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The Oxidative Dehydrogenation of Cyclohexene Catalyzed by $ZrCu(PO_4)_2$

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A kinetic study of the oxidative dehydrogenation of cyclohexene with $ZrCu(PO_4)_2$ as catalyst was carried out. The reaction was found to be first order with respect to both oxygen and hydrocarbon. Activation energies were 11.7 ± 0.4 kcal/mole for the formation of benzene and 6.5 ± 0.3 kcal/mole for the complete oxidation to CO_2 and water. In the absence of oxygen, dehydrogenation takes place with reduction of Cu(II) to copper metal. If the reaction is carried out in a two-step sequence in which the hydrocarbon is first sorbed on the catalyst and then contacted with oxygen, complete burn up of the hydrocarbon is observed. In the reverse sequence in which oxygen is sorbed first high yields of benzene were obtained. A qualitative explanation of possible mechanisms for these reactions is presented.

INTRODUCTION

α-Zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, has a layered structure and behaves as an ion exchanger (*1*). It can be prepared in all degrees of crystallinity ranging from an amorphous gel to single crystals (*2, 3*). The surface area of the exchanger decreases as a direct function of the crystallinity (*4, 5*). In the fully crystalline state the surface is nonporous and can be calculated from the size and shape (hexagonal platelets) of the crystallites. The use of zirconium phosphate as a catalyst or support has several advantageous features. It permits the investigator to examine the effect of increased surface area (with little change in surface structure) on reaction rates for acid-catalyzed reactions (*6*). Alternatively, the protons may be exchanged for transition metal cations which catalyze a variety of reactions.

In this paper we report on the oxidative dehydrogenation of cyclohexene to benzene as catalyzed by the Cu(II) form of zirconium phosphate. It was previously observed that cyclohexene reduced the Cu(II) to metal (*7*) forming benzene in the process. This prompted us to study the hydrogen reduction of $ZrCu(PO_4)_2$ (*8*). It was found that the copper metal was reoxidized to Cu(II) in air and then diffused back into the zirconium phosphate reducing O_2 to $2H_2O$ in the process. Thus, it was felt that a continuous dehydrogenation reaction would proceed over the catalyst in the presence of oxygen.

EXPERIMENTAL

Catalyst preparation. The α-zirconium phosphate was prepared by refluxing a gel in 12 *M* H_3PO_4 for 336 h (*2, 3*). This treatment produces a product of high crystallinity which shall be referred to as α-ZrP (12:336). A weighed amount of dried solid was slurried with the exact amount of a 0.2 *N* copper(II) acetate solution required to completely exchange the zirconium phosphate protons (exchange capacity 6.62 meq/g assuming the presence of 2% Hf). This mixture was refluxed until a negligible amount of copper ions remained in solution (as observed spectrophotometrically). The same procedure was followed in order to prepare catalysts with lesser amounts of Cu(II), i.e., the total copper content of the solution was transferred to the exchanger by the refluxing procedure (*9*). The ex-

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changed solids were washed in distilled, deionized water and dehydrated at 400°C *in vacuo* for 20 h. This treatment is necessary to remove the last traces of water (*10*). Analysis for Cu(II) in the catalyst was carried out by neutron activation analysis or by exhaustive extraction with acid followed by iodometric titration. Weight losses from TG analysis were also used as a measure of the degree of Cu(II) exchange as the unexchanged protons split out as water above 450°C (*11*). Details of the TGA, ESCA, X-ray, and EPR data have been given previously (*7–11*).

Kinetic measurements. The reactions were run in a conventional flow reactor. Degreased glass wool was used to support 0.5–1.0 g of catalyst in a Vycor glass reaction chamber. Oxygen and helium were metered into a gas mixing chamber to produce a mixture of known oxygen partial pressure and this was led into a saturator filled with cyclohexene. The saturator was maintained at different temperatures to yield the desired hydrocarbon partial pressures. The total gas pressure was always 1 atm. Analysis of the gas mixture and the products of the reaction was carried out by gas chromatography using a 8-ft. column of 15% Anakrom ABS, 80/100 mesh. A modified air-circulatory furnace and Barber-Coleman temperature controller was used to maintain constant temperature (usually ±0.1°C). An iron–constantan thermocouple, located inside a thermal well, was placed directly above the catalyst and used to record the temperature of the reaction.

