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Solid-State NMR Investigation of Ethylbenzene Reactions over HMOR and Pt–HMOR Catalysts

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Ethylbenzene reactions on HMOR and Pt–HMOR have been studied by means of solid-state MAS NMR. These experimental findings clearly indicate that disproportionation via the intermediacy of diphenylethane structure constitutes the first steps of this catalytic process over both HMOR and Pt–HMOR. In addition, ethylbenzene is suggested to undergo nonbranching rearrangements via the intermediacy of a two-electron–three-center bond leading to a ^{13}C-label transfer from α- to β-position of the side chain. This appears to be a major catalytic event over both catalysts. At later stages, disproportionation of ethylbenzene via dealkylation/alkylation steps accompanied by secondary reactions of ethylene proceeds freely on HMOR, whereas it is very much suppressed on Pt–HMOR. While dealkylation is very pronounced over Pt–HMOR, alkylation is very much limited by rapid hydrogenation of ethylene to ethane on Pt sites. Based on the spectroscopic evidence of this investigation, a number of schematic representations are illustrated to address the mechanistic approaches taken in this contribution. © 1997 Academic Press

INTRODUCTION

In a modern refinery, the C_8 stream obtained from pyrolysis gasoline and reformate contains *o*-, *m*-, and *p*-xylenes and ethylbenzene. *p*-Xylene is required in large quantities for the synthesis of terepthalic acid which is in turn used for the manufacture of poly (ethylene terepthalate) fibres. There is yet a little commercial demand for the other two xylene isomers and additionally, ethylbenzene, although a major petrochemical intermediate, is mostly made by synthesis from ethylene and benzene. It follows that conversion of the mixture of *o*- and *m*-xylenes and ethylbenzene into *p*-xylene is a significant process in the petrochemical industry. Isomerization of xylenes and ethylbenzene is carried out in the presence of hydrogen on a dual function catalyst consisting of a hydrogenation component (e.g., platinum) and an acid catalyst (e.g., acidic zeolite HMOR).

Isomerization of ethylbenzene over both acidic and Pt-modified acidic zeolites has been broadly studied (1–5). Over monofunction acid catalyst (e.g., HMOR), ethylbenzene is mainly converted into diethylbenzenes and benzene, whereas ethylene, ethane, C_3–C_8, and xylenes are produced in very small amounts. It follows that disproportionation of ethylbenzene is the main reaction pathway accompanied by dealkylation. Ethylene resulting from dealkylation undergoes secondary reactions leading to a variety of C_3–C_8 products. The effect of platinum on this reaction is that it decreases the rate of disproportionation and increases the rate of dialkylation. Furthermore, ethylbenzene is suggested (2–5) to isomerize over a dual function catalyst via the intermediacy of cycloalkenes, formed by hydrogenation, which in turn isomerize and undergo dehydrogenation to form xylenes. Hydrocracking of these highly reactive intermediates is an undesirable secondary reaction which limits the rate of ethylbenzene isomerization, yielding a variety of C_1–C_7 hydrocarbons.

The potential of MAS NMR for monitoring hydrocarbon conversions proceeding inside the catalyst pores using sealed samples has been widely demonstrated (6–18). In our studies the reaction of ethylbenzene over both HMOR and Pt–HMOR was investigated by means of MAS NMR. A large number of organic species were detected at intermediate stages of this catalytic process and successfully identified, producing vital information as to the reaction mechanism of this process.

EXPERIMENTAL

Sample Preparation

Zeolites HMOR and Pt–HMOR were provided by Shell Research and Technology Centre in Amsterdam. Chemical analysis of the as-synthesized samples gives a Si/Al ratio of 5 and a sodium content of ca 0.08 w/w%. The Pt content of Pt–HMOR is 0.4 w/w% and TEM shows a fine dispersion of Pt over the whole sample. Furthermore, these catalysts were fully characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and ^{1}H and ^{27}Al MAS NMR. SEM images picture crystal sizes of 75–300 nm, while the ^{27}Al MAS NMR spectra of both catalysts depict that 15% of aluminum sits in octahedral coordination.

