Selective dehydrogenation of cyclohexene to benzene using Pd-exchanged α-zirconium phosphate

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The dehydrogenation of cyclohexene to benzene with $\sim$ 85% cyclohexene conversion and $>$ 80% benzene selectivity has been achieved over Pd-exchanged α-zirconium phosphate at 200°C.

Keywords: dehydrogenation, cyclohexene, zirconium phosphate, MCM-41, zeolite beta

Catalytic dehydrogenation is an important step in the reforming process. In the reforming process *n*-paraffin molecules are mainly dehydrogenated to produce olefins, diolefins and triolefins which then cyclize and finally produce the aromatics [1,2]. The oxidation of cyclohexene has been used as a model reaction by many investigators to evaluate the catalyst [3–7]. Cation-exchanged zeolites have been known to exhibit high catalytic activity for oxidative dehydrogenation of cyclohexane and cyclohexene [8–11]. However, selectivity of the reaction was found to be dependent on the nature of the ion-exchanged metals. For example, the most active catalyst was Cu(II)-Y for benzene formation (80% selectivity and 10% conversion) whereas Pd(II)-Y was best for carbon dioxide formation [8].

Cheung and Clearfield [12] reported the oxidative dehydrogenation of cyclohexene to benzene over the Cu(II) form of zirconium phosphate, $CuZr(PO_4)_2$. It was observed that, in the absence of oxygen, dehydration takes place with reduction of Cu(II) to Cu metal forming benzene in the process. A similar hydrogen reduction and dehydrogenation study indicated that the copper metal once formed was reoxidized to Cu(II) in air and then diffused back into the zirconium phosphate reducing O_2 to H_2O in the process. In the case of an erionite catalyst [11] using an oxygen atmosphere, the conversion of cyclohexane at 450°C was 11.4% with 54% selectivity to benzene whereas in the case of Cu(II)-ZrP 65–90% conversion with 65% selectivity in the temperature range 260–350°C was achieved [12]. However, in the absence of O_2, Cu(II)-ZrP showed a significant decrease in catalytic activity from 65% to 10% within 60 min of reaction time. In the present case we report $\sim$ 85% cyclohexene conversion with $>$ 80% benzene selectivity at 200°C using Pd-exchanged α-zirconium phosphate in the absence of oxygen. The catalyst was tested for one week and showed no sign of deactivation.

A zirconium phosphate gel, prepared by the method of Clearfield et al. [13], was refluxed in 12 M H_3PO_4 for 100 h. This treatment produces a product of high crystallinity which shall be referred to as α-ZrP. Pd exchange of α-ZrP was carried out as follows. A weighed amount of dried solid α-ZrP was slurried with propylamine (3 mmol/g) at room temperature for two days using an ultrasonic bath. The solid product was recovered by filtration and washing with deionized water and dried at room temperature. To this solid product was added 0.1 N $Pd(NH_3)_4Cl_2$ solution in water. The mixture was again ultrasonicated at room temperature for two days. The yellowish solid product was obtained after washing and drying. As expected, incorporation of $Pd(NH_3)_4Cl_2$ complex in α-ZrP resulted in an increase in the interlayer distance from 7.6 to 11.6 Å. The XPS analysis indicated that Pd is present as Pd(II) and there are 4 nitrogen and 1.6 chlorine atoms for each atom of Pd suggesting that the $Pd(NH_3)_4Cl_2$ complex is intact.

The cyclohexene dehydrogenation reaction was carried out in a conventional glass reactor with 10 mm diameter. A 50 mg sample of Pd-exchanged α-ZrP was loaded in a reactor which was supported on glass wool. Prior to reaction the catalyst was calcined in situ at 200°C for 6 h in a N_2 atmosphere. After activation the N_2 flow was diverted to a saturator filled with cyclohexene and then passed through the reactor. The saturator was maintained at different temperatures to yield desired partial pressures. Analysis of the products was carried out by on-line gas chromatography (Varian 3400) using a J&W Scientific 50 m Alumina PLOT capillary column and FID detector. The outlet lines were heated to ensure no product condensation within the lines. Mass balances were within ±2% of closure, i.e. the moles of carbon in equals to moles of carbon out.

It was observed that the pretreatment/activation of the catalyst is an important step in determining the catalytic activity of Pd-ZrP. Activation of Pd-ZrP in a N_2 atmosphere for less than 6 h resulted in less active material whereas the higher activity remained more or less the

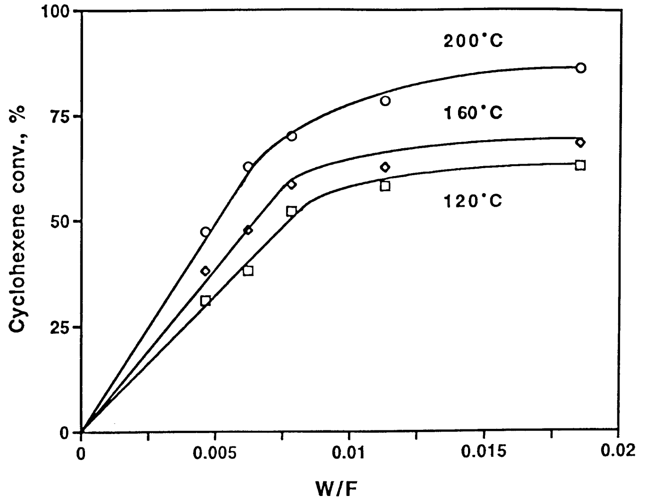
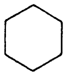
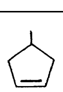
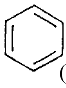
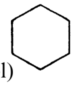


