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Paraffin Dehydrocyclization

VI. The Influence of Metal and Gaseous Promoters on the Aromatic Selectivity

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The addition of tin to a Pt-Al_2O_3 catalyst greatly enhanced the activity and/or decreased the rate of deactivation for the dehydrocyclization of alkanes. There appeared to be an optimum ratio of Pt:Sn = 1:4 for a 0.6% Pt catalyst. The addition of Sn, Ag, or Cu to a Rh-Al_2O_3 catalyst had a similar effect with Sn showing the greatest improvement. The addition of tin altered the ethylbenzene (EB):*ortho*-xylene (OX) ratio from 1:1 for pure 0.6% Pt to EB:OX = 1:2 for the Pt-Sn (1:4) catalyst. The addition of thiophene and the dehydrocyclization of the octenes or octynes also changed the EB:OX ratio to favor the OX in a similar manner. The addition of tin or thiophene greatly decreased the second cyclization to the bicyclic aromatic; e.g., the addition of tin produced a tenfold decrease in the indan (bicyclic)/total aromatic ratio. The results are interpreted to be consistent with a selectivity that is determined by an electronic factor.

INTRODUCTION

In the 1920's, Taylor taught the concept of "active sites" as the seat of activity for heterogeneous catalysts (*1*). Since then, many data have been obtained which were interpreted to support this viewpoint (*2*). More recently, catalytic activity has been attributed to the electronic character of the solid and many studies have attempted to relate catalytic activity to *d*-band holes for metals and *n*- or *p*-type conductivity for semiconductors (*3*). The question of a geometric or electronic effect has still not been resolved. In fact, Fisher (*4*) in a recent review concluded that "no one yet claims to be able to relate specific catalytic activity of metals to such fundamental properties as the electronic spectrum of the solid or the surface structure." The use of a high surface area support for metal catalysts and preparative methods to provide very small metal crystallites increases the complexity beyond present-day descriptive models. It is realized that attempts to relate catalytic behavior to either surface geometry or electronic structure will ultimately fail since it is unlikely that the surface geometry and electronic structure are independent. Still, light presents a dual nature and it has been treated as having either wave or particle properties depending on the particular situation. Hence, it seems appropriate to treat metal catalytic activity as a surface structure or electronic property according to the experimental results at hand.

Recently bimetallic Pt-Re catalysts were introduced for commercial use in naphtha reforming (*5*). Subsequently, Sinfelt (*6*) reported catalytic properties for supported "bimetallic cluster" catalysts where the addition of increasing amounts of copper to the osmium or ruthenium catalysts altered the dehydrogenation and hydrogenolysis activity in a different manner. Sinfelt did not eliminate either the surface or electronic structure as being solely responsible for catalytic activity. Somorjai (*7*) presented data which showed that *n*-heptane dehydrocyclization is very sensitive to the atomic structure of the platinum surface and occurs most readily on stepped surfaces. The reaction was much faster on a stepped Pt (111) surface than on a Pt (100) stepped surface. Somorjai found that "there is a strong correlation between the atomic structure of the surface and the reactivity of that surface in the dehydrocyclization surface reaction." On the other hand, Levy and Boudart (*8*) have reported that the catalytic property of tungsten was altered by conversion to the tungsten carbide and that the carbide catalyst resembled platinum for the conversion of 2,2-dimethylpropane. Boudart as well as subsequent investigators have attributed this to a change in the electron distributions of tungsten by the addition of carbon (*9*). The electronic effect may be influenced by the support (*10*). This was elegantly set forth by Professor Bond (*11*) who stated, "The explanation proposed is that very small supported metal crystallites become electron deficient, and hence electronically similar to the metal to their left in the Periodic Table, by donation of electrons from metal to the support. Thus sufficiently small particles may have their catalytic properties transmuted, so that gold resembles platinum, platinum resembles iridium and palladium resembles rhodium."

We have observed that the aromatic isomer distribution from the dehydrocyclization of alkanes depended on the metal loading for Pt catalysts (*12*) and attributed this to an electronic transmutation in the fashion of Bond. In this report we present results that show that the aromatic selectivity may be altered by "promoting" platinum with other "metals" or with gaseous compounds.

EXPERIMENTAL

Catalysts

Pt-Al_2O_3*-K*. Nonacidic alumina, prepared by precipitation from potassium aluminate with CO_2, was impregnated with aqueous chloroplatinic acid. The catalyst was reduced in hydrogen at 482°C, then washed twice with 5% ammonia to remove chlorine (*13*).

