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Different Mechanisms of Aromatization of Trimethylpentanes over Chromia-Alumina and Platinum-Alumina Catalysts

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A study of the product distributions obtained in aromatization of trimethylpentanes and trimethylcyclopentanes over K_2O-Cr_2O_3-Al_2O_3 and nonacidic Pt-Al_2O_3 at 400–500°C has shown that different mechanisms are required for trimethylpentane aromatization on the different types of catalysts. Cyclopentanes are found to be important intermediates over nonacidic Pt-Al_2O_3 but not over K_2O-Cr_2O_3-Al_2O_3. Weak Lewis acid character is attributed to Pt to explain the ability of the otherwise nonacidic catalyst to cause ring expansion of cyclopentyl species to cyclohexyl species.

INTRODUCTION

Although considerable effort has been devoted to the understanding of the aromatization of paraffins over Cr_2O_3-Al_2O_3 type catalysts, there is still some question about the mechanism of the aromatization of substituted pentanes. Even less is known about the corresponding reaction over supported Pt catalysts because these usually contain acidic components which obscure the results by causing isomerization of the feed and/or products.

Herrington and Rideal (*1*) proposed cyclopentyl intermediates formed by 1,5-closure to explain the product distributions found when substituted pentanes were aromatized over Cr_2O_3-Al_2O_3. Pines (*2*) and other later workers (*3*) have suggested as the result of more sophisticated studies that 1,5-adsorption followed by chain lengthening via cyclopropyl and cyclobutyl intermediates and 1,6-closure of the adsorbed hexyl species better describes the reaction over this type of catalyst. This mechanism, which does not depend on cyclopentyl intermediates, seems to be generally accepted at present.

The situation is less clear with respect to supported Pt catalysts, although intermediate cyclopentanes have been often assumed by extension of the Herrington and Rideal mechanism to these catalysts. Studies with commercial-type Pt-Al_2O_3 catalysts are uninformative because the acidic character of these catalysts is known to cause skeletal isomerization of the feed as well as the products. Kazanski and co-workers (*4*, *5*) have reported the production of up to 35% cyclopentanes over 20% Pt on carbon catalysts at temperatures of 300–350°C. Except for the work of Timofeeva and co-workers (*6*), in which small amounts of 1,1,3-trimethylcyclopentane (TMCP) were reported to form during aromatization of 2,2,4-trimethylpentane (TMP) over K_2O-Cr_2O_3-Al_2O_3, cyclopentanes have not been identified as products over this type of catalyst. The small amount of the cyclopentane found by Timofeeva relative to the large amounts of olefins suggests that it is not an important intermediate unless it is very unstable over the catalyst.

The present work includes a comparison of the product distributions obtained by processing 2,2,4-TMP, 1,1,3-TMCP, and 2,4,4-trimethylpentene-2 (TMP-2) over a K_2O-Cr_2O_3-Al_2O_3 catalyst and over a nonacidic Pt-Al_2O_3 catalyst in an attempt to determine the mechanism of the aromatization reaction and the significance of cyclopentyl species as intermediates over the two types of catalysts.

EXPERIMENTAL

Although some experiments were made in a continuous operation with a 50-cc catalyst bed to permit isolation and rigorous identification of the reaction effluent, the work reported was done with a microreactor-chromatographic apparatus similar in principle to that used by Kokes, Tobin, and Emmett (*7*) and others (*8*). The reactor was the glass injection port liner in an F & M Model 810 gas chromatograph. The injection port heating elements were replaced by larger wattage heaters to permit operation to 550°C. The catalyst loading was 0.5 cc contained in a 1-inch length located at the center of the aluminum block near the thermocouple. The hydrogen carrier gas rate was 140 cc (STP)/min for a residence time of about 0.1 sec. The pressure was slightly above atmospheric due to the small pressure drop across the chromatographic column. Feed was injected into the H_2 stream through a rubber septum in 1-μl shots from a 10-μl syringe.

Mild deactivation was observed with both types of catalysts and they were regenerated whenever necessary. The results reported with each catalyst were obtained on freshly activated catalysts.

ASTM grade 2,2,4-TMP (99%) and 2,4,4-TMP-2 were obtained from the Phillips Petroleum Co. 1,1,3-TMCP (99.5%) and all other hydrocarbons were from Chemical Samples Co., Columbus, Ohio. All were analyzed by gas-liquid chromatography (GLC); the olefin contained about 2% 2,4,4-TMP-1 but no other significant impurities were found.

The 2% K_2O-, 40% Cr_2O_3-, 58% Al_2O_3 catalyst was prepared by adding a solution containing potassium nitrate and chromium oxide (CrO_3) to a slurried gel of Al_2O_3 prepared by hydrolysis of $AlCl_3$ with NH_4OH; the gel had been washed free of chloride (<0.1%) by repetitive reslurrying with distilled water. The mixed slurry was dried at 150°, calcined at 650°, ground and sieved. The material used was 40–60 mesh.

