JOURNAL OF CATALYSIS **15**, 205-208 (1969)

Sorption and Exchange Patterns of Benzene–Phenolic Mixtures over Faujasite Catalyst: Relevance to Phenol Ethylation

P. B. VENUTO AND E. L. WU

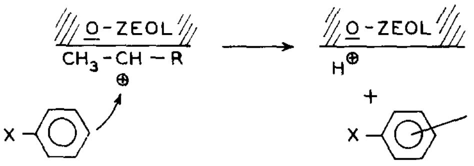
From the Mobil Research and Development Corporation, Applied Research and Development Division, Paulsboro, New Jersey 08066

Received April 15, 1969

Competitive sorption experiments showed that phenol (and anisole) was sorbed preferentially over benzene on hydrogen Y-zeolite at 130°C. Using benzene-d_6, isotopic exchange patterns of these compounds were observed. Benzene-d_6, although less strongly sorbed, communicated with the zeolite surface as shown by isotopic exchange. The deuterium thus exchanged onto the surface was subsequently transferred into the nuclear as well as hydroxyl hydrogen positions of phenol. Further, a temperature higher than 200°C was required to desorb the phenolic compounds. These data provide an explanation of some apparent anomalies previously observed in phenol ethylation.

INTRODUCTION

Modified faujasite-type catalysts have shown broad catalytic activity for alkylation and related electrophilic substitutions (*1*, *2*). For the alkylation of simple aromatic hydrocarbons such as benzene with 1-olefins (R—CH=CH$_2$) at low temperatures, transfer of a catalyst proton to the olefin—with the generation of an adsorbed carbonium ion—has been demonstrated (*2*). Formation of the observed alkylaromatic products was explained by a subsequent Rideal-like attack of the aromatic on the adsorbed electrophile as illustrated in Eq. (1).



(1)

Several apparent anomalies were noted earlier in the alkylation of phenol over modified faujasite catalysts at atmospheric pressure (*1*). First, the alkylation of phenol alone with ethylene occurred at 204°C, a temperature considerably higher than that required for alkylation of the much less nucleophilic benzene nucleus—121°C—under similar conditions. On the other hand, alkylation of phenol with ethanol or C$_{10}$-alkylating agents occurred at temperatures as low as 144–150°C, and imposition of 400 psig pressure on the ethylene–phenol system afforded activity below 100°C. Finally, still higher temperatures were required to ethylate benzene in the *presence of phenol* than those required to ethylate benzene alone.

It seemed plausible that strong adsorption of phenol, with its polar hydroxyl group and electron-rich aromatic π-electron system, might be responsible for these observations. More specifically, if at lower temperatures, phenol were strongly adsorbed at or near the protonic acid sites active for alkylation, the adsorption of a low molecular weight alkylating agent such

TABLE 1
COMPETITIVE SORPTION OF PHENOL AND BENZENE-d_6 OVER HY CATALYST

Time (min)	Temp (°C)	Sample[a] wt (g)	Effluent composition (mole %) (av degree of deuteration)[b]	
			C_6D_6	C_6H_5OH[c]
30	130	3.03	98.0 (5.15)	2.0 (—)
60	130	5.45	66.5 (5.38)	33.5 (0.66)
90	130	7.61	51.3 (5.44)	48.7 (0.59)
111	221[d]	5.92	9.5 (5.15)	90.5 (0.55)

[a] Total recovery of reactants charged: 96.2 wt %.
[b] Values for C_6D_6 are corrected for 0.04 H/mole in charge.
[c] Mass spectroscopic analysis of water-washed phenol sample.
[d] Desorbed fraction.

as ethylene would be hindered. This would prevent the generation of the adsorbed electrophile and the operation of a Rideal-like mechanism until temperatures high enough to desorb phenol from the active sites were obtained. At such elevated temperatures, ethylene could compete for adsorption. We now report the results of competition experiments designed to test this hypothesis, in which mixtures of benzene-d_6 and phenolic compounds were passed over HY catalyst and their sorption–desorption patterns were observed.