Pt-Sn-Cl-Al_2O_3*-A*. Alumina, from the hydrolysis of aluminum isopropoxide, was impregnated with chloroplatinic acid, dried at 120°C, then impregnated with an acetone solution of $SnCl_2 \cdot 2H_2O$. The catalyst, after reduction at 500°C, contained 0.6% Pt (Pt:Sn = 1:4). Other platinum–tin catalysts were prepared in a similar manner or by forming the chloroplatinic acid–stannous chloride complex in acetone before impregnation with the exception that a different Pt-Sn loading or support was used.

Rh-Cl-Al_2O_3*-K*. K_3RhCl_6, dissolved in water acidified with HCl to effect solution, was added to nonacidic alumina and the catalyst dried at 120°C.

Rh-Sn-Cl-Al_2O_3*-K*. $RhCl_3$ and $SnCl_2 \cdot 2H_2O$ were dissolved in absolute ethanol (concentrated HCl was added to effect solution) and added to nonacidic alumina. The catalyst contained 0.6% Rh and Rh:Sn = 1:4.

Rh-Ag-Cl-Al_2O_3*-K*. Sufficient $AgNO_3$ to give a Rh:Ag ratio of 1:4 was dissolved in water and then added to the Rh-Cl-Al_2O_3-K catalyst.

Rh-Cu-Cl-Al_2O_3*-K*. Same as the Rh-Ag catalyst except use $Cu(NO_3)_2$.

Co-Sn-Cl-SiO_2. Cobalt nitrate was dissolved in water and added to SiO_2 to give 0.6% Co. Stannous chloride in acetone was added to the Co catalyst, after drying at 120°C, to give a Co:Sn ratio of 1:4.

Procedure

The catalyst was reduced in flowing hydrogen (5 cm^3/min) at 550°C unless noted otherwise in Results. The reactant was added by a syringe pump and was heated to the reaction temperature by passing over approximately 30 ml of quartz chips placed above the 5-ml catalyst bed. Reaction conditions were (unless otherwise noted): 482°C, atmospheric pressure, LHSV = 0.32, no added carrier gas. Liquid products were collected after passing through a water condenser. Liquid products were analyzed by glc for conversion using a Carbowax 20M column and for aromatic isomer distribution using a Bentone 3,4-diisodecylphthalate column.

RESULTS

It was observed that a Pt-Al_2O_3 catalyst containing chlorine, added in the chloroplatinic acid, aged more slowly during *n*-heptane dehydrocyclization than one which had the chlorine removed by NH_3 washing (*14*). However, this chlorine was slowly lost during the reaction and apparently could not be replaced in the same form as it was initially. This led us to try to replace chlorine ligands with more stable "ligands," another metal. A Pt-Sn catalyst was prepared by impregnating alumina with an acetone solution containing $(PtSnCl_8)^{2-}$ with excess $SnCl_2$ ($SnCl_2$: $PtCl_6^{2-}$ = 4). The impregnated Pt-Sn catalyst had the characteristic red–orange color of the complex whereas a catalyst prepared by impregnation with H_2PtCl_6 was pale yellow. A similar red–orange complex was formed when a catalyst impregnated first with H_2PtCl_6 was dried at 120°C and then impregnated with $SnCl_2$.

The results for the conversion of *n*-octane dehydrocyclization over a Pt-Al_2O_3 and Pt-Sn-Al_2O_3 catalysts are shown in Fig. 1. It is apparent that the Pt-Sn-Al_2O_3 lost dehydrocyclization activity much more slowly than the Pt-Al_2O_3 catalyst. These runs are directly comparable; the Pt-Sn catalyst was prepared by adding $SnCl_2$ to a portion of the Pt-Cl-Al_2O_3 catalyst. The resulting Pt-Sn catalyst did not lose chlorine during the 50-hr run. If this Pt-Sn catalyst was reduced in H_2 and then washed with ammonium hydroxide to remove the chlorine, it was still more active than Pt alone and maintained the superior activity with time stream (Table 1). There was an optimum Pt:Sn ratio for the 0.6% Pt catalyst at approximately 4 Sn/Pt atom (Fig. 2).

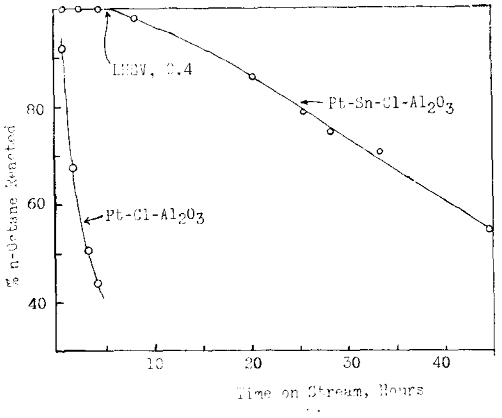


FIG. 1. Conversion of *n*-octane over Pt and Pt-Sn-Al_2O_3-A catalysts. (482°C; LHSV = 0.3; atmospheric pressure; no added hydrogen).