Nonacidic Pt-Al_2O_3 was prepared by the removal of chloride from a commercial-type catalyst and residual acidity was removed by treatment with a basic carbonate. The catalyst was then dried and calcined at 600°C. Pretreatment consisted of passing H_2 at 140 cc/min at 450°C for 2 hr.

The chromatographic column was 25 ft of $\frac{1}{4}$-inch tubing loaded with 80–100 mesh Chromosorb P containing 5 weight percent (wt. %) of Bentone-34 and 8 wt. % of diethylene glycol succinate (DEGS) and was operated at 90°C.

Light gases (C_1–C_3) were not separated and were grouped with the C_4–C_7 products in the calculations.

RESULTS

K_2O-Cr_2O_3-Al_2O_3

The effluent compositions when 2,2,4-TMP, 2,4,4-TMP-2, and 1,1,3-TMCP were passed over 0.44 g of K_2O-Cr_2O_3-Al_2O_3 at 100 cc (STP)/min and 500°C are shown in Table 1.

TABLE 1
COMPOSITION OF EFFLUENTS FROM REACTIONS OVER K_2O-Cr_2O_3-Al_2O_3 AT 500°C

Feed	2,2,4-TMP	1,1,3-TMCP	2,4,4-TMP-2
	Components in effluent (wt. %)		
C_1–C_7	6.6	0.8	24.4
2,2,4-TMP	74.8	0.0	0.0
1,1,3-TMCP	0.0	97.7	0.0
C_8H_{16} (Total)	16.1	0.0	66.1
C_7H_8	0.4	0.1	1.0
p-Xylene	2.1	0.4	8.5
m-Xylene	0.0	0.9	0.0
o-Xylene	0.0	0.1	0.0

It is seen that *p*-xylene is the only C_8 aromatic produced by the paraffin and olefin, and that the cyclopentane yields a mixture of xylenes high in *m*-xylene. Also, it should be noted that the cyclopentane is converted to a much lesser extent than the acyclic hydrocarbons. The olefin is converted to cracked and aromatized products with a distribution very similar to that found with the paraffin, but these reactions are about four times faster with the olefin as feed.

Nonacidic Pt-Al_2O_3

2,2,4-Trimethylpentane. The effluent compositions when 2,2,4-TMP and 1,1,3-TMCP

TABLE 2

COMPOSITION OF EFFLUENTS FROM REACTIONS OVER NONACIDIC Pt-Al_2O_3

Temp. (°C): Feed:	425° 2,2,4-TMP	425° 1,1,3-TMCP	480° 2,2,4-TMP	480° 1,1,3-TMCP
	Components in effluent (wt. %)			
C_1–C_7	21.0	17.0	52.3	41.2
2,2,4-TMP	37.4	14.6	14.9	8.2
1,1,3-TMCP	32.4	59.8	2.4	24.3
C_7H_8	1.3	0.0	12.9	7.8
p-C_8H_{10}	3.2	3.9	7.0	7.1
m-C_8H_{10}	4.7	4.7	10.5	11.0
o-C_8H_{10}	0.0	0.0	0.0	0.4

were passed through nonacidic Pt-Al_2O_3 in H_2 are shown in Table 2.

At each temperature, the paraffin and naphthene yield very similar distributions of xylenes; no ethylbenzene was made (Table 3).

The paraffin was cracked more extensively at both temperatures; hydrogenolysis (ring opening) of the naphthene and cyclization of the paraffin were also observed at both temperatures.

TABLE 3

XYLENE DISTRIBUTIONS OVER NONACIDIC Pt-Al_2O_3

Feed	Temp., (°C)	Xylene distribution		
		p-C_8H_{10}	*m*-C_8H_{10}	*o*-C_8H_{10}
2,2,4-TMP	425°	40.5	59.5	0.0
1,1,3-TMCP	425°	45.3	54.7	0.0
2,2,4-TMP	480°	40.0	60.0	0.0
1,1,3-TMCP	480°	38.4	59.4	2.2

Other trimethylpentanes. Over the nonacidic Pt-Al_2O_3 catalyst at 427°C, 2,2,3-TMP and 2,3,3-TMP were cyclicized to the same cyclopentane (1,1,2-TMCP) at up to 25% conversion and both yielded the same C_8 aromatic distribution: approximately 78% *m*-xylene and 22% *o*-xylene. With the same catalyst, 2,3,4-TMP gave an isomeric mixture of the three expected 1,2,3-TMCP at 427° and an aromatic distribution of 43% each of *para*- and *o*-xylene and 14% of *m*-xylene. Both 1,*cis*-2,*trans*-3- and 1,*trans*-2,*cis*-3-trimethylcyclopentanes gave essentially the same aromatic distribution as the 2,3,4-TMP had at this condition. The two naphthenes were apparently isomerized to *cis–trans* equilibrium as shown in Table 4.