EXPERIMENTAL METHODS

Apparatus and Procedures

An NH_4Y catalyst (2.5 g) was placed in a Vycor glass continuous flow reactor and calcined for 3 hr at 550°C in O_2 *in situ* to produce the hydrogen form (HY). The general experimental techniques, the catalyst analysis, and activation procedure have been described in detail earlier (*1*). After purging the reactor with dried N_2 gas, an equimolar mixture of benzene-d_6 and phenol was passed continuously over the catalyst bed (LHSV 2.9) at 130°C. Samples were removed periodically. After 90 min, the reactant flow was stopped and the catalyst bed temperature was increased to 221°C. The resulting desorbed fraction was collected.

After initial GLC analysis (12-ft 20% silicone gum rubber on Chromosorb column), the benzene-d_6 was separated from the phenol by careful micro-fractional distillation. Each fraction was analyzed by infrared (IR) and mass spectroscopy. The analytical data from this run are shown in Table 1. The results of a similar run employing anisole instead of phenol are shown in Table 2.

Material and Analyses

Benzene-d_6 was obtained from Columbia Organic Chemicals Company and contained 99.3 at. % deuterium. It was purified by distillation over sodium metal and stored over Linde 5A sieve. Phenol was purified by simple distillation. The IR spectra were recorded on a Perkin-Elmer Infracord 337 spectrometer; anisole and benzene-d_6 samples were run neat in an 0.05-mm KBr cavity cell; phenol samples were run neat between NaCl plates. Mass

TABLE 2
COMPETITIVE SORPTION OF ANISOLE AND BENZENE-d_6 OVER HY CATALYST

Time (min)	Temp (°C)	Sample[a] wt (g)	Effluent composition (mole %)	
			C_6D_6	$C_6H_5OCH_3$[b]
30	130	4.13	70.1	29.9
60	130	6.56	54.7	45.3
90	130	6.59	52.5	47.5
102	221[c]	3.69	18.0	82.0

[a] Total recovery of reactants charged: 95.8 wt %.
[b] Calculated on the basis of both anisole and its reaction products.
[c] Desorbed fraction.

spectra were run at 10 eV on a Consolidated Electrodynamics Corporation model 21-104 spectrometer.

RESULTS AND DISCUSSION

Strong Adsorption of Phenol

Table 1 shows that when an equimolar mixture of benzene-d_6 and phenol was passed over HY at a moderately low temperature (130°C), an initial selective adsorption of phenol occurred, with the reactor effluent consisting largely of benzene. Alkylation of phenol with ethylene at one atmosphere does not occur at this temperature. Correspondingly, the sample desorbed at the higher temperature (221°C) was enriched in phenol.

In these experiments, benzene-d_6 functions not only as a competing sorbate but also as a deuterium source via continuous isotopic exchange reactions (*3*) such as shown in Eq. (2). This affords a deuterated catalyst surface, and interaction of phenol with the surface [Eq. (3)] would be revealed by the incorporation of deuterium as O–D or C–D bonds.

$$H^{\oplus}\overset{\ominus}{O}\text{-Zeol} + C_6D_6 \rightleftharpoons D^{\oplus}\overset{\ominus}{O}\text{-Zeol} + C_6D_5H, \quad (2)$$

$$D^{\oplus}\overset{\ominus}{O}\text{-Zeol} + C_6H_6O \rightleftharpoons H^{\oplus}\overset{\ominus}{O}\text{-Zeol} + C_6H_5DO \quad (3)$$

Distilled phenol samples all showed ν_{O-D} (broad, *m*) centered near 2380 cm^{-1} and ν_{C-D} (w) at 2270 cm^{-1} [lit. (*4*) 2270 cm^{-1} in phenol-3-*d*]. Disappearance of ν_{O-D} but retention of ν_{C-D} was observed upon washing the phenol samples with an excess of water. The data in Table 1 show that each phenol molecule contained, on the average, 0.6 atom of deuterium on carbon from isotopic exchange; correspondingly, each benzene molecule contained about 0.7 atom of hydrogen. The deuterium distribution for the 60-min sample is typical (mole %): for phenol: d_0, 50.8; d_1, 35.5; d_2, 11.1; d_3, 2.2; d_4, 0.4; d_5, 0.03; for benzene: d_0, 0.0; d_1, 0.3; d_2, 1.2; d_3, 3.6; d_4, 10.5; d_5, 27.6; d_6, 56.8.