Pulsed experiments. A glass U-shaped reactor was connected directly to the gas chromatograph. A weighed amount of catalyst was degassed in the U-tube and oxygen (at 1 atm) was passed over the catalyst which was kept at 200°C. To ensure saturation of the catalyst the oxygen flow was continued for 1 h. This was followed by flowing helium over the catalyst for 0.5 h to remove any unadsorbed oxygen. Then, pulses of 1 μl of cyclohexene were injected into the helium stream, passed over the catalyst and the effluent analyzed in the gas chromatograph. This process was repeated by first sorbing cyclohexene onto the catalyst, followed by injecting 0.03-cm^3 pulses of O_2.

Reagents. Cyclohexene, cyclohexane and benzene were all reagent grade (Fisher Sci. Co.). They were separately purified by distillation and the center cut, which showed less than 0.01% impurities by gas chromatography, used in the experiments. 1,3- and 1,4-Cyclohexadiene were obtained from Aldrich Chemical Company and similarly treated. Ultrapure O_2 and He (Airco) were further purified by passage over solid KOH to remove CO_2 and dried over a column of zeolite-A.

Oxygen and cyclohexene sorption isotherms. The chemisorption of O_2 and cyclohexene at 200°C onto the catalyst surface was determined by means of a McBain balance. Approximately 200 mg of catalyst in a quartz bucket was suspended from a calibrated quartz spring. Changes in the extension of the spring upon adsorption of gas (O_2 or cyclohexene) were followed with a cathetometer which allowed weight changes to be determined to within ±0.005 mg. The catalyst was degassed overnight at 10^{-6} Torr and 200°C before admitting the sorbant.

RESULTS

Catalyst characterization. The actual Cu(II) content of α-ZrP (12:336) loaded to three different copper ion levels is shown in Table 1. It is seen that the agreement with the expected loading is excellent as is the internal consistency of the three analytical methods used. These preparations were dehydrated prior to use as described in the Experimental section. The lowest copper value was in each case that determined by titration. This may be due to small amounts of Cu^{2+} being retained by the exchanger as it was always slightly blue colored after the acid extraction of copper ions. The X-ray diffraction patterns in the hydrated and dehydrated states were identical to those pub-

TABLE 1

Copper Content of $ZrCu(PO_4)_2$ Catalysts

Degree of Cu^{2+} exchange (%)	Titration	Analytical method[a]	
		Neutron activation analysis	TGA water loss
100	98.87	99.9	99.5
20	19.66	19.7	19.8
10	9.85	10.1	10.0

[a] Cu^{2+} content as percentage of ion exchange capacity.

lished previously (*9, 11*), which for the fully exchanged anhydrous catalyst was phase G, $ZrCu(PO_4)_2$ (*11*). Unless otherwise stated the catalyst used was the 100% Cu(II) exchanged product.

Dehydrogenation of cyclohexene in the absence of oxygen. In the absence of oxygen cyclohexene was converted to a mixture of benzene, 1,3-cyclohexadiene, and cyclohexane. Total conversion of cyclohexene as a function of contact time in the temperature range 259–364°C is shown in Fig. 1. The distribution of products in a typical run is shown in Fig. 2. After rapidly attaining a maximum rate of reaction the percent cyclohexene conversion rapidly falls to zero. X-Ray analysis of the catalyst revealed that a reduction of Cu(II) to metal accompanied the reaction. The first appearance of copper metal in the X-ray powder pattern coincided with the maximum for cyclohexene conversion in Fig. 2. When all the Cu(II) was reduced, no further reaction was observed. The reactions which occur may be represented as

