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Optimization of the Gas-Phase Disproportionation of Cyclohexene Catalysed by Pd/SiO_2–$AlPO_4$

Cyclohexene is an organic compound of great interest in catalysis on account of its occurrence as a reaction intermediate in hydrogenation–dehydrogenation processes involving benzene. On the other hand, it disproportionates to benzene and cyclohexane at low temperatures (*1, 2*). In addition, it can act as a donor in different hydrogen-transfer reduction processes (*3, 4*), as shown by Marinas *et al.*, by using catalytic systems consisting of Pd supported on orthophosphates in the reduction of aromatic nitro compounds (*5*), α,β-unsaturated carbonyl compounds (*6, 7*), benzaldehyde, and substituted benzaldehydes (*8*), as well as in the deprotection of amino acids and N-protected dipeptides (*9*).

This note reports the results obtained in the liquid- and gas-phase conversion of cyclohexene by use of a pulse reactor and Pd/SiO_2–$AlPO_4$ as a catalyst under various reaction conditions.

The catalyst used contained 1% palladium by weight supported on $SiO_2/AlPO_4$ (80 : 20). The support was prepared by precipitation of $AlPO_4$ on commercial silica gel (Merck ref. 7734), using 0.1 *M* NH_4OH up to pH 6 as the precipitating agent. The solid thus obtained was dried in the air and subsequently calcined at 923 K for 3 hr. Its chemical and texture properties were as follows: S_{BET} = 280 $m^2\ g^{-1}$; accumulated pore volume, 0.46 ml g^{-1}; average pore diameter, 35 Å; acidity against pyridine, 3.4 $\times\ 10^{-4}$ meq g^{-1}. The metal catalyst was obtained by impregnation of the support with sodium tetrachloropalladiate. Once dry, the solid was calcined from 373 to 523 K for 2 hr and then reduced by having a hydrogen stream (flow rate 50 ml min^{-1}) at 523 K passed over it for 2 hr.

The metal surface area (S_{met} = 251 m^2/g Pd) was determined by transmission electron microscopy (TEM), by applying the extractive replica technique.

The catalyst acidity was measured spectrophotometrically (*10*) by determining the volume of titrant (generally pyridine) retained chemically by the solid. The level of acidity against pyridine found (3.4 $\times\ 10^{-4}$ meq g^{-1}) seems to indicate that the deposition of the metal salt introduces no significant changes in the support's inherent acidity.

The pulse reactor used was described elsewhere (*11*) and its outlet was coupled directly to a gas chromatograph to facilitate product analysis. The reaction tube, holding the catalyst, was placed in an oven external to the chromatograph working at temperatures between 293 and 773 K. The chromatographic column used to analyse the products was packed with 5% TCEP on Chromosorb G AW-DCMS and was 2 m in length and $\frac{1}{8}$ inch in diameter. Nitrogen was used as a gas carrier.

A 0.02-g amount of the catalyst was placed in the reactor and, after coupling to the gas chromatograph, the flow rate of the nitrogen stream and the reaction temperature were adjusted to the desired levels. Then, reagent pulses of 0.5 to 2 μl were injected and the resultant products emerging from the reactor were analysed by the coupled gas chromatograph.

The liquid-phase experiments were conducted by placing 3.94 $\times\ 10^{-2}$ mol cyclohexene and 0.3 g of the catalyst into a

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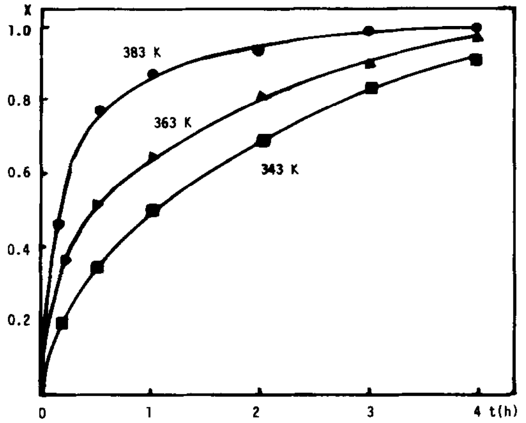

FIG. 1. Variation of conversion as a function of the reaction time for the liquid-phase conversion of cyclohexene.

TABLE 1

Variation of the X_{CHA}/X_{BZ} Ratio Obtained in the Liquid-Phase Disproportionation of Cyclohexene with Reaction Time

T (K)	Reaction time (hr)				
	0.5	1	2	3	4
343	2.0	1.8	1.1	0.9	0.9
363	2.0	1.3	0.8	0.8	0.8
383	1.7	1.0	0.6	0.5	0.5

two-neck flask and fitting a reflux condenser. Once the reaction temperature had been reached ($t = 0$), portions of the reacting mixture were extracted at regular intervals.

Blank assays carried out with no catalyst showed the reaction not to occur in its absence, in neither the liquid nor the gas phase. On the other hand, the working conditions were chosen so as to avoid the influence of diffusion on the results.