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Catalysis-MAS NMR

Ethyl[α-^{13}C]benzene (99% ^{13}C-enriched) was purchased from CDN isotopes. HMOR catalyst (50 mg) was loaded into specially designed Pyrex capsules which were in turn connected to a vacuum line. This catalyst was activated under vacuum at 400°C for 24 h and then loaded with a controlled quantity of the reactant. Pt–HMOR was reduced in H_2 flow at 500°C for 5 h and then transferred to the vacuum line in Pyrex capsules where they were vigorously evacuated to assure removal of physisorbed H_2 prior to loading. Experiments on both catalysts HMOR and Pt–HMOR were carried out with the loading of 1.6 ± 0.1 moles of ethylbenzene per unit cell. Experiments with higher loading were not feasible as condensation of the reactant within the capsule was unavoidable. The sample capsules were sealed (6, 7) and heated at various reaction temperatures for a period of 4 min. All the ^{13}C MAS NMR spectra were recorded at room temperature on a Bruker MSL 400 spectrometer using a Chemagnetics APEX 400 pencil probe. Most of the experiments were carried out by means of single pulse direct excitation with high-power proton decoupling. Pulse delays of 5 s were found adequate to yield quantitatively reliable spectra. Where necessary spectra were recorded with cross-polarization to enhance weak resonances and contact times in these cases were 2 ms. Chemical shifts are referenced to external tetramethylsilane. In our spectra, asterisks denote spinning side bands, whereas background signals are marked and result from the silicon rubber sleeve at 1.2 ppm and impurities at 3.9 and 40 ppm.

RESULTS

^{13}C MAS NMR spectra depicted in this section demonstrate the progression of this catalytic process at different reaction temperatures. During the course of this investigation, only broad and featureless signals, resulting from coke, were detected in the olefinic and aromatic region of the spectrum by means of cross-polarization and therefore, only the aliphatic region is shown.

Figure 1 shows the ^{13}C MAS NMR spectra of ethylbenzene reaction over HMOR catalyst at a range of temperatures. Initially at room temperature (RT), one resonance is observed at 28.8 ppm which is assigned to methene group ($-CH_2-$) in the side chain of ethylbenzene. The strong intensity of this signal results from the selective ^{13}C enrichment at this position. Reaction commences at ca 200°C with the appearance of two signals at 28.2 and 25 ppm. Both of these lines are assigned to diethylbenzenes retaining the label at the α-position of the side chain. The line at 28.2 ppm is attributed to *p*-diethylbenzene and the one at 25 ppm to *o*-diethylbenzene. At 300°C a third strong line at 15.2 ppm appears in the spectrum which is assigned to both ethylbenzene and diethylbenzene isomers accommodating the label at the β-position of the side chain. The ^{13}C label transfer from the α- to the β-position in the side chain appears to be a major catalytic event in this process and interpretation of such an observation merits a great deal of significance in this investigation. The spectrum corresponding to 350°C indicates a considerable increase in the intensity of the line at 15.2 ppm and exhibits two additional weak signals at 20 and 53 ppm. The line at 20 ppm is assigned to methyl groups in toluene or xylene molecules, whereas the resonance at 53 ppm could result from the formation of surface bound alkoxy species and most likely ethoxy groups. The formation of alkoxides has already been reported (8, 10, 19–21), and in several contributions (8, 21) NMR signals in the region of ca 50–55 ppm were assigned to ethoxy groups.