In addition to improving the aging character of Pt-Al_2O_3 catalysts, the addition of tin also altered the aromatic selectivity for *n*-octane dehydrocyclization. Results for the aromatic selectivity are shown in Table 1 for several different Pt-Sn and Pt on nonacidic supports. For a catalyst prepared by impregnation with the $PtSnCl_8^{2-}$ complex the ethylbenzene:*ortho*-xylene ratio was approximately 1:1.9. Preparing a catalyst by impregnation with the $PtSnCl_8^{2-}$ complex, then removing the chlorine by washing with ammonia after reduction to remove the chlorine did not alter the aromatic selectivity. However, a platinum catalyst that was reduced, then washed with ammonia to remove chloride, and then impregnated with $SnCl_2$ to give a Pt:Sn ratio of 1:4 was less selective for *ortho*-xylene than one from the $PtSnCl_8^{2-}$ complex; the ethylbenzene:*ortho*-xylene ratio was approximately 1:1.13. Without tin the ratio was 1:1. A Pt:Sn ratio of 1:3

TABLE 1

Aromatic Distribution from *n*-Octane Dehydrocyclization over Pt-Sn Catalysts[a]

Catalyst	Time-on-stream (min)	Conversion to aromatic (mol%)	C_8-aromatic (mol%)			
			EB	OX	MX	PX
$Pt-Al_2O_3$	36	48	48.3	48.8	1.9	1.0
	78	35	49.0	49.0	1.3	0.7
	120	23	48.2	49.4	1.6	0.8
	160	21	48.1	49.7	1.2	1.0
	201	18	47.4	51.2	0.7	0.7
$Pt-Sn-Al_2O_3-K$[b]	52	84	32.2	59.0	6.1	2.7
	103	82	31.5	58.5	7.1	3.0
	166	79	33.4	59.2	5.0	2.4
	222	82	33.9		66.1	
$Pt-Sn-Al_2O_3-K$[c]	45	90	32.1	57.7	6.9	3.4
	103	88	32.0		68.0	
	158	88	32.9	58.8	5.6	3.0
	218	89	34.1		65.9	
	248	88	33.3	58.0	6.0	2.9
$Pt-Sn-Al_2O_3-K$[d]	41	25	43.6	52.3	2.3	1.4
	80	16	45.4	51.2	2.0	1.2
	135	13	45.2	51.3	2.0	1.6
$Pt-Sn-Al_2O_3-K$[e]	40	87	40.1		59.9	
	87	87	39.1		60.9	
	139	91	37.7		62 3	
	187	92	37.4		62.6	
	242	90	38.3		61.7	
$Pt-Sn-Al_2O_3-K$[f]	35	63	36.6	59.5	2.7	1.2
	80	59	37.9	58.2	2.4	1.6
	125	56	40.2	53.7	4.1	2.1
Pt-Sn-Alon-C[g]	37	37	39.2	57.4	2.6	0.9
	77	40	38.8	54.6	4.3	2.3
	45	62	46.1[i]	47.6	4.5	1.9
$Pt-La-Al_2O_3$[h]	88	40	46.1[i]	48.2	3.9	1.8

[a] 482°C, LHSV = 0.32, atmospheric pressure.

[b] Nonacidic alumina was impregnated with a $PtSnCl_8^{2-}$ complex in acetone.

[c] A portion of the above catalyst was reduced at 482°C in hydrogen, washed with 2% ammonium hydroxide, reduced at 482°C, and washed with 2% ammonium hydroxide.

[d] $Pt-Al_2O_3-K$ was reduced at 482°C, washed twice with 2% NH_4OH, dried at 120°C, then impregnated with an acetone solution of $SnCl_2 \cdot 2H_2O$.

[e] Nonacidic alumina was impregnated with an acetone solution of the $Pt_3Sn_8Cl_{24}^{4-}$ (prepared according to *Inorg. Chem.* **5**, 109 (1966)).

[f] An acetone solution of the 1,5-cyclooctadiene adduct of the Pt-Sn-Cl complex was used to impregnate nonacidic alumina.

[g] Alon-C was impregnated with an acetone solution of the $PtSnCl_8^{2-}$ complex.

[h] A 0.6% Pt on nonacidic alumina was impregnated with $LaCl_3$ solution to give La:Pt = 1:4.

[i] Ethylbenzene may have been a higher percentage since benzene and toluene were formed with this catalyst.

was less selective for *ortho*-xylene than one with a Pt:Sn ratio of 1:4 but still more selective than the Pt catalyst. The addition of $LaCl_3$ (Pt:La = 1:4) did not alter the aromatic selectivity from that of Pt alone.