Figure 1. Cyclohexene conversion over Pd-ZrP at various temperatures.

same for the catalyst pretreated for 6–12 h. The Pd-ZrP at 200°C ($W/F = 0.0185$ min) gave cyclohexene conversion near 86%. Total conversion of cyclohexene as a function of contact time in the temperature range 120–200°C is shown in figure 1. Dehydrogenation of cyclohexene to benzene as well as hydrogenation of cylohexene to cyclohexane occurred simultaneously. No other products such as 1,3- or 1,4-cyclohexadiene were detected. The formation of benzene from cyclohexene without forming 1,3-cyclohexadiene over Pt complexes and Pt supported catalysts is reported in the literature [11,14]. From the slope of the kinetic curves of cyclohexene conversion against contact time in figure 1, initial rates were obtained. The apparent activation energy (E_a) for cyclohexene conversion was 1.9 kcal/mol. Because the apparent activation energy value was very low, several experiments were carried out in this temperature range to check the reproducibility of the results. Again, E_a values were found to be within the same range of experimental errors. The apparent activation energy for the same reaction over Cu-exchanged α-ZrP was found to be 8.5 kcal/mol [12]. This lower E_a may explain why Pd-exchanged α-ZrP is more active than Cu-exchanged α-ZrP. Davis and Somorjai reported [4] an apparent activation energy for the same reaction of at least 8 kcal/mol at 77 Torr but zero at low pressures in the temperature range 25–150°C for Pt supported on SiO_2 surface.

In table 1 we have compared catalytic data of Pd-ZrP, Cu-ZrP and Pd-exchanged beta (microporous) and Pd-exchanged MCM-41 (mesoporous) catalysts for the cyclohexene dehydrogenation reaction. The protonated forms of MCM-41 and beta were obtained using procedures described elsewhere [15–17]. A calculated amount of $Pd(NH_3)_4Cl_2$ solution in water was used to obtain 0.4% Pd-loaded MCM-41 or beta zeolite. From table 1, It is clearly seen that Pd-ZrP is the most active and selective catalyst for the production of benzene. It also produces cyclohexane by hydrogenation. Note that benzene-to-cyclohexane (dehydrogenation/hydrogenation ratio) is > 4.5 and per cent deactivation is 1% < in 4 h. All silica Pd-MCM-41 also showed very high activity with only 8% deactivation. However, this catalyst gave a benzene/cyclohexane ratio of 2. Although, in the case of Cu-ZrP the benzene/cyclohexane ratio was comparable with that of Pd-ZrP, the activity of this catalyst was much lower and the deactivation rate was much higher. In addition to benzene and cyclohexane it produced significant quantities of 1,3-cyclohexene. On Pd-beta and Pd-MCM-41(Si/Al = 15) not only benzene and cyclohexane but also C_6 isomeric products such as methylcyclopentenes are formed. The activity of these catalysts is much lower than Pd-ZrP. It is known that beta and MCM-41 contain Brønsted acid sites resulting in formation of methylcyclopentenes in addition to benzene and cyclohexane. On Pd-MCM-41(Si/Al = 15), isomerization is a main reaction, followed by hydrogenation and then dehydrogenation reactions, whereas on Pd-beta, hydrogenation and isomerization reactions are taking place simultaneously. Again the rate of deactivation is very high for both catalysts. The benzene/cyclohexane ratio is 0.5 and 0.04 for Pd-MCM-41(Si/Al = 15) and Pd-beta, respectively.

Table 1
Cyclohexene dehydrogenation activity of various Pd-exchanged catalysts[a]

Catalyst	Reaction temp. (°C)	Initial con. (wt%)	Deactivation[b] (%)	Product distribution (wt%)				
					 isomers			 /  (mol)
Pd-ZrP	200	86.3	1 <	19.0	–	–	80.0	4.5
Cu-ZrP[c]	260	12.0	99	18.0	–	13.0	69.0	4.1
Pd-MCM-41 (all silica)	200	99.8	8	34.7	–	–	65.2	2.0
Pd-MCM-41 (Si/Al = 15)	200	25.8	96	22.8	66.6	–	10.5	0.5
Pd-beta (Si/Al = 13)	200	37.0	97	58.4	39.4	–	2.1	0.04

[a] Catalyst = 50 mg; activation temp. = 200°C/6 h; $P_{CHE} = 23.9$ mm; N_2 + cyclohexene flow = 27 ml/min.

[b] Defined as $(A_0 - A_t/A_0)100$, where A_0 is activity at time 2 min and A_t is activity at time 4 h.

[c] Data taken from ref. [12].

To summarize, the absence of isomerization reactions and 1,3-cyclohexadiene in the products and a very high relative rate for dehydrogenation over the hydrogenation reaction coupled with a very low deactivation rate clearly indicates that Pd-ZrP is a very effective catalyst for dehydrogenation reaction.

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