

Cyclic Olefins by Selective Hydrogenation of Aromatics

Several investigators, notably Siegel *et al.* (1) and Weitkamp (2), have contended that olefins are intermediates in the hydrogenation of suitably substituted aromatics by analysis of *cis/trans* ratios of cycloparaffin products. As early as 1934, Truffault (3) suggested that cyclohexene is an intermediate in benzene hydrogenation with nickel catalysts based on the amount of cyclohexylbenzene formed when phosphoric acid is present. More recently, Slaugh and Leonard (4) reported on the preparation of cyclohexylbenzene with a wide variety of acid supports and Group VIII transition metals. These latter results, where cyclohexene is trapped by immediate reaction with benzene, show that the olefin is indeed an important intermediate in aromatic hydrogenation with many metals. However, as rapid subsequent hydrogenation of the olefin intermediate occurs at the conditions required to initiate aromatic hydrogenation, the partial saturation process has not been a useful route for producing cyclic olefins. In 1968, Hartog (5) reported the preparation of cyclohexene and methyl cyclohexenes by partial hydrogenation of benzene and toluene, respectively, using a ruthenium catalyst with C₁ through C₄ alcohols as catalyst modifiers. While conversions to the corresponding cyclic olefins were low, Hartog's yields are substantially higher than the trace concentrations usually found in benzene hydrogenation, and this work prompted us to explore the use of aqueous systems with ruthenium catalysts for preparing cyclohexene by selective hydrogenation of benzene. This note summarizes the results of this investigation.

The first catalyst used in this work was

prepared by adding an aqueous solution of ruthenium chloride to a slurry of calcium carbonate. The mixture was dried on a hot plate at approximately 200°C and the powdered catalyst was reduced in hydrogen at 200°C prior to use in a batch-stirred reactor. Other catalysts were prepared in a similar manner. A mixture of ruthenium chloride with nickel, cobalt, or iron chloride was added to either calcium hydroxide or alumina as a slurry, the mixture was dried on a hot plate and activated in hydrogen at 200°C. The ruthenium chloride was obtained from Alfa as RuCl₃ · 1-3 H₂O, the alumina was Alon-C, available from the Cabot Corp. Other reagents used in catalyst preparation were obtained from Mallinckrodt Chemical.

In typical experiments, a 1 liter reactor from Autoclave Engineers was charged with 2 g catalyst, 100 g H₂O, and 280 g benzene, flushed with electrolytic grade H₂ from Matheson, heated to approximately 180°C, and then pressurized to 68 atm with hydrogen. The reaction was followed by removing small samples at periodic intervals and analyzing the hydrocarbon phase by glc using a Carbowax 20 M on Chromosorb P column.

Following the initial work with ruthenium on calcium carbonate catalysts, a polytetrafluoroethylene coating was applied to the exposed internal parts of the autoclave to minimize participation of the metallic components of the autoclave in the reaction.

An indication was obtained from initial work with ruthenium on calcium carbonate catalysts that the selective hydrogenation reaction of aromatics was complex and affected by the reactor walls. Significant hy-

drogenation activity was obtained with 4 g of 0.5% Ru on CaCO_3 , 100 ml H_2O containing 0.25% NaOH and 290 g benzene at temperatures of 180°C and 68 atm pressure. At 30% conversion, the yield of cyclohexane was 12% for a selectivity of 40%. The selectivity decreased slowly, with a peak in cyclohexane concentration at 18% obtained at a benzene conversion of 65%. After hydrogenation to cyclohexane was complete, the reactor was cooled to ambient temperature, the cyclohexane was replaced with fresh benzene, and the hydrogenation process was repeated. This time the reaction was slower and more selective, with a maximum cyclohexene content of 22% at a 60% benzene conversion. Repeating the removal-recharging process gave a catalyst system of low activity, but an initial selectivity to cyclohexene near 80%. It was apparent that something in the system was responsible for the decreased activity and improved selectivity to cyclohexene, so a similar experiment was made using a quartz sleeve in the reactor. Rapid hydrogenation of benzene to cyclohexane was obtained with a flat maximum in the cyclohexene content at just under 1%. After hydrogenation to cyclohexane was complete, the hydrocarbon phase was removed and 0.5 g of powdered 316 stainless steel was added with fresh benzene. The hydrogenation process was now slower and more selective to cyclohexene, giving a maximum cyclohexene concentration of 12% at 35% conversion. Repeating the cooling-recharging process after complete reaction to cyclohexane resulted in improved selectivity to cyclohexene with a maximum concentration of 17% at 71% conversion. The overall activity of the catalyst was also significantly lower.