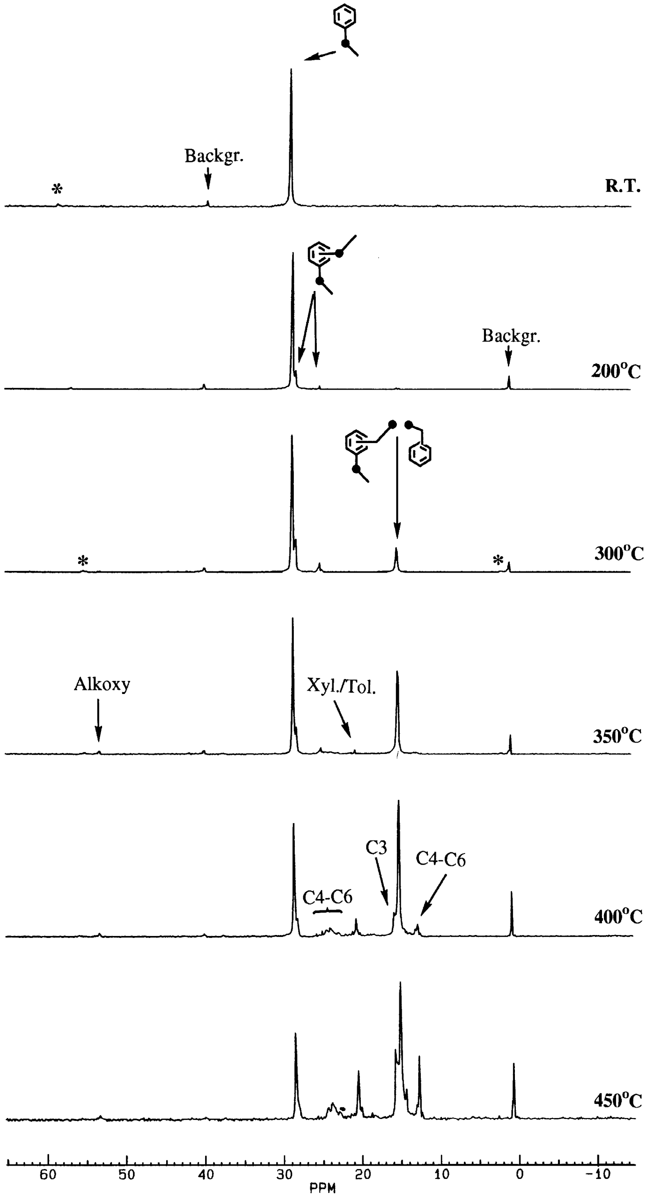


FIG. 1. ^{13}C MAS NMR spectra of ethyl[α-^{13}C]benzene reaction over HMOR (Backgr, background; Xyl, xylenes; Tol, toluene).

Furthermore, rapid interchange of the two carbons in the ethyl group within the NMR time scale has been suggested (21) to average the two carbons, giving rise to one signal in the range of 50–55 ppm. At 400°C, a large number of new resonances are observed in the corresponding spectrum while the intensity of the signal at 15.2 ppm keeps on increasing. The lines at ca 13–14 ppm are attributed to terminal methyl groups of hydrocarbon isomers C_4–C_6 with their internal carbons giving rise to lines in the range of 22–25 ppm. Propane also forms at this reaction stage as evidenced by the lines at ca 15.6 and 15 ppm which are assigned to propane in adsorbed and gas phase, respectively. The spectrum of 450°C exhibits mainly the same pattern as the spectrum above although now the conversion is by far more pronounced.

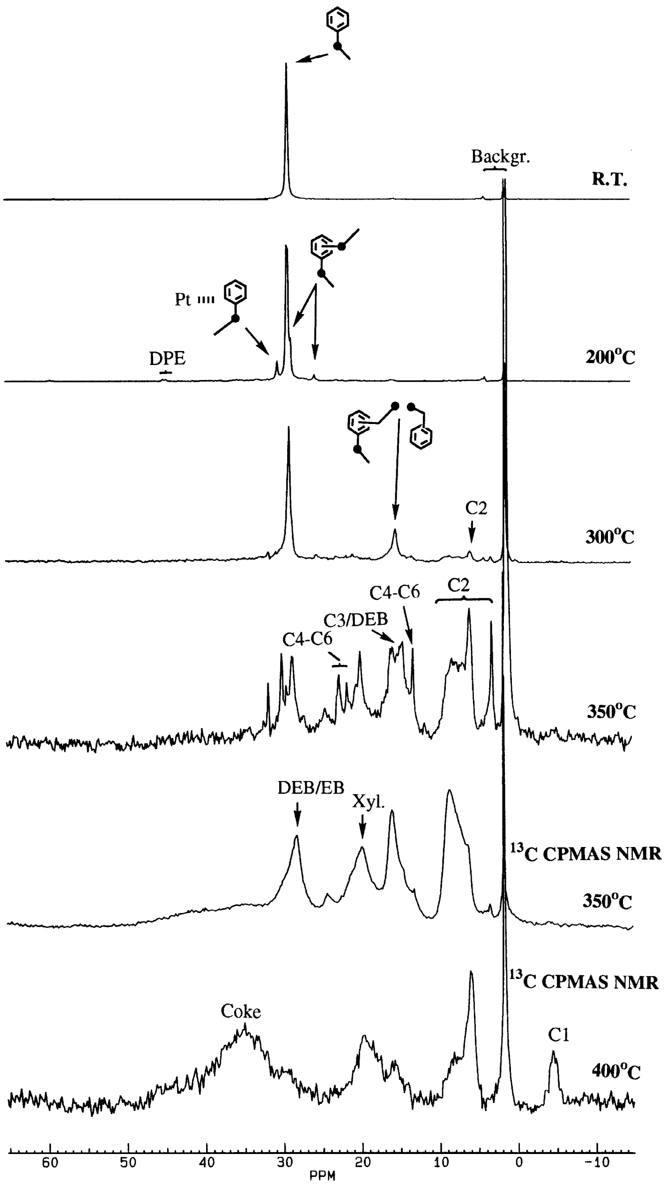


FIG. 2. ^{13}C MAS NMR spectra of ethyl[α-^{13}C]benzene reaction over Pt–HMOR (Backgr, background; DPE, diphenylethane isomers; DEB, diethylbenzenes; EB, ethylbenzene; Xyl, xylenes).