$$C_6H_{10} \xrightarrow{\text{Cat}} C_6H_6 + 2H_2 \quad (1)$$

$$C_6H_{10} \xrightarrow{\text{Cat}} C_6H_8 + H_2 \quad (2)$$

$$ZrCu(PO_4)_2 + H_2 \longrightarrow Zr(HPO_4)_2 + Cu^0 \quad (3)$$

$$C_6H_{10} + H_2 \xrightarrow{Cu^0} C_6H_{12} \quad (4)$$

Reaction (3) was examined separately (*8*) and found to proceed stepwise, hydrogen pressures of 150 Torr or greater being required for reduction to Cu^0. The activation energy for reduction of Cu(II) to Cu(I) was 7.1 kcal/mole and that of Cu(I) to Cu(O) was 5.7 kcal/mole. From the slopes of the curves in Fig. 1 at low contact times it was possible to obtain the initial rates. These values were 0.506, 0.844, 1.27, and 1.90 atm $\cdot$ min^{-1} at 257, 300, 321, and 364°C, respectively. The activation energy computed from these rates, 8.5 kcal/mole, is of the

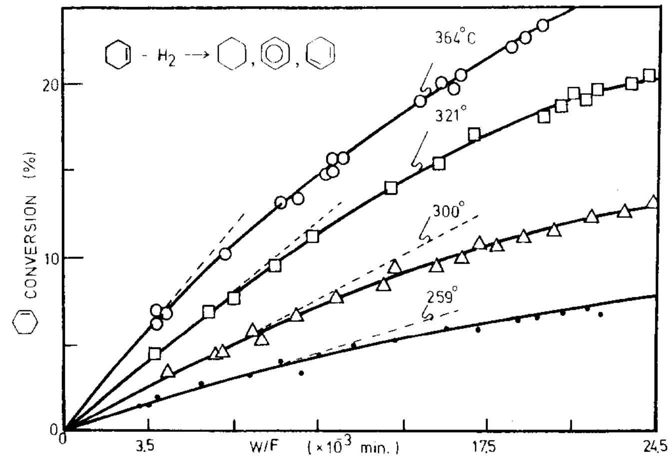

FIG. 1. Percentage conversion of cyclohexene to cyclic products as a function of contact time and temperature. (○) 364°C, (□) 321°C, (△) 300°C, (●) 259°C. The dashed lines indicate the slope of the initial rates.

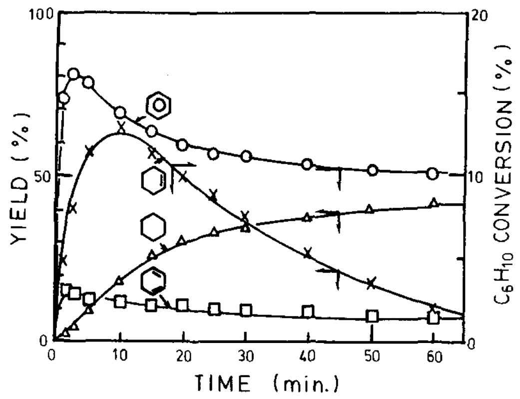

FIG. 2. Dehydrogenation of cyclohexene on Zr $Cu(PO_4)_2$ at 259°C. Yield as a percentage of the products versus reaction time: top curve, benzene; middle curve, cyclohexene; bottom curve, 1,3-cyclohexadiene. Amount of unreacted cyclohexene indicated by ×.

same order of magnitude as for the hydrogen reduction rates of the catalyst. Presumably the increase in cyclohexane with time (Fig. 2) results from the increased hydrogenation activity induced by the production of copper metal.

Oxidative dehydrogenation kinetics. In order to sustain the dehydrogenation reaction it was necessary to add oxygen to the reactant feed. This resulted in continuous conversion of cyclohexene to benzene and CO_2. The conditions could be adjusted to reduce all other oxidation products to less than 0.5% of the total. At higher oxygen levels formaldehyde, methanol, acetaldehyde, acetone, and ethanol, as well as other oxygenated products, were observed. These by-products were appreciable above 350°C and oxygen–hydrocarbon ratios of 4.6. At oxygen/hydrocarbon ratios lower than 1.5, the catalyst was partially reduced and copper metal formed on the surface. More detailed results are contained in Footnote 1.