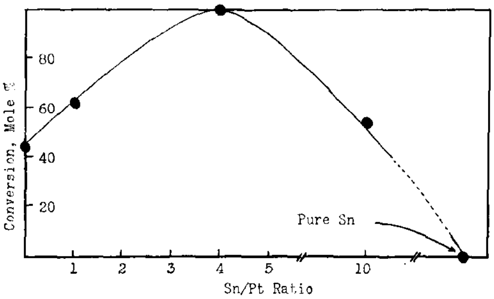


FIG. 2. Conversion of *n*-octane over an 0.6% $Pt-Al_2O_3$ catalyst with an increasing amount of Sn as $SnCl_2$.

In Fig. 3 the dehydrocyclization activities for $Rh-Al_2O_3$ and Rh-Ag-, Rh-Sn, and Rh-Cu bimetallic catalysts are presented. All three bimetallic catalysts aged more slowly than the rhodium catalyst. The most effective metal promoter was tin which was added as the Rh-Sn anion complex; silver and copper were added by a second impregnation and may be more effective if both metals were added as a bimetallic complex ion.

Not all metals "promoted" the platinum catalyst; the addition of Au (1 Pt:4 Au) to the platinum catalyst decreased the dehydrocyclization to a much lower value than the pure platinum catalyst. Likewise, tin did not "promote" all metals. Cobalt is nearly inactive for alkane dehydrocyclization, and the addition of tin (1 Co:4 Sn) did not improve this low activity by a measurable amount.

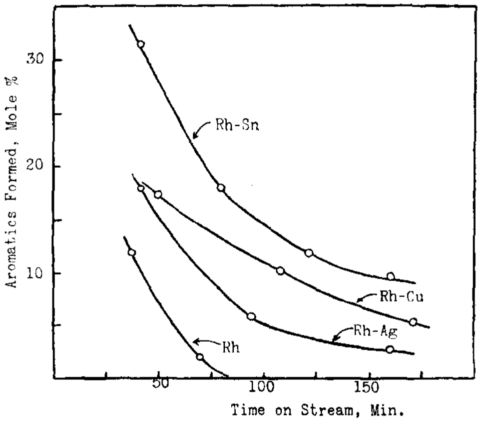


FIG. 3. Comparison of the activity for *n*-octane dehydrocyclization of various bimetallic catalysts (482°C; LHSV = 0.3; atmospheric pressure; no added hydrogen).

TABLE 2

The Aromatic Distribution from the Dehydrocyclization of Octenes and Octynes at 440°C, Atmospheric Pressure, LHSV, 0.4, and No Added Hydrogen over 0.6% $Pt\text{-}Al_2O_3\text{-}K$

Charge	Time-on-stream (min)	Conversion to aromatic (mol%)	Aromatic distribution (mol%)			
			EB	OX	MX	PX
1-Octene	33	10	34	62	2.7	0.8
	70	12	40	60	0.2	0.1
	105	14	43	56	0.3	0.1
2-Octene	32	24	39	52	6.0	3.3
	68	23	45	52	2.1	1.0
trans-4-Octene	37	16	35	56	5.8	2.5
	76	19	38	60	1.4	0.8
1-Octyne	40	24	42	54	2.6	1.4
	96	20	45	51	2.3	1.0
	146	9	44	51	3.2	1.2
2-Octyne	36	21	37	60	1.1	1.1
	72	—	43	55	1.7	0.9
	113	12	41	54	2.3	1.4
4-Octyne	32	25	39	58	2.6	1.5
	67	20	44	54	1.6	1.0
	108	12	42	54	1.5	1.1

A second way to alter the metal catalyst is to add a promoter in the gas phase with the reactant. One surprising "promoter" was the olefin reactant. Data for the conversion of octenes and octynes using the $Pt\text{-}Al_2O_3\text{-}K$ are presented in Table 2. In many runs at 482°C and without added hydrogen, we consistently obtained equal amounts (within 1–2%) of ethylbenzene and *ortho*-xylene from *n*-octane. However, it is obvious that this is not the case with the octenes and octynes where the ethylbenzene:*ortho*-xylene ratio was about 1:1.5 for all reactants. The position of the unsaturation in the charge molecule had no detectable effect on the aromatic isomer distribution.

Sulfur was added as a "promoter" in two forms: β-phenylethanthiol and thiophene. β-Phenylethanthiol rapidly decomposes to form H_2S at the reaction temperature even in the absence of the metal catalyst; hence, the results with the thiol are similar to those using H_2S. Even when as little as 0.1 volume% of β-phenylethanthiol was added to the *n*-octane charge, the catalyst was rapidly deactivated so that less than 2% aromatics were formed even for the first sample (without the thiol, conversion to aromatics was 50–60%).