According to the operational procedure described above, successive pulses of cyclohexene were injected under different conditions (amount of catalyst, reaction temperature, carrier flow rate, reactant pulse volume, etc.).

In Fig. 1 are shown the results obtained for the liquid-phase disproportionation of cyclohexene as a function of the reaction time at different temperatures. As can be seen, the yield increases with increasing temperature and approaches 100% after 4 hr reaction at 383 K. The relationship between the cyclohexane and benzene yields (in mol) was used to determine the selectivity of the processes (Table 1). As can be seen, the ratio of cyclohexane conversion to that of benzene, X_{CHA}/X_{BZ}, decreases with increasing reaction time and depends on the reaction temperature. In addition, low temperatures and short reaction times result in the theoretical value of 2.0 for the X_{CHA}/X_{BZ} ratio, consistent with the following reaction stoichiometry:

$$3 \text{ Cyclohexene} \rightarrow 2 \text{ Cyclohexane} + \text{Benzene}$$

Increasing temperatures and/or reaction times result in gradually decreasing X_{CHA}/X_{BZ} ratios as a result of the conversion of cyclohexane originally formed in the disproportionation. We have checked that, under the same reaction conditions, cyclohexane is converted to benzene by our catalyst.

Table 2 lists the distributions of the products obtained in the gas-phase disproportionation of cyclohexene in terms of the amount of catalyst used. As can be seen,

TABLE 2

Influence of the Amount of Catalyst on the Yield and Selectivity in the Gas-Phase Disproportionation of Cyclohexene

Catalyst weight (mg)	X_T[a] (% mol)	X_{CHA} (% mol)	X_{BZ} (% mol)	X_{CHA}/X_{BZ}[b] (% mol)
10	45.8	30.4	15.2	2.0
20	61.7	40.8	20.9	1.9
25	62.1	39.4	22.4	1.8
35	91.1	50.3	31.7	1.6
50	100	60.8	38.6	1.6
65	100	57.2	42.8	1.3
80	100	54.3	44.7	1.2

Note. Reaction T: 573°K; nitrogen flow rate: 30 ml min^{-1}.

[a] X_T, total conversion of cyclohexene to cyclohexane and benzene.

[b] X_{CHA}/X_{BZ}, molar ratio of cyclohexane to benzene yielded.

TABLE 3

Influence of the Reaction Temperature on the Yield and Selectivity Obtained in the Gas-Phase Disproportionation of Cyclohexene

Nitrogen flow-rate (ml min^{-1})	Reaction temperature (K)									
	353		393		453		513		573	
	X_T	X_{CHA}/X_{BZ}	X_T	X_{CHA}/X_{BZ}	X_T	X_{CHA}/X_{BZ}	X_T	X_{CHA}/X_{BZ}	X_T	X_{CHA}/X_{BZ}
	Pulse volume 0.5 μl									
40	34.0	2.0	94.7	1.7	96.9	0.9	100.0	0.3	100.0	0.2
30	100.0	2.0	100.0	1.7	100.0	0.9	100.0	0.3	100.0	0.2
20	100.0	2.0	100.0	1.7	100.0	0.9	100.0	0.3	100.0	0.1
	Pulse volume 1 μl									
40	37.9	2.0	84.8	1.5	89.8	1.1	92.5	0.6	100.0	0.2
30	100.0	2.0	100.0	1.6	100.0	1.1	100.0	0.6	100.0	0.2
20	100.0	2.0	100.0	1.7	100.0	1.1	100.0	0.6	100.0	0.2
	Pulse volume 2 μl									
40	36.5	2.0	63.5	1.7	73.5	1.0	87.3	1.0	100.0	0.8
30	82.7	1.0	100.0	1.0	100.0	1.0	100.0	1.0	100.0	0.8
20	87.6	1.0	100.0	1.0	100.0	1.0	100.0	1.0	100.0	0.7

Note. For abbreviations, see footnote to Table 2. Amount of catalyst, 20 mg.

increasing amounts of the catalyst result in increasing yields and decreasing X_{CHA}/X_{BZ} ratios.

In Table 3 are given the total conversion (X_T) and X_{CHA}/X_{BZ} ratio obtained as a function of the temperature (K), nitrogen flow rate, and pulse volume in the gas-phase conversion of cyclohexene. As can be seen, low temperatures (353 K) result in the theoretical X_{CHA}/X_{BZ} ratio of 2, thus indicating the occurrence of cyclohexene disproportionation originally. Increasing temperatures or values of the other variables decrease this ratio as a result of the conversion of cyclohexane to benzene. Decreased nitrogen flow rates (i.e., increased contact times) result in slightly decreased X_{CHA}/X_{BZ} ratios. These conditions favour the conversion of cyclohexene to benzene.

Finally, at the higher reaction temperatures (513 and 573 K), the X_{CHA}/X_{BZ} ratios generally increase with the pulse volume as a result of a diminished conversion of cyclohexane to benzene. Thus, by selecting suitable operational variables it is possible to obtain a wide range of X_{CHA}/X_{BZ} ratios from 2.0 (theoretical value for cyclohexene disproportionation) to 0.1.

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