The initial rate of the oxidative dehydrogenation reaction may be written in the general form

$$R_i = k_i P_{O_2}^n P_{che}^m, \qquad (5)$$

where P_{O_2} and P_{che} are the partial pressures of oxygen and cyclohexene, respectively; $R_i = -dP_{che}/dt$ and k_i is the rate constant. In logarithmic form Eq. (5) becomes

$$\log R_i = \log k_i + n \cdot \log P_{O_2} + m \cdot \log P_{che} \qquad (6)$$

under conditions of constant P_{che} Eq. (6) reduces to

$$\log R_i = n \cdot \log P_{O_2} + C. \qquad (7)$$

Thus, a plot of log R_i against log P_{O_2} should reveal the order of the reaction for oxygen. The assumption was made that the formation of benzene and CO_2 may be treated as two separate reactions so that separate plots of Eq. (7) were made as shown in Fig. 3. Both slopes were found to be close to 1 (0.96 and 0.95 for benzene and CO_2, respectively). A similar plot at constant P_{O_2} (0.367 atm) is shown in Fig. 4. Again the slopes are close to 1 (0.98) making the overall reactions second order.

Figure 5 gives a typical set of curves showing the percent conversion of cyclohexene to benzene and carbon dioxide as a function of contact time. The carbon dioxide curve is presented in terms of the amount of cyclohexene consumed in its production.

Rate constants were determined from the second-order rate expression

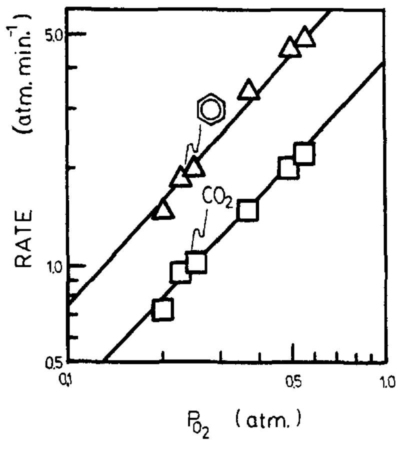

FIG. 3. Log–log plots of the rate of reaction versus pressures of oxygen at constant pressure of cyclohexene (0.119 atm) at 292.5°C: (△) benzene, (□) CO_2.

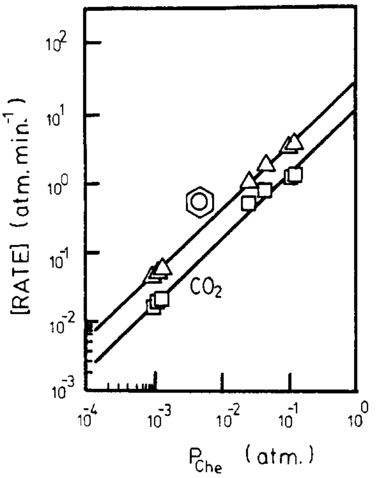

FIG. 4. Log–log plots of the rate of reaction versus pressures of cyclohexene at constant pressure of oxygen (0.367 atm) at 292.5°C: (△) benzene, (□) CO$_2$.

$$kt = \frac{1}{P^{\circ}_{\mathrm{che}}(R-1)} \ln \frac{R-X}{R(1-X)}. \qquad (7)$$

In Eq. (7) t is the contact time defined as the weight of catalyst divided by its density and the flow rate in milliliters per minute, R is the ratio P_{O_2}/P_{che} and X is the ratio of the pressure of a product (either $P_{C_6H_6}$ or P_{CO_2}) to P_{che}. An alternative procedure was to plot the right-hand side of Eq. (7) against t as shown in Fig. 6 and calculate k from the slopes. Arrhenius plots of the results in the temperature range 221–330°C are presented in Fig. 7. A least-squares treatment of the data yielded values for the activation energy of 11.7 ± 0.4 kcal/mole (A = 2.49 ×