The addition of sulfur as thiophene gave results that were very different from those with β-phenylethanthiol. The conversion of *n*-octane with 15–20% thiophene added (6–8% sulfur) was about the same as in the absence of sulfur. Only about half of the thiophene underwent conversion under the reaction conditions; hence, thiophene was always present during the reaction. Also, the catalyst activity did not decline any more rapidly in the presence of thiophene than in its absence. The data in Tables 1 and 3 show that thiophene influences the C_8-aromatic product distribution from *n*-octane in the same direction as tin; both promoters alter the distribution to favor *ortho*-xylene. The aromatic selectivity is approximately the same with the Pt-Sn catalyst in the presence or absence of thiophene; however, the conversion of the *n*-octane is greatly reduced when thiophene was added. Without thiophene, *n*-octane would undergo complete conversion but in the presence of thiophene the conversion to aromatics was less than 10% (Table 3).

Other heterocyclics, furan and pyridine, were also tested but were not as effective as thiophene.

The aromatic distribution from the dehydrocyclization of *n*-octane over a commercial Engelhard E601 Pt-Re catalyst is presented in Table 4. During this run *sec*-butyl amine was added to prevent isomerization of the charge by the dual functional reaction pathway. Alkali metals could not be used to decrease the acidity of a Pt-Re catalyst we prepared because

TABLE 3

Conversion of *n*-Octane in the Presence of Thiophene[a]

Catalyst	Time-on-stream (min)	Conversion to aromatic (mol%)	C_8-aromatic (mol%)				Thiophene
			EB	OX	MX	PX	
Pt-Al_2O_3	50	28	44.4	55.6	tr	tr	9.0[b]
	100	24	44.6	55.4	tr	tr	15
	165	19	43.2	56.8	tr	tr	12
Pt-Sn-Al_2O_3-K	39	9.3	39.8	60.2			6.8[b]
	76	5.6	35.0	64.0			9.5
	115	6.6	37.9	62.1			9.2

[a] 482°C; H_2, 3.5 cm^3/min); LHSV = 0.32).

[b] 15.2% Thiophene in *n*-octane charge.

the alkali metal was a severe catalyst poison. It is apparent that the amount of the two isomers not allowed by direct six-carbon ring formation are present in very small amounts. Also, the *ortho*-xylene: ethylbenzene ratio was nearly 2:1 and is very similar to that obtained with Pt-Sn.

Both gaseous and metal promoters also altered the catalytic property of platinum for the formation of the bicyclic aromatics from *n*-nonane and *n*-decane. Results for the first sample (approximately 50 min) are shown in Table 5. It is apparent that the thiophene and tin decreased the formation of bicyclic aromatics by more than a factor of 10 over the pure Pt catalyst. At later time on stream this decrease in bicyclics was even more pronounced. Results for *n*-nonane over Pt-Al_2O_3-K with and without thiophene are shown in Table 6.

In Table 7 we have compared the C_8-aromatic distribution for the first sample for promoters and loading.

The C_8-aromatic products for the conversion of *n*-octane over Pt-C and Pt-Cl-Al_2O_3-K are shown in Table 8; it is apparent that the selectivity is very similar for both catalysts. However, the Pt-C catalyst was more active for "dealkylation" to C_6- and C_7-aromatics (Fig. 4). The conversion to aromatics for all three Pt-C catalyst was nearly identical for the duration of the runs;

TABLE 4

Aromatic Distribution from the Dehydrocyclization of *n*-Octane over Pt-Re-Al_2O_3 (Engelhard E601) in Presence of *sec*-Butyl amine[a]

Time-on-stream (min)	Conversion to aromatic (%)	C_8-aromatics (mol%)			
		Ethylbenzene	*ortho*-Xylene	*meta*-Xylene	*para*-Xylene
65	35	35.3	60.0	4.23	0.65
130	35	37.3	59.8	2.10	0.84
270	24	37.4	60.0	1.77	1.00
330	22	40.2	57.2	1.48	1.23

[a] LHSV = 0.5; temperature, 482°C; 5 cm^3 of H_2/min; H_2: octane mole ratio = 1:1.4.

TABLE 5

Selectivity for Bicyclic Aromatic Formation over Pt and Moderated Pt Catalysts for the First Sample Collected at about 50 min[a]

Reactant	Pt metal moderator	Total aromatic (glc area %)	Bicyclic aromatic (glc area %)	Bicyclic total cyclic
n-Nonane	None	42	21	0.5
	Thiophene	45	2	0.04
	Tin	66	1.2	0.02
n-Decane	None	23	15	0.4
	Thiophene	45	4.3	0.1
	Tin	72	4.8	0.07

[a] 482°C; atmospheric pressure; LHSV, 0.3.

