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Disproportionation of Ethylbenzene: A Potential Test Reaction for Acidity of Bifunctional Zeolite Catalysts

In previous studies Karge *et al.* (*1–3*) have shown that, under appropriate conditions, acidic zeolites catalyze disproportionation of ethylbenzene in a completely selective manner, yielding benzene and diethylbenzenes as the only products. Since in this reaction no unsaturated polymerizable species are formed, no catalyst deactivation due to polymerization and coke formation occurs. Thus, a well-defined steady-state conversion can be measured which proved to be related to the acidity of the catalyst (*1–3*). Therefore, the rate of ethylbenzene disproportionation seems to be a suitable parameter for characterizing the acidity of monofunctional catalysts.

Acidity is generally considered (*4–6*) to be one of the key properties of bifunctional catalysts influencing both activity and selectivity in, for example, isomerization or hydrocracking of alkanes. Yet the available methods for measurement of acidity of bifunctional catalysts continue to be unsatisfactory. It was therefore decided to extend the investigation of ethylbenzene disproportionation to bifunctional zeolite catalysts. This paper reports on preliminary results obtained with LaNaX zeolite with and without platinum.

A 100-g sample of NaX from Union Carbide was stirred 25 times with 400 cm^3 of a 0.65-wt.% solution of $La(NO_3)_3 \cdot 6H_2O$ at 80°C. The resulting LaNaX sample had the composition $Na_{8.3}La_{26.6}Al_{88}Si_{106}O_{384}$ (degree of exchange: 91%). Portions were subsequently exchanged with $[Pt(NH_3)_4]Cl_2$ solution such as to achieve Pt loadings of 0.05, 0.2, and 0.5 wt.% on an anhydrous basis. The final catalysts are referred to as LaNaX, 0.05 Pt/LaNaX, 0.2 Pt/LaNaX, and 0.5 Pt/LaNaX, respectively. Details of the apparatus for the catalytic experiments have been described elsewhere (*2*). Pretreatment of the catalysts was as follows: 12 h in flowing O_2 (60 cm^3/min, ca. 100 kPa, 573 K); equilibrating overnight over saturated NH_4Cl solution; 12 h in flowing N_2 (60 cm^3/min, ca. 100 kPa, 623 K); 3 h in flowing H_2 (60 cm^3/min, ca. 100 kPa, 573 K); cooling to reaction temperature (423 K). Pretreatments in N_2 and H_2 were done in the reactor. The mass of catalyst was 0.05 g. Ethylbenzene (1.3 kPa) in a He carrier gas (60 cm^3/min, ca. 100 kPa) was then passed over the catalyst. After 5 h on stream H_2 was admixed (ca. 10 kPa) for 2 h. Infrared spectroscopic investigations were carried out (procedures as in Ref. *2*) on samples which had been pretreated according to the above described procedures.

Figure 1 shows the main results for two selected catalysts. After an induction period a constant ethylbenzene conversion was reached for both catalysts, i.e., no deactivation took place. On 0.2 Pt/LaNaX the induction period was much shorter and the steady state conversion was higher than on the Pt-free LaNaX. The molar ratio of benzene to diethylbenzenes (DEBs) was always close to unity. The isomer distribution of DEBs, as obtained from additional GLC analyses of time-averaged samples on a 100-m polypropylene glycol capillary column, was 3% *o*-DEB, 68% *m*-DEB, and 29% *p*-DEB. This is in excellent agreement with the equilibrium distribution of 3% *o*-DEB, 69% *m*-DEB, and 28% *p*-DEB (*7*). (In contrast, when a dealuminated mordenite catalyst (BeM-D, No. 10 of Ref. *2*) was em-