Figure 2 illustrates the ^{13}C MAS NMR spectra of ethylbenzene reaction over Pt–HMOR catalyst at a range of temperatures. At first, one resonance is observed at 28.8 ppm which is assigned to methene group ($-CH_2-$) in the side chain of ethylbenzene. The strong intensity of this signal results from the selective ^{13}C enrichment at this position. Reaction begins at ca 200°C with the appearance of signals at 25, 28.2, 30.4, and 45 ppm. Both lines at 25 and 28.2 ppm are assigned to diethylbenzenes retaining the label at the α-position of the side chain as observed in the previous series of spectra. In addition, a weak interaction between ethylbenzene and Pt is suggested to account for the downfield shift (30.4 ppm) of the ethylbenzene methene group observed in this spectrum. Of great interest is the appearance of two weak lines at ca 45 ppm which could be attributed to the side-chain methyne group $>CH-$ of diphenylethane isomers, intermediates in ethylbenzene disproportionation. The spectrum of 300°C displays a considerable line-broadening arising from a continuously intensifying interaction between the different organic species and Pt. In this spectrum, the presence of two signals at 5.6 and 15.2 ppm becomes apparent. The line at 5.6 ppm is attributed to ethane whereas the resonance at 15.2 ppm is assigned to both ethylbenzene and diethylbenzene isomers accommodating the label at the β-position of the side chain. A large number of catalytic events are pictured in the spectrum of 350°C. The increasing interaction of organic molecules with Pt coupled with coke formation may account for both the substantial line-broadening and the loss in signal intensity. The lines at ca 3, 5.6, and 7 ppm are assigned to ethane in gas, adsorbed, and strongly adsorbed phases, respectively. In the same spectrum, the line at 13.4 ppm is associated with terminal methyl groups of hydrocarbon isomers C_4–C_6 with their internal carbons giving rise to lines in the range of 22–25 ppm. The broad lines in the region of 14–17 ppm are attributed to both propane and diethylbenzene isomers while the resonance at 20 ppm is characteristic of methyl groups in xylene isomers. The next spectrum corresponding to the same reaction stage (350°C) is recorded with cross-polarization. This spectrum, although not quantitative, clearly illustrates a number of intensified broad resonances observed in the above spectrum. The main resonances depicted in this spectrum arise from ethylbenzene, diethylbenzenes, xylenes, and strongly adsorbed ethane, all sharing a substantial lack of mobility. At 400°C, the signal intensity decreases dramatically to an extent that only cross-polarization spectra could feasibly obtain. In the cross-polarization spectrum of 400°C, the broad signal at ca 35 ppm is ascribed to side chains of aromatic coke species, whereas the new line at −5 ppm is attributed to methane in adsorbed phase. Furthermore, ethane, propane, diethylbenzenes, and xylenes are still observed at this late stage of this catalytic process.

Summary of MAS NMR Results

In the above sections, we have seen how the reaction proceeds inside the pores of these catalysts loaded with a certain amount of reactant and heated at various temperatures. For the two catalysts these results are summarized below.

HMOR

—Reaction commences at 200°C with the formation of diethylbenzenes as primary products retaining the ^{13}C label at the α-position of the side chain.

—The amount of diethylbenzenes increases markedly up to the temperature of 400°C. A major catalytic event in this reaction process is the ^{13}C label transfer from the α- to the β-position in the side chain of both ethylbenzene and diethylbenzene.

—In the same temperature region, 200–400°C, a small amount of toluene/xylene and oligomerization products (C_3–C_6) are also produced. Of great interest is the appearance of a weak line at ca 54 ppm which could be assigned to alkoxy species (most likely ethoxy groups).

—At higher temperatures, the amount of diethylbenzenes tend to decrease, whereas an increase in the lines assigned to toluene/xylenes and C_3–C_6 products becomes apparent.

