

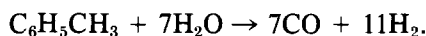
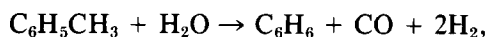
Catalytic Steam Dealkylation of Alkyl Phenols

Presently, the dominant commercial process for synthetic phenol is oxidation of cumene, formed by the reaction of benzene and propylene, to a hydroperoxide followed by mild acid treatment. Because of the complexity and expense of this process, there may be commercial potential for a more direct synthesis route using readily available and inexpensive feedstocks. With further development of coal conversion processes, one such candidate is coal tar acids which contain alkyl phenols.

Several techniques for dealkylation of alkyl phenols have been reported: thermal dealkylation (1), thermal hydrodealkylation (2, 3), and catalytic hydrodealkylation (4, 5). Typical liquid product distributions are presented in Table 1. The catalytic and thermal hydrodealkylation processes are the most effective at moderate tempera-

tures. However, because of the cost of hydrogen, processes utilizing water in lieu of hydrogen are of increasing interest.

The steam dealkylation of toluene to produce benzene is an example for which considerable literature information is available (6-8). The reaction of steam with toluene can proceed according to either of the following reactions:



Previous investigations have found the supported noble metals to have a high selectivity for benzene. Recently, Rabinovich and Mozhaiko (6) and Grenoble (8) reported activity series of these metals for the dealkylation of toluene at 430 and 440°C, respectively. Their results are as follows:

	Metal						Ref.
	Rh	Ir	Pd	Pt	Ru	Os	
Relative activity	100	13	11	5	3	1	(6)
	100	14	34	21	52	3	(8)
Benzene							
selectivity (mole%)	85-87	88-93	96-98	96-98	60-70	88-93	(6)
	83-90	83-90	95-100	95-100	60-70	60-70	(8)

Based on these results, the activities and phenol selectivities of several palladium on γ -alumina catalysts for the steam dealkylation of alkyl phenols were investigated. The feedstock was a commercial grade of cresylic acid consisting of 96.0 wt% *m,p*-cresol, 0.8% *o*-ethylphenol, and 3.2% xylenols. A down-flow macroreactor with a volume of approximately 100 cm³ was employed. For each run, 60 g of a fresh catalyst was loaded into the reactor. The remaining portion of the reactor, approxi-

mately one-half the reactor volume, was filled with tabular alumina. The reactor was heated under nitrogen to 455°C. After the reactor had been at temperature for 1.5 hr, the feed, an emulsion consisting of a molar ratio of water to cresylic acid of 6:1, was pumped through the reactor at a rate of 1 g alkyl phenol/hr/g catalyst at atmospheric pressure. Liquid samples were collected in an ice trap and analyzed by gas chromatography.

All of the catalysts, except 1% Pd + 20%

TABLE I
 Dealkylation of Alkyl Phenols

Method	Thermal dealkylation (1)		Thermal hydrodealkylation (3)		Catalytic hydrodealkylation (4)
	o-cresol	m-cresol	o-cresol	m-cresol	o-cresol
Temperature (°C)	871	871	621	621	500
Pressure (psi)	?	?	450	450	750
Catalyst	—	—	—	—	Active charcoal
Conversion (mole%)	43.6	21.2	63.5	24.5	64.5
Liquid product composition (mole%)					
Benzene	15.8	9.2	24.2	2.1	4.6
Toluene	16.3	4.1	15.8	15.3	14.7
Phenol	11.5	7.9	22.4	6.6	45.2
<i>m,p</i> -Xylene	} 56.4	} 78.8	1.1	0.5	—
<i>o</i> -Cresol			31.2	—	30.3
<i>m,p</i> -Cresol			3.9	74.6	2.8
Xylenols			1.4	0.9	2.4
Product selectivity (mole%)					
Benzene	36.2	43.4	38.1	8.8	7.1
Toluene	37.4	19.3	24.9	62.4	22.8
Phenol	26.4	37.3	35.3	27.0	70.1
<i>m,p</i> -Xylene	—	—	1.7	1.8	—

Cr₂O₃/γ-Al₂O₃, were obtained from United Catalyst. The 1% Pd + 20% Cr₂O₃/γ-Al₂O₃, was prepared by impregnation of 20% Cr₂O₃/γ-Al₂O₃, purchased from United Catalyst, with an aqueous solution of (NH₄)₂PdCl₄. After impregnation, the catalyst was dried overnight at 110°C and reduced for 1 hr at 500°C.

