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Paraffin Dehydrocyclization

VII. Comparison of Aromatic Distribution from *n*-Octane Conversion over Pt at Atmospheric and 200 Psig

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A similar C_8-aromatic distribution was obtained for the dehydrocyclization of *n*-octane at atmospheric pressure and at a pressure of 200 psig. Furthermore, the aromatic distribution changed in a similar manner for both pressures to favor *ortho*-xylene when tin was added to the Pt catalyst. The aromatics were those expected for a direct six-carbon ring formation.

INTRODUCTION

The aromatic product distribution for the dehydrocyclization of paraffins has been widely investigated (*1*). These studies have included both metal and metal oxide catalysts. With few exceptions (*2*), these studies have been interpreted to favor a direct C_6-ring formation. However, most of these dehydrocyclization studies have been carried out at atmospheric pressure.

In the reforming of naphthas, a total pressure of 200–400 psig is normally used. Few results of dehydrocyclization have been reported for these pressures and it is not possible to decide whether the results obtained at atmospheric pressure can be extrapolated to higher pressures used in the commercial operation. In this paper, we report the results of a study of the aromatic distribution for *n*-octane dehydrocyclization at 200 psig using Pt on nonacidic alumnia catalysts and compare the results with those obtained at atmospheric pressure.

EXPERIMENTAL METHODS

Methods

The atmospheric pressure runs were carried out in an apparatus previously described (*2*). The higher pressure runs were done in a single pass reactor in which the liquid hydrocarbon was charged by a piston pump and mixed with hydrogen at the inlet of the preheater section. The catalyst, 5 ml of 8–14 mesh pellets, was supported on a stainless steel fritted disc in a stainless steel reactor with 40 ml of quartz chips placed above the catalyst bed to act as a preheater. The reactor was heated by an electrical furnace with automatic temperature control. The temperature was measured in the center of the catalyst bed. Liquid samples were collected in a dropout pot at the operating pressure.

Catalysts

Pt–Sn–Al_2O_3–K. "Nonacidic" alumina was calcined at 550°C for 5 hr. The alumina was impregnated with an acetone solution of chloroplatinic acid and $SnCl_2 \cdot 2H_2O$ (Pt:Sn = 1:4) to give a catalyst with 0.6% Pt. The catalyst was dried in air and reduced at 482°C in flowing hydrogen. The chlorine was removed by washing the reduced catalyst with NH_4OH (*2*). A second Pt–Sn catalyst was prepared by the same procedure except the Pt:Sn ratio was 4:1 rather than 1:4.

Rh-Sn-Cl-Al_2O_3*-K.* $RhCl_3$ (0.48 g) and 1.5 g $SnCl_2 \cdot 2H_2O$ were dissolved in 100 ml of ethanol with the aid of 1 ml of conc HCl. Calcined (600°C in air) nonacidic alumina (30 g) was added to the solution and the ethanol was removed by evaporation.

Pt-Cl-Al_2O_3. A commercial alumina from Continental Oil was impregnated with an aqueous solution of chloroplatinic acid to give a final catalyst with 0.6% Pt.

RESULTS

The C_8-aromatic distribution for the dehydrocyclization of *n*-octane over Pt supported on an acidic alumina at 50 psig total pressure is shown in Fig. 1. Over this catalyst, the total conversion to C_8-aromatics decreased with time on stream but the aromatic selectivity did not change. The C_8-aromatics not allowed by direct C_6-ring formation, *m*- and *p*-xylene, comprise nearly 50% of the C_8-aromatics formed and most likely result from the cyclization of methylheptanes formed by a dual functional metal–acid catalyzed reaction. A similar C_8-aromatic distribution was obtained at 200 psig with the same catalyst.

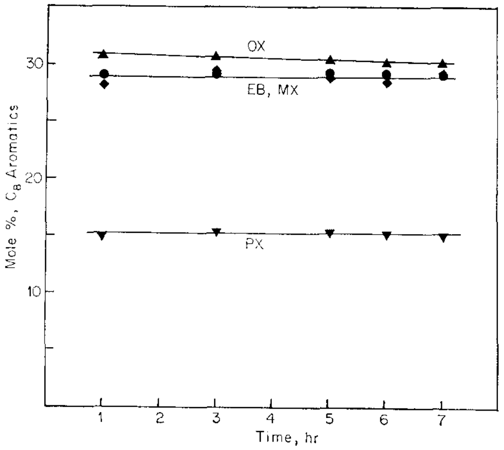


FIG. 1. C_8-Aromatic distribution from the dehydrocyclization of *n*-octane over Pt on acidic alumina (50 psig total pressure; H_2:hydrocarbon = 10:1; *T*, 482°C).

