

## The Dehydrogenation of Cumene to $\alpha$ -Methylstyrene over High-Purity ZnO

In cumene cracking, the ionic mode of cracking and the free radical mode of cracking are known to yield different types of reaction products. The dealkylation reaction to benzene and propylene presumably occurs through a carbonium ion intermediate while the dehydrogenation reaction to  $\alpha$ -methylstyrene and hydrogen occurs through a free radical intermediate. The product distribution for cumene cracking has been used as an indication of the relative amounts of carbonium and free radical activity of a catalyst (1). Although studies have reported the activity of certain promoted ZnO catalysts for cumene conversion to  $\alpha$ -methylstyrene (2), which is one of the free radical products in cumene cracking over acid catalysts, related studies of the catalytic activity of high-purity ZnO are lacking.

Recent EPR work has shown that strong crystal fields exist on the surface of ZnO, and that the intensity of these fields is comparable to those found on active zeolites (3, 4), which also show activity for cumene conversions (1). This communication reports experiments utilizing a microcatalytic technique designed to determine the activity of high-purity ZnO with respect to cumene conversion. For comparison purposes, the cracking of cumene over silica-alumina and alumina was also investigated. It is known that cumene cracking on silica-alumina occurs through a carbonium ion mechanism (5) while both the carbonium and free radical mechanism have been reported for high-purity alumina (6).

The reactions in these experiments were performed by periodically injecting 0.5  $\mu$ l of cumene over a catalyst bed (0.31 g catalyst) packed in a Vycor glass micro-reactor. The reactor was heated by a furnace, and the temperature of the catalyst bed was controlled to  $\pm 1^\circ\text{C}$ . The

chromatographic column was a 3 ft  $\times$  1/4 inch copper tubing column packed with  $\beta,\beta'$ -oxydipropionitrile on 60-80 mesh firebrick. The helium carrier gas, maintained at a flow rate of 31 cc/min, was passed through Linde 4A molecular sieve. Chromatographic analysis of the products encountered in these reactions was optimum at a column temperature of 91°C. The cumene was purified by passing it through a column of activated alumina and was then stored in a nitrogen atmosphere. The specific catalysts used were Houdry silica-alumina, a high-purity Catapal alumina used in catalytic work by Tung (6), and ZnO of high purity (S.P. 500) from the New Jersey Zinc Company. The alumina and ZnO were mixed with distilled water and extruded into pellets.

Pretreatment of the ZnO and silica-alumina catalysts consisted of heating slowly to 550° under a flow of helium (31 cc/min) with subsequent heating at this temperature for 2 hours. The alumina catalyst was heated to 600° under similar conditions. The surface areas for the catalysts were as follows: ZnO 5 m<sup>2</sup>/g; silica-alumina 270 m<sup>2</sup>/g; alumina 280 m<sup>2</sup>/g.

The data for the product gas composition for the cumene conversions appear in Table I. The reaction products observed in cracking over alumina and silica-alumina compare favorably with those reported elsewhere (7). The conversion over ZnO consistently yielded only one product,  $\alpha$ -methylstyrene, over the temperature range 350-400°. At 450°, traces of benzene were observed for the ZnO-catalyzed conversion.

Although the cumene used for these experiments was dehydrated, it was interesting to note that in the ZnO-catalyzed conversions, no significant changes in the reaction products were observed when a cumene-water emulsion was used, or when a small volume of water was added back

TABLE 1  
PRODUCT GAS COMPOSITION IN CATALYZED CUMENE CONVERSION

Gas effluent mole % aromatics)	Silica-alumina		Zinc oxide			Alumina
	300°	350°	350°	400°	450°	450°
Benzene	51	84	—	—	—	9
$\alpha$ -Methylstyrene	—	—	17	39	73	5
Cumene	49	16	83	61	27	86

to the catalyst. This observation along with the failure to observe more than a trace of benzene in the product may be taken as evidence that there are few, if any, Brönsted acid sites on the surface of high-purity ZnO.

As preliminary work in our laboratory suggested that the cumene conversions under discussion were first order, the present data have been treated using a first order relation. For a first order micro-catalytic reaction it has been shown (8) that the rate constant  $kK$  can be calculated according to the relation  $kK = (F^0/273 RW) \ln[1/(1-x)]$ , where  $F^0$  is the flow rate in cc(NTP)/min;  $R$ , the gas constant;  $W$ , the catalyst weight in grams; and  $x$  is the fraction converted. Correcting for surface area of the catalyst, a rate constant product  $kK/A$  can be determined, where  $A$  is the surface area of the catalyst in m<sup>2</sup>/g.

The following rate constant products  $kK/A$  were determined from the conversion data: ZnO at 350°, 0.072; silica-alumina, 350°, 0.010; ZnO, 450°, 0.420; alumina, 450°, 0.0009;  $kK$  has the dimensions mole atm<sup>-1</sup> sec<sup>-1</sup> m<sup>-2</sup>. As determined from the slope of the plot of  $\ln kK$  vs.  $1/T$ , the apparent activation energy for the ZnO-catalyzed dehydrogenation was found to be 15 kcal/mole.

These results establish that high-purity

ZnO is an active catalyst for the dehydrogenation of cumene to  $\alpha$ -methylstyrene. Such free radical reaction may be initiated by strong interactions of low-symmetry crystal fields with adsorbed cumene. Experiments designed to further explore this mode of interaction are currently in progress.

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