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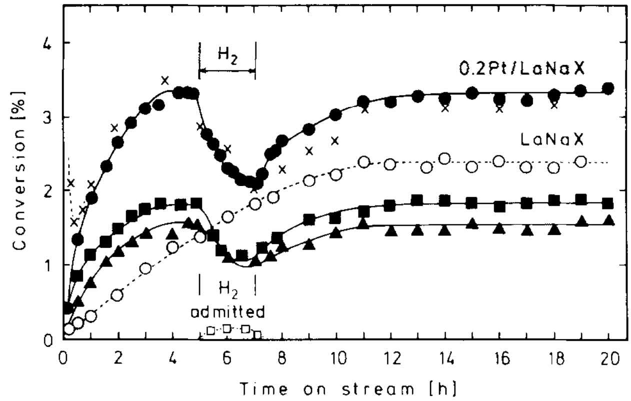

FIG. 1. Conversion of ethylbenzene (× × ×), as determined via ethylbenzene disappearance; conversion to benzene (■■■), to diethylbenzenes (▲▲▲), to benzene plus diethylbenzenes (●●●), and to ethylcyclohexane (□□□) over 0.2 Pt/LaNaX; conversion of ethylbenzene to benzene plus diethylbenzenes (○○○) over LaNaX.

ployed, the distribution was 1% *o*-DEB, 50% *m*-DEB, and 49% *p*-DEB, indicating a clear effect of shape selectivity on BeM-D.)

Hydrogen admission affected the two catalysts in a significantly different manner: on LaNaX there was no measurable effect while on 0.2 Pt/LaNaX the conversion dropped markedly. The yield of benzene decreased somewhat faster than that of DEBs; we tentatively attribute this to a faster hydrogenation of benzene compared to DEBs. Indeed, small amounts of cyclohexane could be detected in the product stream as long as H_2 was admitted. However, the main new component during the same period was ethylcyclohexane; up to 0.1% of the ethylbenzene feed (i.e., about 5% of the ethylbenzene converted) was converted into ethylcyclohexane. In future experiments it will be checked whether ethylbenzene conversion without and with H_2 admission is suitable for a simultaneous characterization of acidity and hydrogenation activity of bifunctional catalysts. The formation of ethylcyclohexane immediately ceased when H_2 admission was stopped. Subsequently, the conversion of ethylbenzene slowly approached the same upper level that had been obtained prior to H_2 admission.

The results shown in Fig. 1 for 0.2 Pt/LaNaX could be reproduced several times. Furthermore, the catalysts with a different Pt content exhibited a similar qualitative behavior. With increasing Pt content the upper conversion level increased and the duration of the induction period decreased (Table 1). After H_2 admission the conversion always dropped to a value between 2.0 and 2.5%. It is interesting to notice that the steady-state conversion over Pt-free LaNaX is in this same range. In the case of

TABLE 1

Induction Period and Conversion in Ethylbenzene Disproportionation with and without H_2 Admission

Zeolite	Catalyst composition	Induction period [h]	Φ_{max}[a] [%]	Φ_{H_2}[b] [%]
1	LaNaX	11.5	2.35	2.4
2	0.05 Pt/LaNaX	12.5	3.75	2.5
3	0.2 Pt/LaNaX	4.0	3.35	2.1
4	0.5 Pt/LaNaX	2.0	6.90	2.0
5	0.5 Pt/LaNaX (without H_2 pretreat.)	3.5	2.70	

[a] Φ_{max}: maximum conversion of ethylbenzene in disproportionation to benzene and diethylbenzenes.

[b] Φ_{H_2}: minimum conversion of ethylbenzene in disproportionation to benzene and diethylbenzenes after H_2 admission.

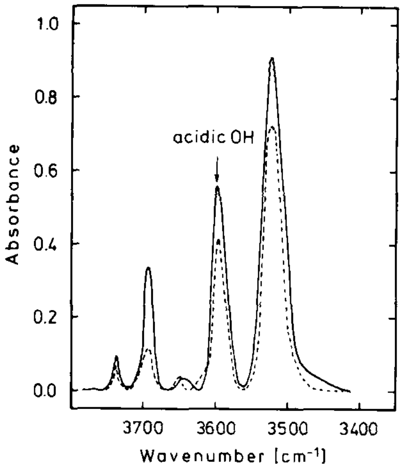

FIG. 2. The ir spectrum of the OH stretching region of 0.5 Pt/LaNaX before (dashed line) and after (solid line) reduction by H_2 at 573 K.