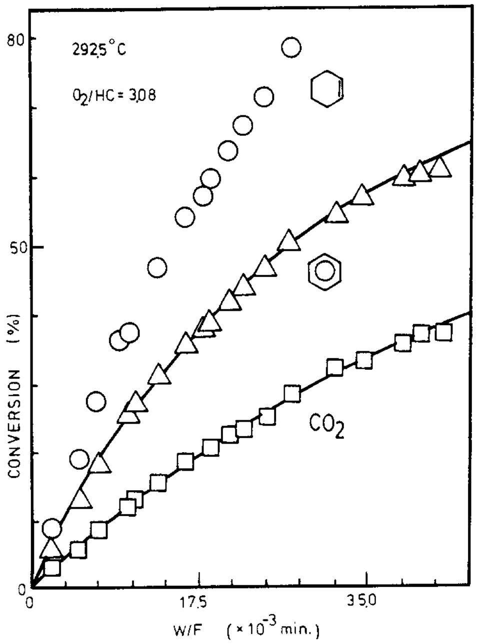

FIG. 5. Kinetic curves of percentage conversion of cyclohexene versus W/F at 292.5°C, O$_2$/HC = 3.08. Reactant gas composition; 36.70% oxygen, 11.93% cyclohexene, and 51.37% helium.

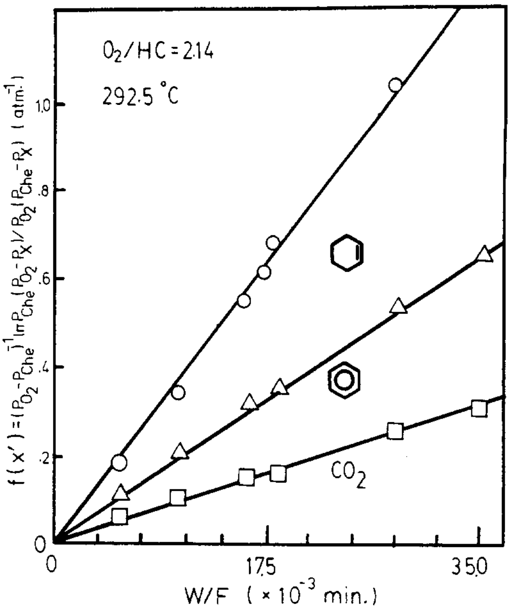

FIG. 6. Second-order rate plot, $f(x')$ versus W/F according to Eq. (7). (○) Cyclohexene, (△) benzene, (□) CO$_2$. O$_2$/HC = 2.14 at 292.5°C.

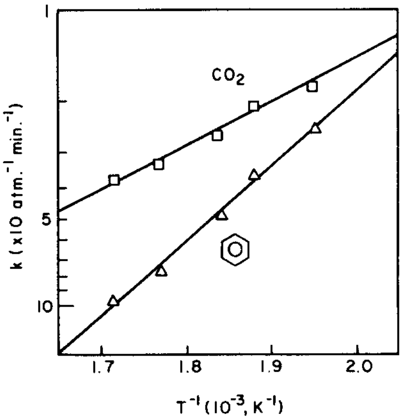

FIG. 7. Arrhenius plot of log k against $1/T$ for the formation of (△) benzene and (□) CO$_2$.

10^6 atm^{-1} min^{-1}) for formation of benzene and 6.5 ± 0.3 kcal/mole (A = 994 × 10^3 atm^{-1} min^{-1}) for carbon dioxide.