Pt–HMOR

—Reaction commences at 200°C with the formation of diethylbenzenes retaining the label at the α-position as above. At the same time, ethylbenzene starts interacting with Pt, whereas diphenylethane isomers, intermediates in ethylbenzene disproportionation, are detected.

—At 300°C, the ^{13}C label transfer from the α- to the β-position in the side chain of both ethylbenzene and diethylbenzene is observed , whereas ethane is also seen as a main product at this reaction stage.

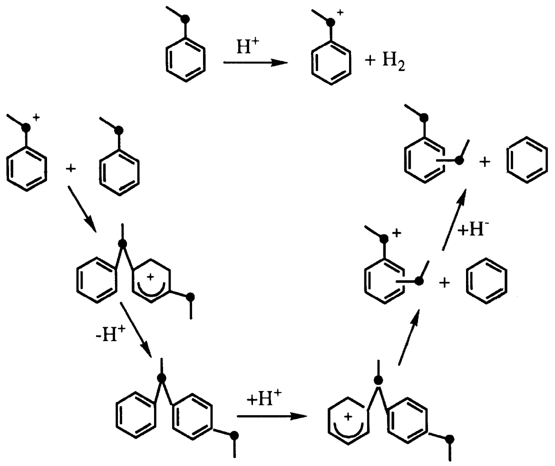
—At 350°C, the strong interaction of Pt with hydrocarbons coupled with coke formation makes lines extremely broad and weak. However, ethane C_3–C_6, xylenes, and diethylbenzenes lines are still observed.

—In the spectrum corresponding to the last stage of this reaction process (400°C), the main resonances are assigned to methane, ethane, propane, xylenes, diethylbenzenes, and aromatic coke.

DISCUSSION

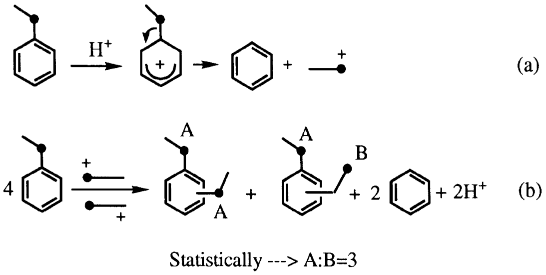
Ethylbenzene on HMOR

The first reaction stages. Investigation of a catalytic process by MAS NMR yields spectra picturing different stages including the onset of a catalyzed reaction process. In these experiments, the reaction commences at 200°C with the formation of diethylbenzenes as primary products. At this reaction stage, the ^{13}C label is retained at the α-position in the side chain of both ethylbenzene and diethylbenzene and this appears to be vital information as to the mechanistic pathway of disproportionation. This observation strongly suggests that disproportionation, at this early reaction stages, proceeds via the intermediacy of diphenylethane structure (1–5) as shown in Scheme 1. In such a mechanistic route the ^{13}C label is necessarily retained at the α-position of the side chain.



SCHEME 1

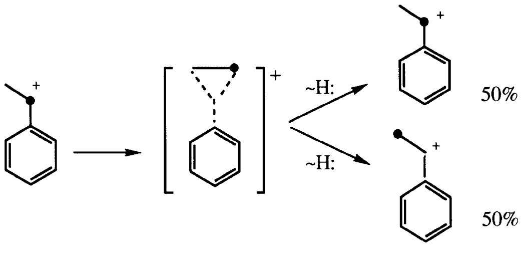
Conversely, disproportionation via dealkylation/alkylation steps (4) would necessarily lead to a statistical distribution of the ^{13}C label in the side chain of diethylbenzene isomers as shown in Scheme 2. In this scheme, methene group is labeled A and observed at 28.2 and 25 ppm, whereas methyl group is marked as B and observed at 15.2 ppm in the side chains of diethylbenzenes. Based on this reaction route, one would expect to observe a ratio of A/B = 3 in the NMR spectra of this process. The complete absence of signal B at this reaction stage confirms our mechanistic approach pictured in Scheme 1. Furthermore, dealkylation/alkylation of ethylbenzene entails the formation of primary ethyl



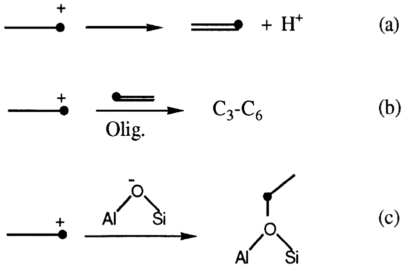
SCHEME 2

carbenium ions and must be rejected on energetic grounds, considering the relatively low reaction temperature (200°C).