TABLE 6

Conversion of *n*-Nonane in the Presence and Absence of Thiophene[a]

Catalyst	Time-on-stream (min)	Conversion to aromatics (mol%)	Thiophene in product (mol%)	C_9-aromatics (mol%)					
				PrBz	OEt	MEt	PEt	Indan	Indene
$Pt-Al_2O_3-K$ (no thiophene)	37	40		25.6	47.7	6.1	0.6	15.2	5.5
	74	31		25.2	49.8	6.5	1.2	12.5	4.8
	111	24		24.8	51.0	6.7	1.9	11.4	4.3
	149	21		23.5	50.2	7.9	0.2	11.7	4.6
	186	18		23.6	52.8	7.3	1.6	10.6	4.1
$Pt-Al_2O_3-K$ (with thiophene)	39	45	7.2[b]	30.3	65.5	tr	tr	4.2	tr
	79	31	8.2[b]	30.8	69.2	tr	tr	tr	—
	123	28	8.6[b]	—	—	—	—	—	—
	161	22	8.6[b]	30.1	68.5	tr	tr	tr	—

[a] 482°C; 3.5 cm^3 of H_2/min; LHSV = 0.3.

[b] 15.1% thiophene in the *n*-nonane charge.

thus the different amounts of dealkylation over the three catalysts cannot be attributed to differences in the conversion. Furthermore, the same amount of support was present for all three catalysts; if the dealkylation was occurring on the support, it should have contributed equally (or even more over the low-loading catalyst). Hence we believe dealkylation must be attributed to the metal function.

Three runs were made with *n*-octane over the Pt-C catalysts in which water vapor was added in a hydrogen stream during the run but not during the reduction. Results for the dealkylation activity of the 2.2 wt% Pt catalyst, with and without added water, are shown in Fig. 5. The addition of 0.72 H_2O molecules/hour/Pt atom had little effect on the dealkylation activity but did decrease total conversion by about 20%. The addition of more water, 5.9 H_2O molecules/hour/Pt, decreased the dealkylation activity to about 40% of the Pt-C and also decreased the dehydrocyclization activity to about 40% of the Pt-C catalyst. The addition of 5.9 H_2O molecules/hour/

TABLE 7

Product Distribution from Dehydrocyclization of *n*-Octane over $Pt-Al_2O_3$ ("Nonacidic" Alumina) and Moderated $Pt-Al_2O_3$ after Approximately 3 hr on Stream

Catalyst	C_8-aromatic (mol%)			
	Ethylbenzene	*para*-Xylene	*meta*-Xylene	*ortho*-Xylene
0.6% Pt	48.3	1.0	1.9	48.8
Pt-Sn	32.2	2.9	6.3	59.0
Pt-thiophene	44.4	trace	trace	55.6
0.2% Pt		43.0		57.0
Olefin	43	0.4	0.6	56
Alkyne	42	1.0	1.5	54

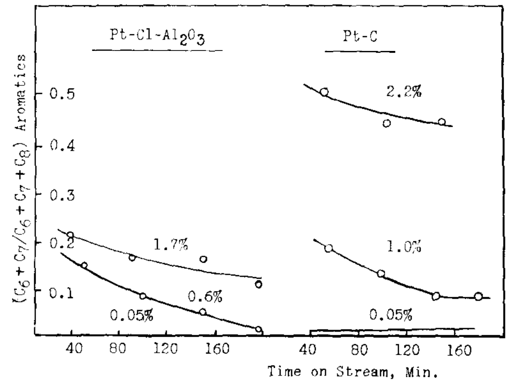


FIG. 4. Aromatic dealkylation activity for $Pt-Al_2O_3$ and Pt-C catalysts.

TABLE 8

Distribution of C_8-Aromatic Isomers for Dehydrocyclization of *n*-Octane at 482°C[a]

