

Mechanism of Dehydrocyclization of n-Alkanes over Platinum-Alumina Catalysts

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ABSTRACT

In order to examine whether the metal function or the acid function is "critical" for the reforming reaction, the dehydrocyclization of n-hexane, n-heptane and n-octane was carried out over acidic and non acidic platinum-alumina catalysts. It is concluded that the metal function is the "critical" parameter with the C₆ and C₇ alkanes whereas both the metal and acid could be important with n-octane.

INTRODUCTION

There has been much discussion as to whether the reforming of n-alkanes to aromatics follows the classical bifunctional mechanism involving both the metal and the acid sites [1] or a monofunctional mechanism involving only the metallic sites [2,3]. In a recent study, Shum et al. [4] identified the metal function as the "critical" parameter in reforming catalysts. Their reasoning was based on studies using a chlorine-free (non-acidic) model catalyst and n-hexane as the feedstock. As "real" catalysts contain chloride (acidity) and also are used to aromatize other hydrocarbons such as C₇ and C₈ alkanes, it was decided to verify whether the conclusions of Shum et al. [4] are also valid for these catalysts and hydrocarbons. Also, Shum et al. [4] used a mechanical mixture of a non-acidic platinum catalyst and alumina, with which the effect of acid centres will not be noticeable because of the large distances separating the acid and the metal sites and the consequent difficulties in transporting the olefins formed on the metal sites to the acid centres. Therefore, we used a commercial platinum-alumina-chloride catalyst and its sodium-poisoned analogue in the reforming of n-hexane, n-heptane and n-octane. Similar studies using acidic and potassium-doped catalysts have been carried out earlier by Davis [5] and Davis and Venuto [6] using n- and iso-octane and -nonane as feedstocks. However, no comparative data examining the effect of carbon number on the dehydrocyclization ability of acidic and non-acidic catalysts are available.

EXPERIMENTAL

The acidic catalyst (A) was a commercial platinum–alumina catalyst containing 0.6% platinum and 1.0% chlorine. The non-acidic catalyst (NA) was prepared from catalyst A by impregnation with a solution of sodium carbonate to give 1% Na₂O in the catalyst. The feeds (n-hexane, n-heptane and n-octane) were >99% pure and contained <1.0 ppm sulphur. The reactions were carried out at atmospheric pressure using 2 g of fresh catalyst without pre-sulphidation. The catalyst was reduced at 753 K for 2 h prior to introduction of the feed. The reaction conditions were: temperature, 733 K; WHSV = 2 h⁻¹; and hydrogen:hydrocarbon molar ratio = 6.

Product analysis was carried out using a capillary column (Hewlett-Packard PNA Analyser).

RESULTS AND DISCUSSION

The experimental results are presented in Table 1.

n-Hexane

The acidic and non-acidic catalysts (A and NA) produce nearly identical amounts of benzene after both 1 h and 4 h on-stream. This result confirms the

TABLE 1

Reforming of n-alkanes on acidic and non-acidic platinum–alumina catalysts*

Feed	Catalyst	Time-on-stream (h)	Product distribution (wt.%)						
			Aromatics			Iso-products**		Naphthenes**	
			C ₆	C ₇	C ₈			5-membered ring	6-membered ring
n-C ₆	A	1	11.8	0.6	1.8	16.5	7.8	—	
		4	7.4	0.5	1.4	11.1	7.5	—	
	NA	1	12.9	0.2	—	7.7	9.6	—	
		4	9.9	—	—	3.4	8.1	—	
n-C ₇	A	1	1.6	13.6	1.0	10.9	2.8	2.0	
		4	0.9	7.7	0.6	9.5	2.7	0.8	
	NA	1	2.2	12.1	—	2.2	2.3	4.1	
		4	1.1	9.8	—	1.8	2.0	3.7	
n-C ₈	A	1	1.2	3.2	17.0	8.0	1.6	1.0	
		4	0.8	2.2	9.6	7.6	1.2	0.8	
	NA	1	1.4	1.8	10.0	1.8	1.1	2.0	
		4	1.0	1.0	8.3	1.6	2.0	2.0	

*Conditions: $P = 1$ atm, $T = 733$ K, $\text{WHSV} = 2 \text{ h}^{-1}$, hydrogen:hydrocarbon molar ratio = 6.