Table 2 demonstrates the phenol, benzene, toluene, and xylene comparative selectivities and overall liquid product com-

positions obtained with each catalyst after approximately 50 min on stream. The phenol selectivity exceeds 90 mole% for all the catalysts except γ-Al₂O₃. As was common for all the catalysts and is reflected by the data in Table 3, phenol selectivity improved with an increase in catalyst age and concurrent decrease in catalyst activity. Within the catalyst age range 0.5 to 1.0 ml feed/g catalyst, the mean value of the phenol selectivity varies in the order:

$$1\% \text{ Pd} + 20\% \text{ Cr}_2\text{O}_3 > 0.3\% \text{ Pd} + 0.3\% \text{ Cr}_2\text{O}_3 > 20\% \text{ Cr}_2\text{O}_3 > 1\% \text{ Pd}$$

95.7 92.2 90.6 89.0 mole%

The role of the support is suggested by the results illustrated in Fig. 1, where the dealkylation activity of 1% Pd/α-Al₂O₃ is compared to that of 1% Pd/γ-Al₂O₃. The low activity of 1% Pd/α-Al₂O₃ (<2%) in comparison to that of 1% Pd/γ-Al₂O₃ sug-

gests that (1) little thermal dealkylation is occurring, and (2) γ-Al₂O₃ must be activating the stream to promote dealkylation, in agreement with the recent results of Grenoble (8).

Comparison of the results for 1% Pd/γ-

TABLE 2
Product Composition and Corresponding Results

	Catalyst				
	1% Pd/ γ -Al ₂ O ₃	0.3% Pd + 0.3% Cr ₂ O ₃ / γ -Al ₂ O ₃	1% Pd + 20% Cr ₂ O ₃ / γ - Al ₂ O ₃	20% Cr ₂ O ₃ / γ -Al ₂ O ₃	γ -Al ₂ O ₃
Catalyst age, (ml feed/g catalyst)	0.86	0.83	0.85	0.83	0.84
Product composition (mole%)					
Methanol	0.10	1.02	0.17	0.17	0.00
Benzene	1.25	0.21	0.05	0.50	1.54
Toluene	0.90	0.79	0.28	1.27	3.61
Phenol	27.16	22.03	11.91	22.18	23.61
<i>m,p</i> -Xylene	0.27	0.38	0.15	0.46	1.43
<i>o</i> -Cresol	5.71	5.04	2.50	4.63	10.43
<i>m,p</i> -Cresol	56.20	62.98	78.80	60.68	41.38
Xylenols	8.41	7.55	6.14	10.11	18.00
Conversion (mole%)	29.6	23.7	12.4	24.4	30.2
Product selectivity, (mole%)					
Benzene	4.23	0.92	0.45	2.06	5.10
Toluene	3.04	3.36	2.25	5.19	11.96
Phenol	91.83	94.07	96.08	90.87	78.20
<i>m,p</i> -Xylene	0.90	1.65	1.22	1.88	4.74

Al₂O₃ with γ -Al₂O₃ demonstrate a second function of the support and suggest the role of palladium. As the data in Table 2 illustrate, at comparable catalyst life the cresol conversion levels are approximately equal: 29.6 mole% for 1% Pd/ γ -Al₂O₃ and 30.2

mole% for γ -Al₂O₃. The phenol yield is higher for 1% Pd/ γ -Al₂O₃, 27.2 mole%, versus γ -Al₂O₃, 23.6 mole%. The xylenol and *o*-cresol levels are higher for γ -Al₂O₃, 18.0 and 10.4 mole%, versus 1% Pd γ -Al₂O₃, 8.4 and 5.7 mole%, respectively. These data

TABLE 3
Summary of Cresol Conversion and Phenol Selectivity

	Catalyst				
	1% Pd/ γ -Al ₂ O ₃	0.3% Pd + 0.3% Cr ₂ O ₃ / γ -Al ₂ O ₃	1% Pd + 20% Cr ₂ O ₃ / γ - Al ₂ O ₃	20% Cr ₂ O ₃ / γ -Al ₂ O ₃	γ -Al ₂ O ₃
Catalyst age, (ml feed/g catalyst)	0.18–1.03	0.34–1.00	0.51–1.49	0.34–1.51	0.33–1.66
Cresol conversion, (mole%)	50.2–25.0	44.3–19.0	28.6–4.2	43.3–10.9	36.7–23.9
Phenol selectivity (mole%)	79.3–92.6	90.7–94.1	95.3–96.1	85.8–91.4	69.2–89.2