Liquid sample	Ethylbenzene		*ortho*-Xylene		*meta*-Xylene		*para*-Xylene	
	Pt-C	Pt-Al_2O_3	Pt-C	PtAl_2O_3	Pt-C	Pt-Al_2O_3	Pt-C	Pt-Al_2O_3
0.05% Pt-Al_2O_3-K; 0.05% Pt-C								
1	36.0	41.3	57.3	57.3	4.9	0.9	2.1	0.6
2	40.8	44.8	53.8	55.2	3.3	tr	2.1	tr
3	44.4	43.2	50.8	56.4	2.6	0.2	2.3	0.2
0.6% Pt-Cl-Al_2O_3-K; 1.0% Pt-C								
1	43.5	43.8	46.2	45.5	7.6	9.1	2.5	1.6
2	48.7	—	42.2		6.1	—	3.2	—
3	48.3	43.6	41.2	49.1	6.7	6.6	3.7	0.8
4	47.5	42.0	41.9	48.3	6.8	6.7	3.9	3.2
1.7% Pt-Cl-Al_2O_3-K; 2.2% Pt-C								
1	45.5	34.9	38.3	40.7	11.4	17.7	5.0	6.9
2	45.7	—	36.8	—	11.2	—	6.2	—
3	44.7	36.3	36.3	42.4	12.5	15.6	6.7	5.8

[a] Atmospheric Pressure, no added H_2; LHSV, 0.3.

Pt to the 1.0 wt% Pt-C catalyst completely poisoned the catalyst for aromatic formation. The addition of 5.9 H_2O molecules/hour/Pt to the 2.2 wt% Pt-C catalyst altered the aromatic selectivity to favor more ethylbenzene (EB), probably by decreasing the selective dealkylation of EB, and also the amount of *meta-* and *para*-xylene.

Figure 6 shows results for Rh and Rh-Sn catalysts. These runs were made at 400 psig and clearly demonstrate that the selectivity of a metal catalyst can be altered for operation under high H_2 pressure conditions.

For Rh-Al_2O_3 at 470°C and 400 psig, methane was practically the only product. At 500°C with Rh, temperature run-away resulted in even greater conversion to methane. The Rh-Sn-Al_2O_3 catalyst produced about five times as much aromatics as Rh-Al_2O_3 at 400 psig even though the

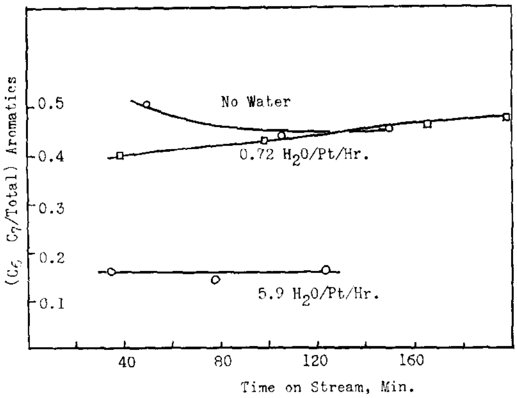


FIG. 5. Influence of water on the aromatic dealkylation activity for a Pt-C catalyst.

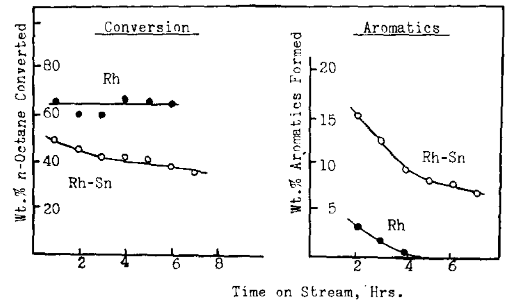
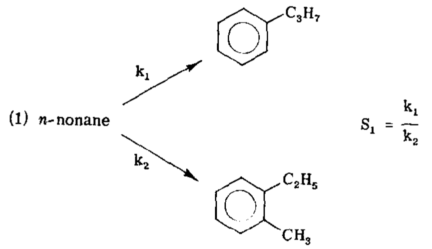


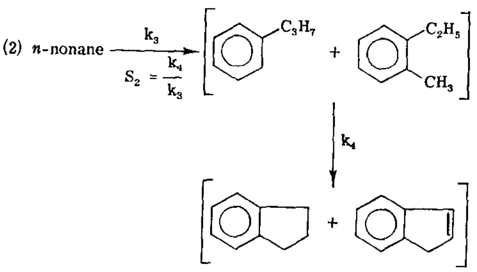
FIG. 6. Comparison of the activity and aromatic selectivity for the conversion of *n*-octane over Rh and Rh-Sn-Al_2O_3 at 400 psig total pressure (H_2:H.C. = 1:10; temperature, 482°C; LHSV = 1.2).

total conversion was less (Fig. 6). During he t7-hr run the activity of the catalysts decreased; the Rh-Sn-Al_2O_3 dehydrocyclization activity declined to about half its early activity. We did not include the isomerization of *n*-octane to iso-octanes in the total conversion (Fig. 6). With the Rh-Sn-Al_2O_3 catalyst about 80% of the C_8 paraffins were iso-octanes; this corresponds to the equilibrium conditions if the iso-octanes are only 2-, 3-, and 4-methylheptanes. In contrast, less than 5% of the C_8 paraffins were iso-octanes for the Rh-Al_2O_3 catalyst. An Sn-Al_2O_3 catalyst was inactive with the same experimental conditions.