**Those having the same carbon number as the feed.

TABLE 2

Distribution of isomers in the C₈ aromatic fraction*

Catalyst	Time-on-stream	Total C ₈ aromatics	Relative mol%			
			Ethylbenzene	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene
A	1	17.0	31.8	29.7	25.3	13.2
	4	9.6	25.2	32.4	28.4	14.0
NA	1	10.0	53.9	33.4	7.4	5.3
	4	8.3	51.0	32.9	9.8	6.3

*Feed, n-octane; conditions as in Table 1.

observation of Shum et al. [4] that metal sites are the "critical" parameter, at least with n-hexane. However, in contrast to their observations [4], in this work considerable amounts of methylcyclopentane were obtained over both catalysts. As the non-acidic catalyst produces more methylcyclopentane than the acidic catalyst, it is likely that the methylcyclopentane was formed directly on the metal sites by a 1,5 ring closure rather than by an acid-catalyzed isomerization of cyclohexane. Also, cyclohexane was not detected in the product. The metal-catalyzed interconversion of five- and six-membered rings is reported to proceed by a ring-opening step, leading to a n-alkene [3].

n-Heptane

n-Heptane gave very similar results to n-hexane. The acidic and non-acidic catalysts have nearly identical dehydrocyclization activity. Dimethylcyclopentanes (mostly 1,2-dimethylcyclopentane), ethylcyclopentane and methylcyclohexane are also present in the product. Although 1,2-dimethylcyclopentane can be formed by the isomerization of methylcyclohexane over acid sites, it is difficult to explain the formation of ethylcyclopentane from methylcyclohexane. The major route to ethylcyclopentane would be direct 1,5 ring closure of n-heptane.

n-Octane

The dehydrocyclization activity of the acidic catalyst (Table 1) is greater than that of the non-acidic catalyst, especially after 1 h on-stream (17% for catalyst A vs. 10% for catalyst NA). However, after 4 h the results are similar for the two catalysts. Apparently, in the initial stages at least, acid sites promote the dehydrocyclization of n-octane. This implies that during the commercial reforming of full-range naphtha or the C₈ cut for xylenes, the acid sites also play a role in the DHC reaction.

The degradation of the C₈ aromatics is presented in Table 2. The major components are ethylbenzene and *o*-xylene, which are formed directly by the 1,6 ring closure of n-octane.

More *p*- and *m*-xylene are formed with catalyst A than NA. These isomers can be formed by the 1,6 ring closure of methylheptanes. More isooctane is produced on the acidic catalyst and therefore more *p*- and *m*-xylene are formed. The larger amount of ethylbenzene obtained with the NA catalyst (Table 2) is due to the greater probability of occurrence of 1,6 ring closure between the C-1 and C-6 carbon atoms than between the C-2 and C-7 carbon atoms. The near identical amounts of ethylbenzene and *o*-xylene observed with the acidic catalyst are a consequence of the acid-catalyzed interconversions between these C₈ aromatics. Such interconversions are not likely with the non-acidic catalyst.

Examination of the naphthenic fraction (Table 1) shows the presence of both C₅ and C₆ naphthenes. The prominent naphthenes are 1,2-dimethylcyclohexane, ethylcyclohexane, isopropylcyclopentane and 1-ethyl-2-methylcyclopentane. It is possible that some of the cyclopentanes are formed by the isomerization of cyclohexanes. However, the presence of isopropylcyclopentane can only be explained by invoking a 1,5 ring closure between the C-1 and C-5 carbon atoms. Such a ring closure will produce n-propylcyclopentane, which can be expected to isomerize rapidly to isopropylcyclopentane.

CONCLUSIONS

Based on the above results, it is concluded that in general the observation of Shum et al. [4] that the metal function is the "critical" parameter of a reforming catalyst is valid for the C₆ and C₇ alkanes. With n-octane, the acid centres are also important. Although the results support the 1,6 cyclization mechanism of Davis [5] and Davis and Venuto [6] with n-octane, it appears that 1,5 ring closure is also an important reaction with n-hexane and n-heptane.

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