

Figure 7. Pressure dependence, rhodium and palladium catalysts.

fluence of ruthenium and palladium catalyst concentration. Substantially larger concentrations of palladium are required to achieve the same results as ruthenium, and the bulky nature of the palladium causes the control to switch from a chemical to a physical step at catalyst loadings larger than 5%. Compared with the results obtained with Raney nickel (Wisniak, *et al.*, 1974) it can then be concluded that for similar conditions the rate decreases according to Ru > Ni > Rh > Pd.

Pressure. The effect of pressure on k is shown in Figures 6 and 7 for different temperatures levels. It is seen that all three catalysts have a similar overall behavior. The rate increases with increasing pressures up to about 600 psig and then remains constant.

Ruthenium is active at all pressure levels whereas, for rhodium and palladium (Figure 7), the rate drops rapidly to negligible values below 200 to 300 psig. This indicates that hydrogen is not adsorbed in significant amounts and that its adsorption constant is weakly temperature dependent. These results can be partially explained by an analysis of the mechanism of reaction as shown below.

Mechanism of the Reaction. The following conclusions can be drawn from the experimental values of k that appear in Figures 1-7.

1. Mass transfer resistance in the gas phase is negligible as the phase is essentially hydrogen.

2. Mass transfer resistances in the liquid phase are also negligible as shown by the independence of the reaction rate at high agitation rates and its linear variation with catalyst loading. The process can then be assumed to be controlled by the chemical steps and can be further analyzed by Langmuir-Hinshelwood mechanisms, as developed by Hougen and Watson (1947), if it is assumed that the hydrogen pressure is a measure of hydrogen concentration at the surface of the catalyst. Experimental results show that, in the range of variable explored here, hydrogen solubility follows Henry's law (Wisniak, 1973).

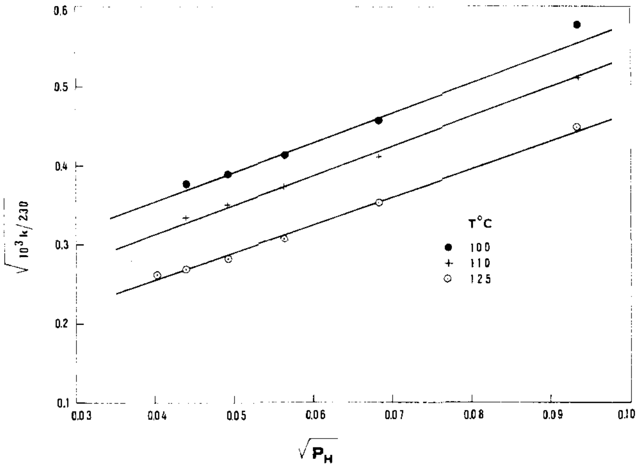

Figure 8. Test of the kinetic mechanism.

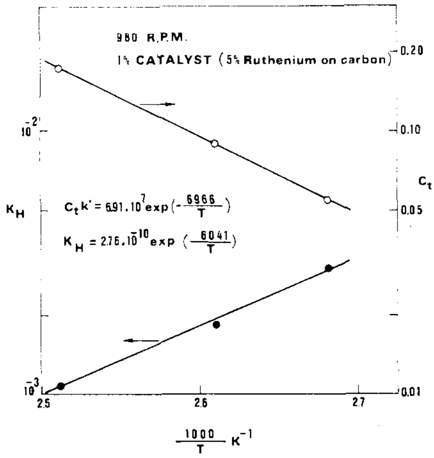

Figure 9. Kinetic constants for the surface reaction.

3. The adsorption of hydrogen is not rate controlling because this would require the rate to vary proportionally to the hydrogen concentration and inversely proportionally to the xylose concentration.

4. The adsorption of xylose is not rate controlling as this would require a decrease in the rate with increase in hydrogen pressure.

5. The desorption of xylitol cannot be rate controlling. If it were, the rate would grow to a constant value when the hydrogen pressure and/or xylose concentration are increased.

6. The rate-controlling step is not the impact of an unadsorbed species on an adsorbed one. This would require a first order reaction in hydrogen, which is not the case.

Under these assumptions the 17 mechanisms of Hougen and Watson reduce to one in which the reaction occurs between atomic chemisorbed hydrogen and unadsorbed xylose, and the surface reaction controls the overall rate.

This hypothesis is substantiated by the knowledge on the chemisorption of hydrogen in platinum metals. For all transition metals below 100°K, the γ phase present will adsorb hydrogen only in molecular form. At higher temperatures the β phase desorbs hydrogen with second-order kinetics indicating that the gas is adsorbed in an atomic form (Smith, 1948; Lapujoulade, 1972).

The rate equation for this mechanism is as follows

$$r = \frac{k' C_t^2 K_H}{(1 + K_s C_s + \sqrt{K_H P_H})} C \cdot P_H \qquad (2)$$

Combining eq 2 with eq 1 and neglecting the adsorption of xylitol, the following is obtained.

$$k = \frac{k' C_t^2 K_H P_H}{(1 + \sqrt{K_H P_H})^2} \qquad (3)$$

This equation can be easily linearized as follows

$$\frac{1}{\sqrt{k}} = \frac{1}{C_t\sqrt{k'}} + \frac{1}{C_t\sqrt{k'}}\,\frac{1}{\sqrt{K_H P_H}} \qquad (4)$$

If the assumed mechanism is correct then a plot of $1/\sqrt{k}$ against $1/\sqrt{P_H}$ should yield a straight line. The intercept and slope of this line would then provide information of the hydrogen adsorption constant and the surface reaction constant. Figure 8 indicates that the test is satisfied for the two isotherms of ruthenium plotted in Figure 6. Not enough information was available for a similar test with rhodium and palladium. Figure 9 contains the kinetic constants of the surface reaction.

From the slope and intercept, the following Arrhenius type equations are obtained

$$K_H = 2.76 \times 10^{-10} \exp\left(-\frac{12,000}{RT}\right) \qquad (5)$$

$$C_t^2 k' = 6.91 \times 10^7 \exp\left(\frac{13,840}{RT}\right) \qquad (6)$$

The heat of adsorption for hydrogen on ruthenium is similar to that obtained by Nakano, *et al.* (1973), for rhodium on alumina (10,226 cal/mol).

Conclusions

During the hydrogenation of xylose to xylitol with ruthenium, rhodium, and palladium catalysts under conditions of pressure, temperature catalyst concentration, and agitation that assured chemical control, the following observations were made.

1. The hydrogenation ability decreased in the order Ru > Rh > Pd.
2. The reaction followed a pseudo-first-order course with an activation energy of 5 kcal/mol for 1% ruthenium at 200 psig.
3. The rate-controlling step involved the surface reaction between chemisorbed hydrogen and unadsorbed xylose. For ruthenium the energy of adsorption of atomic hydrogen was 12 kcal/mol and the energy of activation for the surface reaction was 13.8 kcal/mol.
4. Temperature had a weak effect on the catalytic activity of rhodium and palladium.

Nomenclature

C = xylose concentration
C_s = concentration of adsorbed xylitol
C_t = total concentration of active sites
k = pseudo-first-order reaction constant, min
k' = surface reaction rate constant
K_H = adsorption constant of atomic hydrogen
K_S = adsorption constant of xylitol
P_H = hydrogen pressure
r = rate of reaction
t = time

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