DISCUSSION

There are two types of selectivity, illustrated below for *n*-nonane, for the dehydrocyclization of paraffins.



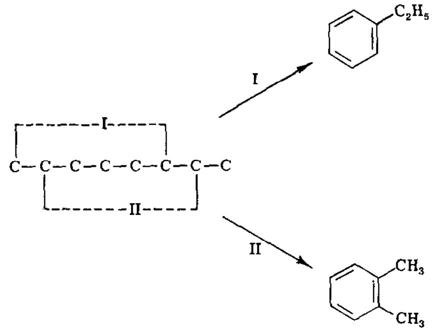


The results with *n*-octane clearly demonstrate the addition of tin or sulfur as thiophene alters the selectivity, S_1, from that of platinum. S_1 is 1 for platinum alone whereas it is decreased to nearly 0.5 when tin or thiophene is present. For *n*-nonane the influence of tin or thiophene on S_1 is complicated by the formation of the indane system from *n*-propylbenzene and ethyltoluene. The addition of tin and thiophene to the 0.6% Pt-Al_2O_3 catalyst decreased S_1 in a manner similar to the previously reported influence of decreasing the Pt loading on the alumina or carbon support (*15*). Thus, the selectivity may be altered from $S_1 = 1$ for the 0.6% Pt-Al_2O_3 to approximately $S_1 = 0.5$ by (a) the influence of the support as the metal content is decreased from 0.6%, (b) the addition of suitable metals to the 0.6% Pt catalyst, and (c) the addition of suitable gaseous promoters during the reaction.

S_2 also shows the influence of tin and sulfur, since S_2 was decreased by a factor of 10 when Sn was added to the Pt.

We favor an electronic effect to explain the influence of the metal environment on the selectivity S_1 and S_2. The selectivity S_1 should be determined by chemical reasons if the aromatics are formed only by direct 1,6-ring closure. It does not appear that the selectivity could be affected by mass transport since the products do not undergo isomerization after their formation; furthermore, desorption rates should be similar for both products.

For *n*-octane there are two direct 1.6-ring closure pathways as shown below:



Ring closure by pathway II involves only secondary C–H bonds in –CH_2– groups. However, ring closure by pathway I must involve a primary C–H bond in a –CH_3 group. It is well known that it requires more energy to rupture a primary C–H bond than a secondary C–H bond.

We believe that for sufficiently electron-deficient metals, the heat of adsorption will be sufficiently large to make the energy difference of primary and secondary C–H bonds negligible with respect to the heat of adsorption. Then for some large electron deficiency we would expect the $-CH_3$ and $-CH_2$ adsorption to be equal; hence S_1 should approach 1, and equal amounts of ethylbenzene and *o*-xylene would be formed. As the electron deficiency becomes smaller, the heat of adsorption should become smaller and the energy difference of primary and secondary C–H bonds become increasingly important, until at low heats of adsorption the selectivity will be determined by the C–H bond. Thus, for a slightly electron-deficient metal, the ratio of S_1 should approach the ratio of the ease of breaking a C–H bond in $-CH_2-$ and $-CH_3$. Qualitatively we should expect S_1 to become less than 1. Our experimental results for S_1 are in agreement with the above predictions.

The selectivity for the second cyclization, S_2, is compatible with the above explanation. The cyclization of propylbenzene to indane can be catalyzed by acids. An acid and metal such as platinum are similar in that they are both electron-deficient species. Thus, it does not seem unreasonable that S_2 should decrease with decreasing electron deficiency of the metal.

This explanation would require that adsorption is the slow step in the reaction. Competitive conversion of mixtures of paraffins or of paraffins and napthenes are in agreement with this explanation (*15*).

However, the electronic effect could operate in a different manner to influence S_1 and S_2. For example, the addition of tin to the Pt catalyst greatly decreases S_2. This suggests that the aromatics from *n*-nonane, *n*-propylbenzene, and ethyltoluene are desorbed before they undergo the second cyclization. It is obvious that the paraffin C–H bond is readily ruptured under our experimental conditions since paraffins are readily converted to aromatics. Thus it seems reasonable to expect the alkylaromatic to be absorbed more strongly by the alkyl group than the aromatic ring. A decrease in electron deficiency would decrease the adsorption of the alkyl group so that the rate of desorption of the aromatic should increase; this in turn would decrease the amount of bicyclic formed from the alkylaromatic. If this speculation is true, then benzene should not decrease the rate of dehydrocyclization whereas an alkylaromatic such as *n*-propylbenzene should.

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