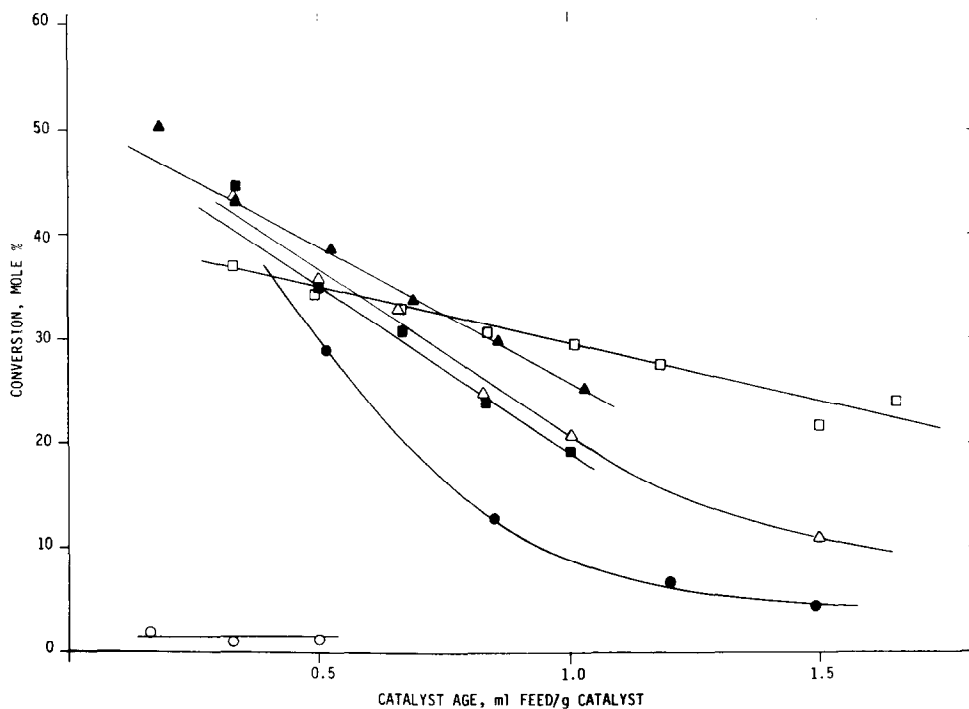


FIG. 1. The conversion of cresylic acid as a function of catalyst age at 455°C and 1 atm; (▲) 1% Pd/ γ -Al₂O₃; (■) 0.3% Pd + 0.3% Cr₂O₃/ γ -Al₂O₃; (●) 1% Pd + 20% Cr₂O₃/ γ -Al₂O₃; (△) 20% Cr₂O₃/ γ -Al₂O₃; (□) γ -Al₂O₃; (○) 1% Pd/ α -Al₂O₃.

demonstrate that γ -Al₂O₃ promotes an isomerization-disproportionation reaction similar to that previously reported for silica-alumina (9). In addition, the data also suggest that reduction in the yields of *o*-cresol and xylene and an increase in the phenol yield in the presence of palladium are due to either (1) a neutralization of the support sites which promote isomerization-disproportionation with a concurrent introduction of a selective dealkylation function of the palladium, or (2) the activation of the intermediate of the isomerization-disproportionation reaction. In both cases, a palladium-activated species apparently reacts with the activated steam to yield carbon monoxide and hydrogen.

As illustrated in Fig. 1, all of the γ -Al₂O₃-based catalysts suffer rapid deactivation attributed to coke formation. As is also illustrated in Fig. 1, the rate of deactivation appears to increase as the level of palladium or chromia increases. These data sug-

gests that the dehydrogenation function of the metal may at least partially contribute to the rapid rate of catalyst deactivation. Intermediate species adsorbed on the surface are dehydrogenated to form new species, more strongly adsorbed and less reactive. Further dehydrogenation of these new species eventually leads to the formation of carbon and total catalyst deactivation.

In conclusion, steam dealkylation of alkyl phenols over γ -alumina-supported noble metals is highly selective toward phenol, more so than other processes previously reported. However, the catalytic dehydrogenation nature of these catalysts appears to also contribute to the rapid rate of catalyst coking and resultant deactivation.

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