

## TRANSFORMATIONS OF CYCLOHEXANOL ON A PLATINUM-ALUMINA CATALYST: EFFECT OF POISONS<sup>1</sup>

S. Sivasanker<sup>2</sup> and L. M. Yeddanapalli<sup>3</sup>

Loyola College, Madras, 600 034, India

Received July 12, 1977

Accepted September 9, 1977

Vapor-phase dehydrogenation/dehydration of cyclohexanol has been investigated over a bifunctional platinum-alumina catalyst. The products of the reactions are cyclohexane, cyclohexene, benzene, cyclohexanone and phenol. Studies using the poisons CO, H<sub>2</sub>S and NH<sub>3</sub> have been made in order to elucidate the nature of the sites responsible for the formation of the various products.

Парофазные дегидрирование/дегидратация циклогексанола были исследованы на катализаторе платины на окиси алюминия с двойной функциональностью. Продуктами реакции являются циклогексан, циклогексен, бензол, циклогексанон и фенол. Исследования путем отравления CO, H<sub>2</sub>S и NH<sub>3</sub> были проведены с целью выяснения природы центров, приводящих к образованию различных продуктов.

### INTRODUCTION

Platinum on alumina is a bifunctional catalyst; the metallic function brings about hydrogenation-dehydrogenation reactions, while the acidic function initiates isomerization, cracking and dehydration reactions. The reactions of cyclohexanol over platinum supported on a moderately acidic alumina have been investigated by

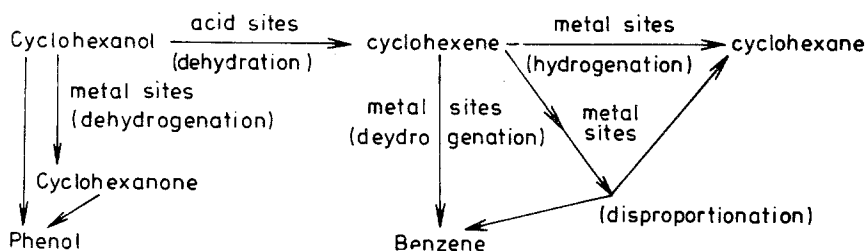
<sup>1</sup> Part of the Ph. D. thesis of S. Sivasanker

<sup>2</sup> Present address: Indian Institute of Petroleum, Dehradun, 248 005, India

<sup>3</sup> Late Head of the Chemistry Department, Loyola College, Madras

the authors /1/. The influence of various poisons on these reactions are reported in this paper.

Cyclohexanol undergoes numerous transformations on a Pt-alumina catalyst. Cyclohexanol undergoes partly dehydration on the support and partly dehydrogenation on the metal. The following reactions take place:



## EXPERIMENTAL

The catalyst used was prepared by impregnating a commercial alumina (BET area 80 m<sup>2</sup>/g, obtained from Sarabhai Merck Co., India) with the required amount of a solution of chloroplatinic acid to yield a material containing 0.6 wt. % Pt.

The reactions were carried out at atmospheric pressure in a vertical flow reactor made of pyrex glass. The liquid reactant was fed through a motor-activated syringe. Before introduction of the feed or the poisons, the catalyst was always reduced at 250 °C for 6 hrs.

Three types of poisoning experiments were performed: (1) the poison was passed along with H<sub>2</sub> through the catalyst bed at the reaction temperature, and then the poison flushed out with pure H<sub>2</sub> at the same temperature; (2) the poison was passed but no flushing was done; (3) the poison (along with H<sub>2</sub>) was passed together with the feed.

Analysis of the reaction products was carried out using a Perkin-Elmer Model 90 P3 gas chromatograph.

## RESULTS AND DISCUSSION

Table 1 gives the product distributions obtained after various poisoning operations. The products benzene and cyclohexane are formed on metal sites mostly from cyclohexene, which is itself produced through dehydration over the acid sites. The sum of the products cyclohexene, cyclohexane and benzene may be taken as a measure of the "total dehydration". Phenol and cyclohexanone are the products of dehydrogenation over the metal sites /2/.

H<sub>2</sub>S and CO poisoning. Carbon monoxide and hydrogen sulfide are known to be poisons for Pt. The operations involving CO and H<sub>2</sub>S (code named B, C and E) lead to losses in the yield of benzene, cyclohexane and phenol, indicating poisoning of the metallic function. The data reveal that H<sub>2</sub>S is a stronger poison than CO. Also H<sub>2</sub>S poisoning is much less reversible than CO poisoning, as indicated by the effect of flushing with hydrogen (operations B and E). The yield of cyclohexanone is increased by operations B, C, and E, which can be considered to have effected mild poisoning of the metal. However, when strong poisoning takes place (operations D and F), there is a drastic fall in all the dehydrogenation products including cyclohexanone. In all cases, the yield of cyclohexene increases due to a build-up consequent to poisoning of the sites responsible for its being converted into cyclohexane and benzene. In the absence of poisons, the metallic function acts as a scavenger converting the less easily desorbable cyclohexene into the more easily desorbed products benzene and cyclohexane. The ease of desorption of the three products on an alumina surface has been shown to follow the order: cyclohexane > benzene > cyclohexene /3/. The scavenging action of Pt explains why a total of nearly 40% of dehydration products is formed on Pt-alumina (case A), in spite of competing dehydrogenation reactions, even though Al<sub>2</sub>O<sub>3</sub>-0.6% HCl itself dehydrates only 36% of the feed cyclohexanol under the same reaction conditions /1/. Also, when the yield of benzene and cyclohexane is lower, there is an increased production of cyclohexanone (operations B, C, and E). Strong poisoning of the