One or more of the metallic components in 316 stainless steel was responsible for the decreased activity of the ruthenium catalyst and the sharp increase in selectivity to the cyclic olefin. The problem

remaining was to identify what element or combination of elements was responsible for the change, so the aqueous catalyst phase was filtered, concentrated by evaporation and analyzed by spectrographic techniques. This approach was not especially rewarding, as small amounts of iron, chromium, nickel, manganese, copper, and lead were detected in the concentrate. The iron, chromium, nickel and manganese can be traced to the 316 stainless steel, while copper and lead are components of the bearings used in the agitator assembly. From previous work by Maxted and Marsden (6,7), all these cationic materials, except chromium, are known to dramatically alter the hydrogenation activity of platinum metal catalysts. Thus, in order to study the role of specific transition metals on the aromatic hydrogenation reaction, we first coated the internal parts of the reactor with polytetrafluoroethylene and then introduced small amounts of the metals with the catalyst in order to determine their effect on the reaction rate and selectivity.

This approach was followed using calcium hydroxide as a support, and the results for catalysts containing 0.05% Ni, Co or 0.07% Fe with 0.5% Ru on $\text{Ca}(\text{OH})_2$ are given in Fig. 1. The cobalt modified catalyst gave the highest yield of cyclohexane, 20.3% at 58% conversion. The initial selectivity with nickel and iron modified catalysts was slightly higher, but the cyclohexane concentration peaked at a lower level, and the iron catalyst lost activity during the hydrogenation. Varying the amount of cobalt added to the catalyst produced some variation in selectivity, with those containing either 0.03 or 0.08% Co giving somewhat lower selectivities than the 0.05% Co-0.5% Ru on $\text{Ca}(\text{OH})_2$ catalyst shown in Fig. 1. The amount of modifier required to alter selectivity is apparently very small. Only 1 mg of cobalt is introduced with 2 g of catalyst, and in a basic solution the solubility of metal hy-

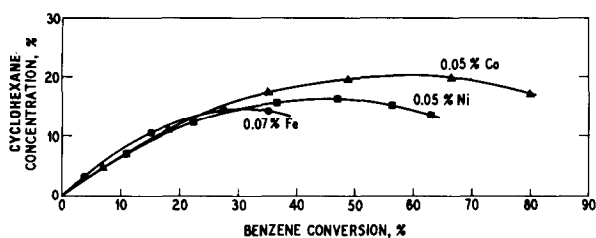


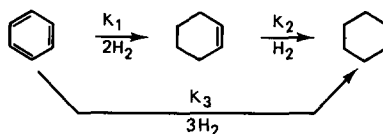
FIG. 1. Cyclohexene concentration vs conversion 0.5% Ru on $\text{Ca}(\text{OH})_2$.

dioxide could limit the cobalt concentration in the aqueous phase to some even smaller value. At these low concentrations, pin holes in the plastic coating and accidental contamination could also contribute to the selectivity of the reaction.

The improved selectivity to the corresponding cyclic olefin with ruthenium catalysts in the aqueous phase is not limited to basic supports, and similar effects are obtained with alumina supported catalysts where the pH of the aqueous phase is acidic, $\text{pH} < 5$. Data for 0.5% Ru on Al_2O_3 with 0.05% Ni are given in Table 1, where a coated reactor is used. The data are similar to those obtained using CaCO_3 or $\text{Ca}(\text{OH})_2$ supported catalysts.

There is little question that supported ruthenium catalysts respond favorably to the addition of small amounts of transition metal ions when the desired product is the olefin. The results suggest that the sites that give cyclohexane by a zero order reaction path are modified and the olefin

intermediate is formed, by a first order reaction, on either the cation modified site or a less active ruthenium metal site. In somewhat more quantitative terms, the reaction scheme depicted by Slauch and Leonard (4) gives, at a constant hydrogen pressure, Eqs. (1) and (2) using mole fraction units for concentration.



$$\frac{d(\text{C}_6\text{H}_{10})}{dt} = k_1(\text{C}_6\text{H}_6) - k_2(\text{C}_6\text{H}_{10}), \quad (1)$$

$$-\frac{d(\text{C}_6\text{H}_6)}{dt} = k_1(\text{C}_6\text{H}_6) + k_3. \quad (2)$$

Dividing Eq. (1) by (2) and letting $\alpha = k_2/k_1$ and $\beta = k_3/k_1$ one obtains Eq. (3).