The results using a "nonacidic" alumina support differ greatly from those using an acidic alumina support. Over two Pt–Sn catalysts and a Rh–Sn catalyst 90% or more of the C_8-aromatics are those expected from a direct six-carbon ring formation. Results for the conversion of *n*-octane and then a run with a 1:1 mixture of *n*-octane and 3-methylheptane over a Pt–Sn catalyst (Pt:Sn = 1:4) at 200 psig are shown in Fig. 2. At an early time on stream about 55% of the C_8-aromatics were *m*- and *p*-xylene; however after 7 hr on stream, these aromatics had decreased to less than 10% of the total C_8-aromatics. At later times on stream the ratio *ortho*-xylene:ethylbenzene (OX:EB) becomes about 2:1. The traces of benzene and toluene in the liquid products could not significantly alter the OX:EB ratio for the 200 psig run. This ratio of OX:EB is about the same as that obtained over a Pt–Sn catalyst with a 1:4 loading ratio at atmospheric pressure with no added hydrogen (Table 1). Hence, the OX:EB aromatic selectivity is the same at atmospheric and 200 psig with hydrogen. After treating the catalyst with hydrogen overnight at 482°C, a second run was made with a 1:1 molar mixture of *n*-octane and 3-methylheptane. Again, after 4 hr on

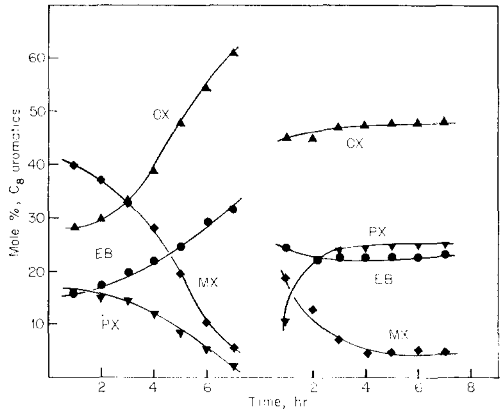


FIG. 2. C_8-Aromatic distribution from the conversion of *n*-octane (left) and then a 1:1 mole ratio mixture of *n*-octane:3-methylheptane over a Pt:Sn (1:4) on nonacidic alumina catalyst (200 psig; H_2:hydrocarbon = 10:1; *T*, 482°C).

TABLE 1

Conversion of *n*-Octane and 3-Methylheptane over a Pt– and Pt–Sn–Al_2O_3–K Catalyst[a]

Catalyst	Charge	Time-on-stream (min)	Conversion (mole%)	C_8-Aromatic (%)			
				EB	OX	MX	PX
Pt–	Octane	36	48	48	49	1.9	1.0
		78	35	49	49	1.3	0.7
		120	23	48	49	1.6	0.8
		160	21	48	50	1.2	1.0
		201	18	47	51	0.7	0.7
Pt–Sn–	Octane	52	84	32	59	6.1	2.7
		103	82	32	59	7.1	3.0
		166	79	33	59	5.0	2.4
		222	82	34	← 66 →		
Pt–Sn–	3-Methyl heptane	40	80	14	28	7.8	51
		93	72	15	27	6.0	52
		145	74	15	28	6.8	50

[a] 1 Pt:4 Sn; 482°C; LHSV 0.32; 1 atm pressure; no added hydrogen.

stream the aromatics expected from direct C_6-ring formation comprise 95% of the total C_8-aromatics. Neglecting the MX, we calculate an aromatic distribution: OX, 49.5; PX, 26.4; and EB, 24.2%. In Table 1 we see that the OX:PX:EB ratio from 3-methylheptane dehydrocyclization at 1 atm over a Pt–Sn (1:4 loading) catalyst was approximately 2:1:1 and that the two paraffins underwent equal conversion to C_8-aromatics when passed over the catalyst as an equal molar mixture (*4*). If we assume a similar aromatic selectivity for the 3-methylheptane at 200 psig and the 2:1 OX:EB from *n*-octane we calculate an aromatic distribution of: OX, 44.7; PX, 26.4; EB, 28.9%. This calculated distribution is in good agreement with the experimental results and is consistent with the same reaction pathway at atmospheric pressure and 200 psig.

The results in Fig. 3 are for the dehydrocyclization of *n*-octane at 200 psig over a Pt:Sn = 4:1 loading. An obvious difference from the Pt:Sn = 1:4 catalyst is that even at the early time on stream, only a small amount of MX and PX are formed. But more important is the difference in the relative amounts of the OX and EB isomers; OX:EB is approximately 2:1 for the 1 Pt:4 Sn and 1.05 for the 4 Pt:1 Sn catalyst. Thus, with increasing tin concentration the catalyst becomes more selective for the formation of OX; a similar

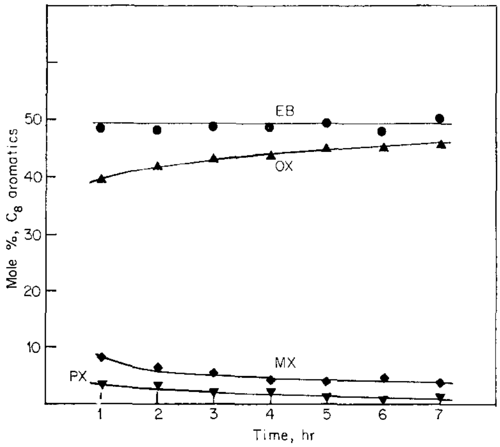


FIG. 3. C_8-Aromatic distribution from the conversion of *n*-octane over a Pt:Sn (4:1) on nonacidic alumina catalyst (200 psig; H_2:hydrocarbon = 10:1; *T*, 482°C).