TABLE 4

1,2,3-TMCP ISOMER DISTRIBUTION, 427°C

Starting isomer	Product isomer (%)		
	1,*trans*-2,*cis*-3	1,*cis*-2,*trans*-3	1,*cis*-2,*cis*-3
1,*cis*-2,*trans*-3	62.3	27.4	10.3
1,*trans*-2,*cis*-3	62.2	26.4	11.4

DISCUSSION

Although Herrington and Rideal (*1*) originally proposed a mechanism for aromatization of substituted pentanes over Cr_2O_3-Al_2O_3 involving cyclopentyl intermediates, the results of Pines and Csicsery (*2*) and Canning *et al.* (*3*) were used to argue persuasively for mechanisms requiring 1,5-diadsorbed species which are converted to 1,6-diadsorbed species by methyl insertions involving cyclopropane and/or cyclobutane intermediates. The large differences found in the present work in rates and C_8 aromatic distribution between the expected cyclopentane on the one hand and 2,2,4-TMP and 2,4,4-TMP-2 on the other, would seem to be conclusive proof that cyclopentanes are not intermediates in the aromatization of such paraffins over this type of catalyst. In fact, the C_8 aromatic distribution obtained from 1,1,3-TMCP is consistent with the suggestion that six-carbon chain acyclic hydrocarbons formed by ring opening are intermediates in the aromatization of C_5 naphthenes. For example, scission of the bond between the 1- and 2-carbon atoms would give a 2,5-dimethylhexyl moeity which can readily cyclicize to *p*-xylene, while scission at the less hindered 1–5 bond would give a 2,4-

dimethylhexyl species which leads to *m*-xylene.

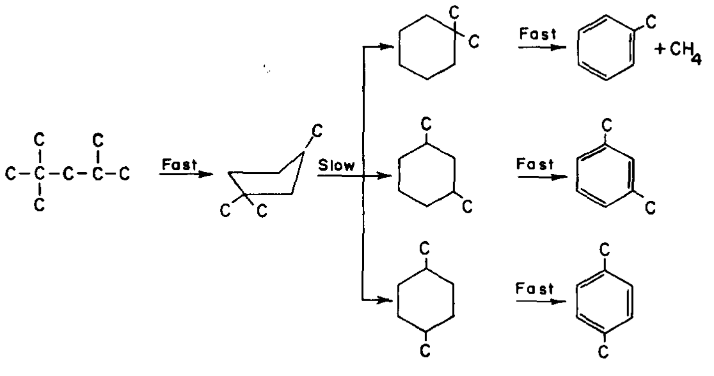
1,1,3-TMCP was not found in the product when 2,2,4-TMP was processed in a continuous plant at 500–600°C and 4:1 $H_2:C_8H_{18}$ ratio with the K_2O-Cr_2O_3-Al_2O_3 catalyst. However, Timofeeva, Shuikin, and Dobrynina (*6*) have reported that in similar experiments, very small amounts of 1,1,3-TMCP were found, while the major products were C_8 olefins and aromatics. If 1,1,3-TMCP were an important intermediate, one would expect to find considerable quantities of it since our results show it to be far more stable to the K_2O-Cr_2O_3-Al_2O_3 catalyst than either 2,2,4-TMP or 2,4,4-TMP-2.

Although the more obvious differences in behavior of oxide and supported metal catalysts are well known, the results obtained on oxide-type catalysts are sometimes used to predict the behavior and mechanism on metal catalysts when the same overall general reaction is found to occur on both types. However, our results indicate that the aromatization of substituted pentanes does not permit such extrapolation because it would appear that the mechanism and the resulting product distribution are very different on supported platinum catalysts than on Cr_2O_3-Al_2O_3.