$$\frac{-d(\text{C}_6\text{H}_{10})}{d(\text{C}_6\text{H}_6)} = \frac{(\text{C}_6\text{H}_6) - \alpha(\text{C}_6\text{H}_{10})}{(\text{C}_6\text{H}_6) + \beta}. \quad (3)$$

By setting

$$\begin{aligned} X &= (\text{C}_6\text{H}_6) + \beta, \\ Y &= \alpha(\text{C}_6\text{H}_{10}) + \beta, \\ V &= Y/X, \end{aligned}$$

one obtains a linear differential equation that can be solved in terms of X and Y or V and X . The solution for V is given in Eq. (4).

$$V = \left(\frac{X}{(1 + \beta)} \right)^{\alpha-1} \cdot \left(\frac{\alpha}{1 - \alpha} + \frac{\beta}{1 + \beta} \right) - \left(\frac{\alpha}{1 - \alpha} \right). \quad (4)$$

TABLE 1
BENZENE HYDROGENATION-RATE DATA^a

Time (min)	Conversion (%)	Selectivity (%)
8	8.8	
10	15.0	56.4
15	21.7	51.5
20	30.2	45.5
25	37.3	40.7
35	50.4	32.7
40	60.4	26.3
60	68.5	16.1
81	94.5	10.9

^a 0.5% Ru-0.05 Ni on Al_2O_3 ; 200°C. 68 atm. 0.07 g cat/g benzene.

The rate of benzene disappearance, Eq. (5), is obtained directly by integration of Eq. (2), where f is used to denote the fraction of benzene reacted.

$$\ln(1 + \beta - f) = \ln(1 + \beta) - k_1 t. \quad (5)$$

Estimates for the ratios of rate constants can be obtained from the experimental data relating selectivity to conversion. The initial selectivity for cyclohexene gives β from Eq. (3), and the point where the cyclohexene concentration is a maximum establishes α by setting Eq. (1) to zero.

$$\frac{1}{1 + \beta} = \frac{\Delta(C_6H_{10})}{\Delta(C_6H_6)} @ (C_6H_6) = 1, \quad (6)$$

$$\alpha = \frac{(C_6H_6)}{(C_6H_{10})} @ (C_6H_{10})_{\max}. \quad (7)$$

Shown in Fig. 2 are the experimental selectivity-conversion data for Table 1 and the curve calculated from Eq. (4) using estimates of α and β established by Eqs. (6) and (7). Figure 3 gives the conversion-time data using the same estimate of β , and again the model gives alignment of the data.

The results obtained show that transition metal ions in low concentrations alter the activity of supported ruthenium catalysts for aromatic hydrogenation in the aqueous phase. The addition of small amounts of iron, cobalt or nickel to the system, typically, decrease the activity of the supported ruthenium catalyst to one-

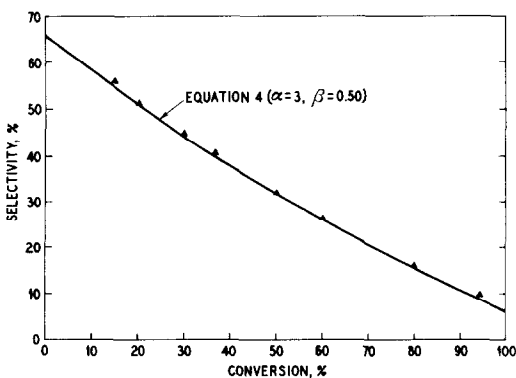


FIG. 2. Selectivity-conversion data of Table 1.

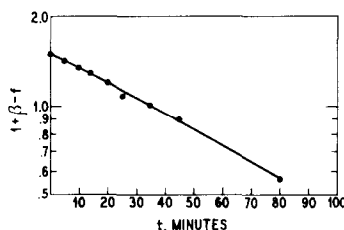


FIG. 3. Rate data of Table 1; $\log(1 + \beta - f)$ vs t .

fifth the original rate, but, at temperatures near 200°C, useful yields of cyclic olefins can be obtained. It appears that the very active sites that give cyclohexane as a principal product are modified by chemisorption of the ions, and that cyclic olefin intermediates are formed on sites that hydrogenate aromatics and the olefin intermediates at elevated temperatures by a first order reaction. The amount of nickel, cobalt or iron required to produce the change in activity-selectivity is very small, and progressive poisoning of the catalyst occurs in stainless steel reactors. In addition fundamental work that follows, exact attention must be given to details of catalyst preparation and source of contamination to elucidate the role played by transition metal ions.

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M. M. JOHNSON
G. P. NOWACK

Phillips Petroleum Company
Research and Development
Bartlesville, Oklahoma 74004

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