RADIOCARBON $^{14}$C STUDY OF THE CATALYTIC ACTIVITY OF THE CaY - CO$_2$, CaY' - CO$_2$, AND CaNdY' - CO$_2$ SYSTEMS IN BENZENE ALKYLATION BY ETHYLENE AND THE INTERACTION OF CO$_2$ WITH ZEOLITES

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The effect of CO$_2$ on zeolite catalysts depends on the reaction being catalyzed and the reaction conditions [1]. The present paper will report the results of a study of the interaction of $^{14}$C-labeled CO$_2$ with catalysts, more particularly with dealuminated CaY' and CaNdY' zeolites which differ in composition and catalytic activity, and with the CaY zeolite of [2], all of which are active in benzene alkylation by ethylene.

EXPERIMENTAL

Experiments were carried out in a circulating system, working at atmospheric pressure and following the procedure outlined in [2, 3]. The moisture content of the CO$_2$ was 13 mg/liter, that of the N$_2$ 17 mg/liter, that of the toluene 0.007%, and that of the benzene 0.01%. The following zeolites were used as catalysts: 0.67 CaNaY (SiO$_2$/Al$_2$O$_3$ mole ratio = x = 4.4; degree of Na$^+$-by-Ca$^{2+}$ exchange, 67%) which had been used in the work of [2]; 0.66 CaNaY' (x = 5.9), and 0.30 Ca$^{0.32}$NdNaY' (x = 5.9), the latter prepared from a NaY' (x = 5.9) which itself had been obtained by dealuminating a NaY zeolite (x = 4.9) with ethylenediaminetetraacetic acid [4]. The mixed calcium-neodymium samples were prepared by simultaneous replacement of the Na$^+$ of NaY' by Ca$^{2+}$ and Nd$^{3+}$. The CO$_2$ content of the zeolites was determined by the methods of [2], the only difference being that the radioactivity was measured with a flow counter (Instrument 2154-I-1M) rather than with the less-sensitive end counter. IR spectra of the catalysts, before and after CO$_2$ adsorption, were obtained with the UR-20 spectrometer.

DISCUSSION OF RESULTS

It is seen from Fig. 1 that C$_2$H$_4$ conversion to ethyl- and diethylbenzene (A) increased during the initial period of reaction on the 0.67 CaNaY zeolite in a current of CO$_2$, passed through a maximum, and then began to fall off. The time required for reaching maximum activity (the development time $\tau$) diminished with rising temperature, going from 4 h at 225°C to 3 h at 275°C. The CO$_2$ content of the catalyst (C) increased steadily during the course of the reaction, the value rising with an increase in the temperature. A and C varied in parallel during the initial period of reaction, and this despite the fact that the activity of the CaY-CO$_2$ system was clearly not determined solely by the zeolite CO$_2$ content. Similar observations have been reported from a study of toluene disproportionation [2], a reaction which differs from C$_2$H$_4$ alkylation by ethylene insofar as the value of C is less by a factor of 2-4 and the time dependence of C, though of the same general type as before, results in a maximum essentially independent of the temperature. It is possible that these differences trace back to differences in the working temperatures (225-275°C in the case of alkylation and 400-450°C in the...
Fig. 1. Time variation of the conversion of \( \text{C}_2\text{H}_4 \) to ethylbenzenes (\( A \)) (1-3), and the \( \text{CO}_2 \) content (\( C \)) (1'-3'), for alkylation on zeolite 0.67 \( \text{CaNaY} \). Space velocity of benzene (\( v \)), 0.6 \( \text{h}^{-1} \); \( \text{C}_6\text{H}_6 : \text{C}_2\text{H}_4 : \text{CO}_2 \) mole ratio = 3:1:2.4; temperature, °C: 1, 1') 225; 2, 2') 250; 3, 3') 275.

Fig. 2. Variation of the time rate of change of \( A \) (1, 2) and \( C \) (1', 2'), on 0.67\( \text{CaNaY} \) with the moisture content of the \( \text{CO}_2 \), mg/liter: 1, 1') 1.3; 2, 2') 13. 275°, \( v = 0.6 \text{ h}^{-1} \); \( \text{C}_6\text{H}_6 : \text{C}_2\text{H}_4 : \text{CO}_2 \) mole ratio = 3:1:2.4.

Fig. 3. Time variation of the degree of toluene disporportionation (\( A_1 \)), \( \text{C}_2\text{H}_4 \) conversion to ethylbenzenes (\( A_2 \)), and \( \text{CO}_2 \) content (\( C_1 \) and \( C_2 \)), on zeolite 0.67\( \text{CaNaY} \) during disporportionation of toluene and alkylation of benzene by ethylene at 300°C; \( v = 0.6 \text{ h}^{-1} \); \( \text{C}_6\text{H}_5\text{CH}_3 : \text{CO}_2 \) mole ratio = 1:0.8 and \( \text{C}_6\text{H}_6 : \text{C}_2\text{H}_4 : \text{CO}_2 = 3:1:2.4 \).

Fig. 4. Variation of \( A \) (1), and \( C \) (2), for 0.67\( \text{CaNaY} \) in experiments involving replacement of \( \text{CO}_2 \) with \( \text{N}_2 \) at 275°C; \( v = 0.6 \text{ h}^{-1} \); mole ratio \( \text{C}_6\text{H}_6 : \text{C}_2\text{H}_4 : \text{gas} = 3:1:2.4 \); 3) in \( \text{N}_2 \).

In the case of disproportionation, or to differences in the moisture content of the \( \text{CO}_2 \) (13 and 1.8 mg/liter, respectively), or to differences in the nature of the reaction itself. In fact it was observed that the \( \text{CO}_2 \) content of the zeolite increased considerably on changing over to a gas with higher moisture content (Fig. 2). On the other hand, a tenfold increase in the \( \text{H}_2\text{O} \) content of the \( \text{CO}_2 \) increased the value of \( C \) by only \( \sim 0.3\% \) (10\%, relative). This same increase in the \( \text{CO}_2 \) moisture content increased the conversion of the \( \text{C}_2\text{H}_4 \) by a factor of 2. Increasing the moisture content of the \( \text{CO}_2 \) reduced the value of \( \tau \), just as in the toluene disproportionation [5]. Taken together, these results again indicated that development of the \( \text{CaY-CO}_2 \) system was not merely a matter of increasing the \( \text{CO}_2 \) content of the catalyst. Important factors here are water buildup in the system through the