Effect of Cu(II) loading on catalyst activity. The possibility exists that some of the Cu(II) ions are reduced to Cu(I) or metal during the reaction. Reduction is accompanied by production of P—OH acid sites on the catalyst as shown by X-ray and IR data (*8*). Therefore, we wished to determine the effect that such groups would have on the reaction. Catalysts were prepared containing 85 to 98% of the theoretical Cu(II) loading and reaction rates determined as before. Below 90% loading a high proportion of the products consisted of oxygenated compounds (acetone, methanol, acetaldehyde). These results indicate extensive cracking and oxidation resulting from the action of the acidic sites as well as the Cu(II) sites. Above 90% Cu(II) loading the amount of cyclohexene produced increased dramatically while that of the oxygenated products resulting from cracking decreased correspondingly. The results from 90 to 100% loading are depicted in Fig. 8. It is seen that at higher loadings the total conversion and selectivity for cyclohexene continues to increase with loading.

Oxygen and hydrocarbon adsorption on $ZrCu(PO_4)_2$. Two types of adsorption experiments were carried out. The first type was the classical gravimetric adsorption isotherm as shown in Fig. 9. The temperature at which the isotherms were run was 200°C. For O_2 the amount sorbed at 1 atm was 4.3×10^{-6} mole per g of catalyst. This corresponds to 0.44 mole of O_2 per mole of Cu(II) ions on the surface of the catalyst. The later figure was derived from the surface area of the catalyst (2.8 m^2/g by BET N_2 sorption). Each phosphate group occupies 24 m^2 of surface (*5*) and each Cu(II) ion is associated with two phosphate groups. Thus, at 100% exchange there are 9.69×10^{-6} mole of Cu(II) ions on the surface.

The isotherm for cyclohexene could only be determined up to about 0.2 atm as larger hydrocarbon pressures brought about some reduction of Cu(II). In this pressure range the sorption of cyclohexene was about half that of oxygen.

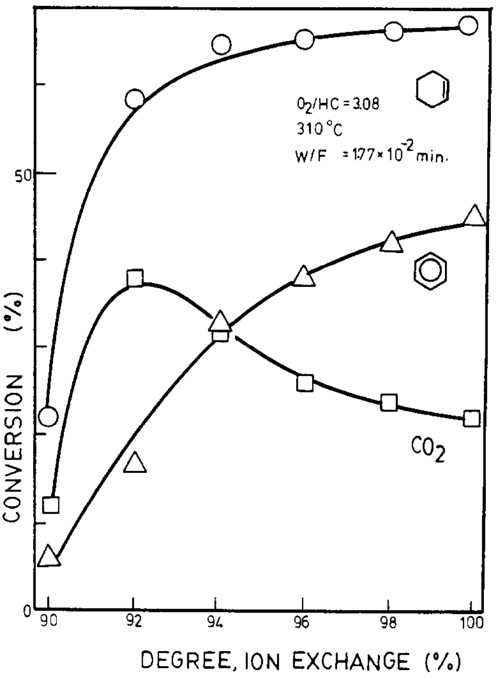

FIG. 8. Effect of cupric ion loading of zirconium phosphate on oxidative dehydrogenation of cyclohexene at T = 310°C, O_2/HC = 3.08, and W/F = 0.0177.

The amount of each component sorbed could also be determined by means of a gas chromatography method. Oxygen was sorbed onto the catalyst by flowing the pure gas over it for 1 h at 1 atm and 200°C. Physisorbed oxygen was then removed by purging the catalyst with helium. Then 1-μl pulses of cyclohexene were injected into the catalyst chamber and the amount converted to products determined. Twenty five or more pulses were required until no reaction was observed. The amount of oxygen consumed was then calculated using the equations

$$C_6H_{10} + O_2 \rightarrow C_6H_6 + 2H_2O \quad (8)$$

$$C_6H_{10} + \tfrac{17}{2} O_2 \rightarrow 6CO_2 + 5H_2O \quad (9)$$

For cyclohexene reactions the total O_2 sorbed was found to be 3.3×10^{-6} mole/g