Pt-free LaNaX, H_2 was also admitted during steady-state operation; again the conversion of ethylbenzene was not affected. Furthermore, a similar steady-state conversion was observed on 0.5 Pt/LaNaX if the H_2 pretreatment step was omitted; the induction period, however, was much shorter in this case than on LaNaX (Table 1).

Figure 2 demonstrates the effect of H_2 pretreatment on the surface chemistry (OH groups) of 0.5 Pt/LaNaX. After reduction the following bands in the ir spectrum are markedly intensified: 3690 cm^{-1} (chemisorbed water), 3598 cm^{-1} (acidic OH groups, absorbance increased by 37%), and 3525 cm^{-1} (OH's attached to La^{3+} cations). The same holds for the 1640-cm^{-1} band (physically adsorbed water) which is not shown in Fig. 2. The acidic nature of the OH groups represented by the band at 3598 cm^{-1} was ascertained by recording additional ir spectra: upon adsorption of ammonia the 3598-cm^{-1} band disappeared and it reappeared upon progressive desorption of ammonia at temperatures from 200 to 300°C. Moreover, the spectrum shown in Fig. 2 as well as the above assignments are in principal agreement with those reported by Hoser *et al.* (*8*) for a CeNaX zeolite. Unlike 0.5 Pt/LaNaX, the band at 3598 cm^{-1} indicating acidic OH groups remained unaffected by H_2 treatment with the platinum-free LaNaX.

We therefore suggest that the increase of activity towards ethylbenzene disproportionation with increasing Pt loading is due to the formation of additional (strong) acidic sites when the platinum cations are reduced (*9*). At this stage of the investigation, however, an alternative explanation cannot be ruled out, viz., that the presence of metallic platinum accelerates carbenium ion generation via styrene.

The existence of a pronounced induction period in ethylbenzene disproportionation (*1–3*) and the strong influence of the Pt content on its duration are presently not understood in mechanistic terms. It is tempting to attribute the drop of ethylbenzene conversion after H_2 admission to poisoning by hydrogenation products. However, ethylcyclohexane is easily desorbed, as indicated by the fact that it disappears from the product stream as soon as H_2 admission is stopped. The ease of ethylcyclohexane desorption from the Pt-loaded catalyst was confirmed when it was followed by ir. Alternatively, ethylcyclohexenes or ethylcyclohexadienes could be formed although they were not detected in the product stream. Indeed, if they had formed they would have been held irreversibly on the catalyst under reaction conditions (*10*). However, evidence against this explanation stems from the fact that the initial upper activity level is restored when H_2 admission is stopped. Therefore, it appears to be more likely that H_2 admission results in a decrease in acidity of the Pt-containing catalysts.

Although it is too early to advance a detailed explanation of such a decrease in acidity, our observations are in line with a hypothesis published by Chick *et al.* (*11*). Hydrogen dissociatively adsorbs on platinum group metals and then, according to the above authors, the activated hydrogen spills over onto Lewis acid sites adjacent to acidic Brønsted centers. Adsorption of dissociated hydrogen at such Lewis sites is claimed to decrease the acid strength of Brønsted OH groups. This would result in a decrease of the rate of ethylbenzene disproportionation which has been clearly shown to require strong Brønsted acidic sites (*3*).

In the original work Chick *et al.* (*11*) were led to the above hypothesis in an attempt to explain the decrease in the rate of *n*-hexane cracking upon incorporation of palladium into hydrogen mordenite. Note, however, that after admission of H_2 our LaNaX and Pt/LaNaX zeolites do not differ substantially in their activity towards ethylbenzene disproportionation.

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