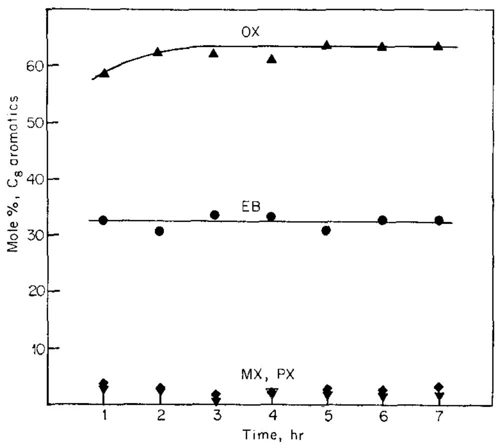


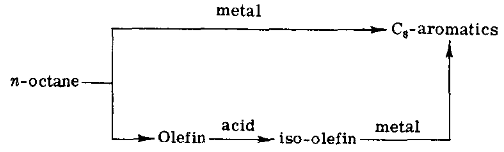
FIG. 4. C_8-Aromatics from the conversion of *n*-octane over Rh:Sn (1:3) on nonacidic alumina (200 psig; H_2:hydrocarbon = 10:1; *T*, 482°C).

result was observed for the dehydrocyclization of *n*-octane at 1 atm.

Results for the dehydrocyclization of *n*-octane over a Rh–Sn = 1:3 catalyst at 200 psig are presented in Fig. 4. The amount of MX and PX is less than 5% of the C_8-aromatic and the OX:EB ratio is about 2:1. A 0.6% Rh–Al_2O_3–K catalyst without Sn could not be used under the same experimental conditions since it was so active for hydrogenolysis of *n*-octane to methane that the temperature could not be controlled and nearly complete conversion of the *n*-octane to methane occurred at a temperature of 600°C rather than 483°C.

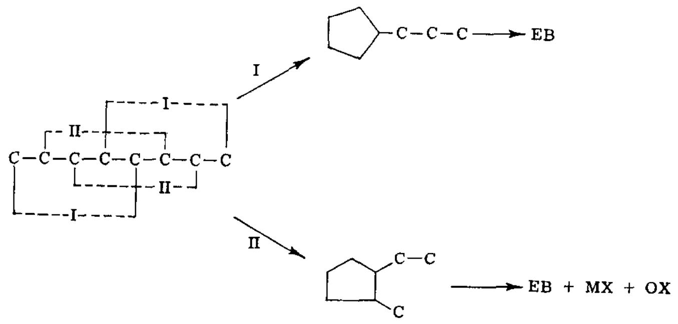
DISCUSSION

The aromatic distribution over the Pt–Al_2O_3–A catalyst is what would be expected for the dual functional metal–acid reaction pathway:



However, we have not experimentally eliminated the isomerization of the aromatic by the acid function after formation on the metal function. But over the metal on "nonacidic" alumina the aromatics, at least after a few hours on stream, are the ones expected for a direct cyclization to C_6-carbon rings, EB and OX.

It has been proposed that cyclization over Pt occurs by a C_5 as well as C_6-ring formation. For *n*-octane, C_5 cyclization would lead to



For reaction pathway II, we would expect at least as much MX as OX to be formed and, due to the steric effect of the methyl group, probably more MX than OX. Over the Pt:Sn = 4:1 the amount of MX is about 5% of the C_8-aromatic but about 45% of OX is present. Thus, the contribution of C_5-carbon ring intermediate to xylene formation must be small. Since there is little difference between pathways I and II, we expect the contribution of a C_5-carbon ring intermediate to be small for EB formation as well.

For dehydrocyclization of *n*-octane at

atmospheric pressure Davis *et al.* (*3*) found that the EB:OX distribution changed to favor OX at low Pt loading and when Pt was promoted with Sn, thiophene, or olefins. A similar change in selectivity is observed at 200 psig. The EB/OX ratio is 1.05 for the Pt:Sn = 4:1 but changes to 0.5 for Pt:Sn = 1:4. Thus, the aromatic selectivity, as well as the cyclization pathway for aromatics, remains the same at 200 psig as it was at 1 atm.

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