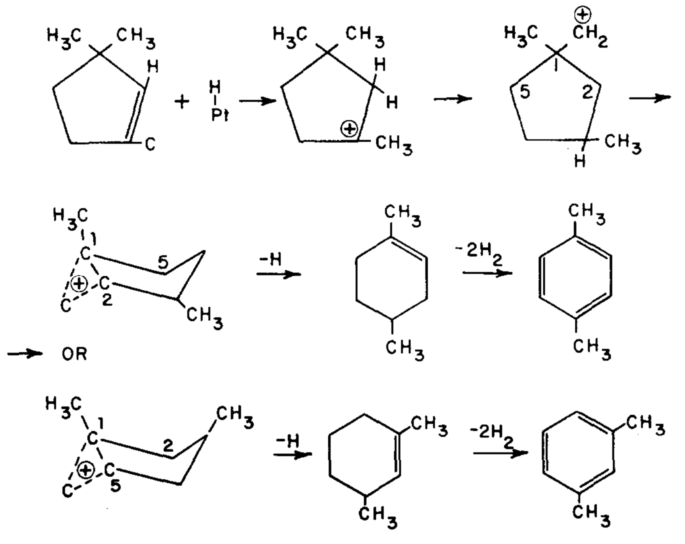
The considerable degree of acid character in commercial platinum reforming catalysts has effectively masked these differences in earlier work because the aromatic products tend toward the equilibrium distribution through acid-catalyzed isomerization; skeletal isomerization of the starting material may also occur. Accordingly, in this effort to determine the mechanism over supported Pt catalysts, the acidity function was attenuated by the removal of most of the halogen and inclusion of a basic oxide as a neutralizing agent for the remaining acidity. This catalyst is not capable of isomerizing C_8 aromatics or of causing skeletal isomerization of paraffins at our conditions. The hydrogenation–dehydrogenation function was not significantly altered, and reactions requiring this function only (such as *cis–trans* isomerization of naphthenes) were observed as usual. Aromatization of cyclohexanes was very rapid and the expected products were found in good yield; for example, 1,4-dimethylcyclohexane gave only *p*-xylene and a trace of toluene.

The close agreement of the aromatic distribution produced over this catalyst from 2,2,4-TMP and from 1,1,3-TMCP suggests that the cyclopentane is an important intermediate over this catalyst. The rate of aromatization of 2,2,4-TMP is about the same as the rate for the 1,1,3-TMCP, which indicates that the ring formation is probably not the rate-determining step. Since cyclohexanes are converted to aromatics very rapidly at these conditions over this catalyst, the slow step appears to be ring expansion of the cyclopentane (Scheme 1).

Although it is conceivable that the ring expansion occurs on unneutralized acid sites on the alumina, it is worth considering the possibility that platinum may be the active catalyst for this reaction. Barron *et al.* (*9*)



SCHEME 1



Scheme 2

and others (*10*) have observed isomerization of paraffins over platinum films; in addition, Barron studied the aromatization of 1,1,3-TMCP and obtained a C_8 aromatic distribution of 65% *m*-xylene and 35% *p*-xylene at 300–330°C, which is similar to that reported here. In view of the ease with which ring expansion occurs with acidic catalysts, it is tempting to suggest that the platinum acts as an electron sink for adsorbed cyclopentenes, creating electron-deficient species which can rearrange in a manner analogous to carbonium ions (*11*) (Scheme 2).

Removal of cyclohexenes by rapid aromatization is a strong driving force for the sequence of reactions to the right. The product xylene is determined by whether a geminal methyl inserts between the 1- and 2-carbon atoms or the 1 and 5. The slight excess (60:40) of *m*-xylene over *p*-xylene reflects a slight steric interference by the 3-methyl group to 1,2-insertion which leads to *p*-xylene. Insertion of the 3-methyl can lead to 1,1-dimethylcyclohexenes which are rapidly converted to toluene; the small amounts of *o*-xylene sometimes found are probably also produced from these intermediates. At the lower temperature, where aromatic demethylation is slight, toluene is a minor product relative to *m*- and *p*-xylenes. This may be due to a stabilizing effect of the methyl group on the cyclopropyl group formed as a transition state during insertion of a geminally substituted methyl group.

Barron and co-workers (*9*) proposed that aromatization of 1,1,3-TMCP on Pt films involved ring expansion by means of an α, α, γ, γ-tetradsorbed species (*d–p*) π-bonded to metal atoms. Such a mechanism is not excluded by the present results but a mechanism requiring removal of four hydrogens from two methyl groups would seem to be less reasonable than the present one which involves ring dehydrogenation followed by a 1,4-intramolecular H transfer and methyl insertion via an electron-deficient bicyclohexyl species. Barron discarded the possibility of a cyclopropane intermediate with the unsupported statement that adsorbed cyclopropane species cannot be formed on metal surfaces.

Overall, the suggested mechanism for metal-catalyzed ring expansion can be thought of as formation of an electron-deficient cyclopentyl species by electron withdrawal from a half-hydrogenated cyclopentene by Pt, followed by either a 1,4-hydrogen shift or a series of 1,2-hydrogen shifts and ring insertion of a methyl carbon via a bicyclohexyl intermediate to form a half-hydrogenated cyclohexene which is quickly dehydrogenated to an aromatic.

It is not proposed that aromatization

over commercial acidic Pt-alumina necessarily occurs in the manner discussed above because the acidic sites present on such a catalyst are much more active for ring expansion than platinum. However, the difference may well be of degree rather than kind, in which case platinum is behaving as a Lewis acid.

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