Thus phenol has undergone isotopic exchange with catalyst deuterium at both the hydroxyl and nuclear hydrogen positions. The former exchange is probably an extremely rapid equilibration, since exchange of the phenolic hydroxyl with D_2O is virtually instantaneous (*5*). Since hydrogen was observed in all benzene-d_6 samples, it is evident that, although phenol is more strongly adsorbed at the active sites, benzene also communicates with the surface and undergoes exchange. It is this organic barrier of phenol—and some benzene—that effectively blocks ethylene from the catalyst surface at low temperatures.

Strong Adsorption of Anisole

The methyl ether of phenol showed a sorption pattern similar to that observed with phenol. As shown in Table 2, strong selective adsorption of anisole occurred initially when an equimolar mixture of anisole and benzene-d_6 was passed over HY at 130°C. Desorption of anisole took place when the temperature was raised to 221°C. The IR spectra of all anisole fractions showed ν_{C-D} (*m*) near 2260 cm^{-1} [lit. (*4*) 2255 cm^{-1} in anisole-3-*d*] and all the corresponding benzene-d_6 fractions showed ν_{C-H} near 3040 cm^{-1}. From 1 to 5 wt % of the anisole in each fraction was transformed to a mixture of phenol and methyl anisoles, with traces of cresols and other products.

Thus isotopic exchange of *nuclear* hydrogens with catalyst deuterium has mainly occurred in anisole, and the data in Table 2 show that the presence of the *free hydroxyl group* is by no means the only factor involved in strong adsorption of phenol derivatives. However, some attack of D^+ on the ether oxygen with CH_3–O bond scission must have occurred as evidenced by the transmethylation reactions. Considerable NMR and absorption spectroscopic evidence exists for C-protonation of methoxybenzenes when these are dissolved in strong protonic acids, although more recent work shows that protonation of alkoxybenzenes may occur as well, or exclusively, at the oxygen atom (*6*).

CONCLUSIONS

These data are interpreted as supporting the hypothesis proposed above, that at low temperatures, adsorption of phenol—and anisole—occurs at catalyst protonic sites. The strongly adsorbed aromatic effectively blocks the active sites from ethylene, preventing its adsorption to form an electrophile. Such a mechanism would also be consistent with the observed (*1*) alkylation of phenol at lower temperatures with polar or higher molecular weight alkylating agents, which can compete more favorably with phenol for adsorption. It would also explain, in part, the beneficial effect of pressure in alkylation with ethylene. The failure of propylene to alkylate naphthalene over a faujasite catalyst until a temperature of 205°C was reached (*1*) may be explained by a similar adsorption process.

REFERENCES

1. VENUTO, P. B., HAMILTON, L. A., LANDIS, P. S., AND WISE, J. J., *J. Catalysis* **5**, 81 (1966).
2. VENUTO, P. B., HAMILTON, L. A., AND LANDIS, P. S., *J. Catalysis* **5**, 484 (1966).
3. VENUTO, P. B., WU, E. L., AND CATTANACH, J., *in* "Molecular Sieves," p. 117. *Soc. Chem. Ind., London,* 1968.
4. MÜLLER, E., RIEKER, A., AND SCHEFFLER, K., *Ann. Chem.* **645**, 92 (1961).
5. HART, H., *J. Am. Chem. Soc.* **72**, 2900 (1950).
6. BROUWER, D. M., MACKOR, E. L., AND MACLEAN, C., *Rec. Trav. Chim.* **85**, 109 (1966).