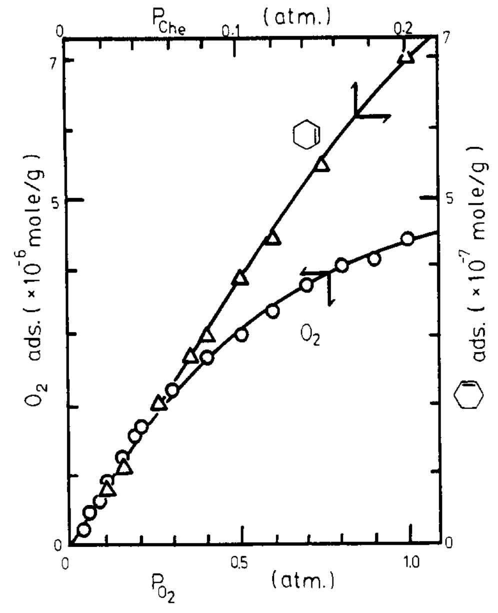

FIG. 9. Gravimetric adsorption isotherms of (O) oxygen and (Δ) cyclohexene on $ZrCu(PO_4)_2$ at 200°C. The weight of catalyst for O_2 absorption was 184.43 mg, for cyclohexene, 171.60 mg.

which is about 77% of the value determined by the gravimetric method.

In the case of cyclohexene sorbed onto the catalyst, the only product was carbon dioxide (and water). No benzene was produced and the total amount sorbed was 4.4×10^{-7} mole/g. This is very close to the value obtained by the gravimetric method for the cyclohexene pressure used (0.119 atm). Similar experiments were run with cyclohexane and cyclohexadiene. In both cases burn up to CO_2 and water was obtained. However, when oxygen was preadsorbed and pulses of these hydrocarbons admitted, conversions to benzene comparable to (or higher than in the case of cyclohexadiene) those achieved with cyclohexene were obtained.

DISCUSSION

Any mechanism proposed for the dehydrogenation reaction must account for the following facts; the overall second-order kinetics, the rapid decrease in product yield below 94% Cu(II) loading and the formation of benzene only when oxygen was preadsorbed or simultaneously adsorbed with the cyclohexene. We need also to explain the burn up of hydrocarbon to CO_2 and H_2O.

The surface structure of the $ZrCu(PO_4)_2$ catalyst can be inferred from the known structure of α-zirconium phosphate layers (*13, 14*). The zirconium atoms are arranged in a hexagonal array and bridged by phosphate groups above and below the metal atom plane. Three oxygens bond to metal and the fourth. The fourth oxygen is bonded to a proton and points away from the layers. The layers are staggered such that zeolite-like cavities are formed by the P—OH groups. Half-cavities would exist on the surface. Each cavity has the equivalent of two protons, so that at 100% exchange each cavity is filled by one Cu(II) ion. On the surface every other half cavity must be occupied. This places copper ions adjacent to each other in rows which are alternately filled and empty.

We propose that the O_2 molecules sorb by bridging two copper ions in adjacent half-cavities. The distance between the copper ions in the cavities is 5.3 Å. However, they are free to move toward each other to accommodate the oxygen bridging. A process such as this occurs in the protein hemocyanin where the copper(II) ions are 5.6 Å apart (1b), but on sorbing oxygen to form oxyhemocyanin, approach each other more closely (≈3.6 Å) (*16*).

The conversion of cyclohexene to benzene and water requires a transfer of four protons and four electrons to the oxygen. The sequence of steps may be visualized as follows: The hydrocarbon, either sorbed or in the gas phase, transfers a proton to the PO^- group adjacent to the copper oxygen dimer. The hydrocarbon now exists as $[C_6H_9]^-$ and transfers electrons to the Cu(II) which in turn can transfer them to the oxygen so that this latter species acquires a negative charge. Finally the proton from the $P—O^-$ migrates to the newly created negative oxygen site and the cycle repeats itself until benzene is produced.