Table 1  
Effect of poisons on the transformations of cyclohexanol over  
Pt(0.6%) $-Al_2O_3$  at 250 °C

Poisoning operation <sup>1</sup>		Conversion (mol %)	Product distribution (mol%)				
Code	Nature of operation		C-ane	C-ene	B	C-anone	Phen
A	No Poison	70.6	9.6	8.1	22.0	21.6	9.3
B	CO passed, H <sub>2</sub> flushed <sup>a</sup>	70.6	0.2	13.6	5.5	43.3	8.0
C	CO passed <sup>b</sup>	69.5	0.3	12.8	3.3	47.9	5.2
D	CO and H <sub>2</sub> passed <sup>c</sup>	19.6	0.7	14.2	0.0	4.3	0.4
E	H <sub>2</sub> S passed, H <sub>2</sub> flushed <sup>a</sup>	60.6	5.9	9.5	0.7	44.5	0.0
F	H <sub>2</sub> S passed <sup>b</sup>	16.5	0.2	15.7	0.0	0.6	0.0
G	No poison	63.8	4.7	2.0	12.5	31.5	13.1
H	NH <sub>3</sub> passed, H <sub>2</sub> flushed <sup>a</sup>	57.5	4.1	2.6	12.0	28.9	9.9
I	NH <sub>3</sub> passed <sup>b</sup>	44.6	2.6	2.2	11.1	22.6	6.1
J	NH <sub>3</sub> and H <sub>2</sub> passed <sup>c</sup>	28.4	0.5	0.6	5.1	2.9	19.3

C-ane: Cyclohexane; C-ene: Cyclohexene; B: Benzene; C-anone: Cyclohexanone; Phen: Phenol

A-F: Feed rate 0.05 mol hr<sup>-1</sup>g<sup>-1</sup>; atmospheric pressure

G-J: Feed rate 0.06 mol hr<sup>-1</sup>g<sup>-1</sup>; atmospheric pressure

<sup>1</sup>All poisoning and flushing operations carried out at 250 °C

<sup>a</sup>Poison passed along with H<sub>2</sub> (partial pressure 0.1, flow rate 3 l hr<sup>-1</sup>) for 30 min and then flushed with H<sub>2</sub> for 2 hrs (flow rate 3 l hr<sup>-1</sup>)

<sup>b</sup>Poison passed along with H<sub>2</sub> (partial pressure 0.1, flow rate 3 l hr<sup>-1</sup>) for 30 min

<sup>c</sup>Poison and H<sub>2</sub> passed along with feed (10% of total feed; poison to H<sub>2</sub> ratio 1/10)

surface decreases the yield of cyclohexanone. Thus, the formation of cyclohexanone may be attributed to mildly poisoned sites or to sites that have escaped poisoning by virtue of their energetic weakness. Strong poisoning blocks all the metal sites, leading to negligible production of cyclohexanone.

NH<sub>3</sub> poisoning. Ammonia is known to poison acidic sites responsible for dehydration reactions. The results presented in Table 1 indicate that there is mild poisoning of alumina sites by ammonia (cf. yield of total "dehydration products") during operations H and I, and very strong poisoning during operation J. The lowered yields of phenol due to operations H and I do indicate mild poisoning of the metal surface by ammonia, but the poisoning effect (in the presence of hydrogen) is more pronounced on the acidic sites than on the metal sites (case J), as shown by the production of large amounts of phenol even though the other products are absent. The large yield of phenol and the low yield of cyclohexanone indicate that acidic sites are necessary for the formation of cyclohexanone and not for the production of phenol.

The increased yield of phenol after operation J is attributable to the following reasons: (1) more cyclohexanol is available for dehydrogenation; (2) the hydrogen passed along competes with ammonia for the metal surface, but does not so for the alumina surface (acidic sites); (3) the water produced in dehydration converts the adsorbed ammonia molecules into NH<sub>4</sub><sup>+</sup> ions, which do not poison metal sites /4/.

## CONCLUSIONS

Some reactions proceed on multiple sites arranged in specific configurations, while some require only one or two sites. The greater the number of atoms involved in the catalytically active configuration, and the greater the requirement of a specific configuration, the more susceptible the reaction is to poisoning. We find that the susceptibility to poisoning increases in the order cyclohexanone>cyclohexane>benzene>phenol. Consequently, the active sites required for the forma-

## SIVASANKER, YEDDANAPALLI: EFFECT OF POISONS

tion of these compounds involve an increasingly greater number of multiple sites and/or more stringent steric requirements. Cyclohexanone production occurs most probably on single metal sites and is therefore unhindered by mild poisoning. The reaction also seems to require an acidic site as evidenced by the poisoning effect of ammonia.

\*

Acknowledgement. Thanks are due to the authorities of Loyola College for their cooperation and help when the above work was carried out.

## REFERENCES

1. S. Sivasanker: Ph. D. Thesis, University of Madras, 1970.
2. Y. Yamamuchi, S. Yada, S. Kudo: Abstract from Shokubai; J. Catal., 5, 198 (1966).
3. I. P. Kutanov, M. A. Syadzeltsova, B. G. Udarov, Yu. A. Eltekov: Vestsi Akad. Navuk B. SSR, Ser. Khim. Navuk, (3), 34-8 (1965); C.A., 64, 11902E (1966).
4. E. B. Maxted: Adv. Catal., 3, 129 (1951).