In the case where the hydrocarbon is sorbed without the presence of oxygen we may assume that the hydrocarbon is sorbed in the empty half-cavities. The hydrocarbon again transfers a proton to the PO^- group forming P—OH and $C_6H_9:^-$. Continuation of this process would result in transfer of electrons to the Cu(II) ions with formation of Cu(I) and would finally lead to copper metal and benzene as was observed if the temperature is high enough. However, at 200°C this reaction is slow and injection of oxygen results in attack at the hydrocarbon electrophilic center to form $C_6H_9OO^-$. Abstraction of the transferred proton then yields a hydroperoxide and burn up then proceeds through the well-recognized free radical autocatalytic pathway (*17*).

Finally we may infer that when oxygen is not present, the carbanion, $C_6H_9:^-$, transfers electrons stepwise (*8*) to the copper(II) ions reducing them to Cu(I) and then to copper metal. As the surface becomes depleted of Cu(II) ions, the hydrogen ions diffuse into the interior and displace Cu(II) ions which then diffuse out to the surface. This part of the mechanism would be much like that of the hydrogen reduction mechanism.

Second-order kinetics was also observed for the same reaction using activated alumina (*18*) and Cu(II) exchanged erionite (*19*) as catalysts. In the latter case the total conversion of hydrocarbon at 450°C was 11.4% with a 54% selectivity for benzene. In the present study 65 to 90% conversions were routinely obtained with 65% selectivity in the temperature range of 280–350°C. The marked difference in catalyst performance may well result from the different arrangement of Cu(II) ions in the catalysts which produce different dehydrogenation mechanisms.

ACKNOWLEDGMENTS

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REFERENCES

1. Clearfield, A., Ed., "Inorganic Ion Exchange Materials." CRC Press, Boca Raton, Fla., 1982.

2. Clearfield, A., and Stynes, J. A., *J. Inorg. Nucl. Chem.* **26,** 117 (1964).

3. Clearfield, A., Oskarsson, A., and Oskarsson, C., *Ion Exch. Membr.* **1,** 91 (1972).

4. Clearfield, A., and Djuric, Z., *J. Inorg. Nucl. Chem.* **41,** 903 (1979).

5. Clearfield, A., and Berman, J., *J. Inorg. Nucl. Chem.* **43,** 2141 (1981).

6. Thakur, D. S., and Clearfield, A., *J. Catal.* **69,** 230 (1981).

7. Clearfield, A., and Pack, S. P., *J. Catal.* **51,** 431 (1978).

8. Clearfield, A., Thakur, D. S., and Cheung, H., *J. Phys. Chem.* **86,** 500 (1982).

9. Clearfield, A., and Kalnins, J. M., *J. Inorg. Nucl. Chem.* **38,** 849 (1976).

10. Cheung, H.-C., Ph.D. dissertation, pp. 42–52. Texas A&M University, Tex., 1982.

11. Clearfield, A., and Pack, S. P., *J. Inorg. Nucl. Chem.* **42,** 771 (1980).

12. Clearfield, A., *J. Catal.* **56,** 296 (1979).

13. Clearfield, A., and Smith, G. D., *Inorg. Chem.* **8,** 431 (1969).

14. Troup, J. M., and Clearfield, A., *Inorg. Chem.* **16,** 3311 (1977).

15. Co, M. S., and Hodgson, K. O., *J. Amer. Chem. Soc.* **103,** 3200 (1981).

16. Co, M. S., Hodgson, K. O., Eccles, T. K., and Lontie, R. J., *J. Amer. Chem. Soc.* **102,** 4210 (1980).

17. Kochi, J. K., "Organometallic Mechanisms and Catalysis: The Role of Intermediates in Organic Reactions." Academic Press, New York, 1978.

18. Uchida, A., Nakazawa, T., Oh-Uchi, K., and Matsuda, S., *Ind. Eng. Chem. Prod. Res. Dev.* **10,** 153 (1971).

19. Minachev, Kh. M., Tagiev, D. B., Zulfugarov, Z. G., and Kharlamov, V. V., *Kinet. Katal.* **20,** 399 (1979).