The ^{13}C label transfer from α to β-position. Of great interest is the ^{13}C label transfer to the β-position of the side chain as observed in the next reaction stage (300°C), and this turns out to be a major catalytic event throughout this reaction process. Methyl groups in the side chain of both ethylbenzene and diethylbenzene isomers come very close at ca 15.2 ppm and separation of these lines is not feasible. Hence, the line at 15.2 ppm in our spectra (signal B) is assigned to methyl groups in both ethylbenzene and diethylbenzenes. The question now remained to address is how does the ^{13}C label move to the β-position of the side chain in such a high rate. As Scheme 2 illustrates, disproportionation via dealkylation/alkylation steps could account for this ^{13}C label transfer. However, such a mechanistic pathway would produce A and B signals in a ratio of A/B = 3. Bearing in mind the intensity of A signals in the spectrum corresponding to the previous reaction stage (200°C), one would now expect to observe a ratio of A/B > 3. In the spectrum of 300°C, a ratio of A/B = 1.5 is observed and thus dealkylation/alkylation steps fail to explain the strong intensity of the signal B. Additionally, dealkylation/alkylation processes are often accompanied by secondary reactions of ethyl carbenium ions, leading to a variety of C_3–C_6 hydrocarbons (4, 5). In our spectra, lines assigned to C_3–C_6 products are observed only at later reaction stages. This verifies even further the argument that disproportionation via dealkylation/alkylation steps has not started contributing to this catalytic process as yet. Since the ^{13}C label transfer can be accounted for by neither of the two disproportionation pathways, a third mechanistic approach should be considered. Nonbranching rearrangement of ethylbenzene via the intermediacy of a two-electron–three-center bond (22, 23), as shown in Scheme 3, is suggested to take place at this reaction stage. This nonskeletal rearrangement simply entails 1, 2 shift of the phenyl group via the intermediacy shown in Scheme 3. The resulting ion may be stabilized by 1, 2 hydride shifts (∼H:), and finally desorb as ethylbenzene by hydride transfer. It is worth noting that 50% of the ^{13}C label involved in this process, will be located at the β-position, giving rise to signal B, whereas the rest will return back the original α-position of the side chain. Such a mechanistic route could explain both the ^{13}C label transfer, yielding signal B, and thus the relatively low ratio of A/B signals at this reaction stage.



SCHEME 3



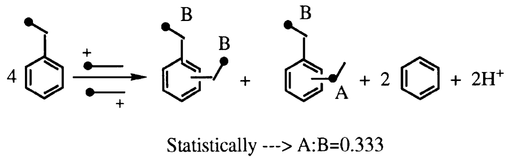
SCHEME 4

Naturally, after the label is transferred to the β-position in ethylbenzene molecules, these may undergo disproportionation via Scheme 1 to produce diethylbenzenes retaining the label in the β-position of the side chains. Hence, signal B may result from both ethylbenzene and diethylbenzene accommodating the label in the β-position, whereas signal A is entirely derived from diethylbenzenes. Considering the limited growth rate of signal A (from 200 to 300°C) which parallels that of disproportionation via Scheme 1, one could see that the monomolecular nonbranching rearrangement of ethylbenzene is very much favored over the bimolecular disproportionation at this reaction stage. Bearing in mind the low loading of the catalysts in these experimental procedures (0.2 moles/acid site), the high nonbranching rearrangement/disproportionation ratio observed above seems to be entirely reasonable.

Disproportionation via dealkylation/alkylation steps. At higher temperatures (350–450°C), dealkylation/alkylation of ethylbenzene accompanied by secondary reactions of ethylene leading to a variety of C_3–C_6 hydrocarbon products, as shown in Scheme 4, start contributing to this catalytic process. Moreover, the energy barrier of primary ethyl carbenium ions, involved in this case, may now be overcome at these elevated reaction temperatures. Following the dealkylation reaction (Scheme 2a), ethyl carbenium ions may attack the aromatic ring to yield diethylbenzenes (Scheme 2b). Alternatively, ethyl carbenium ions may desorb as either ethylene, which in turn undergoes oligomerization/isomerization reactions, yielding a variety of C_3–C_6 products (Schemes 4a and 4b) or ethylate the zeolitic framework forming alkoxides (Scheme 4c).

As evidenced by the strong intensity of signal B, nonbranching rearrangement of ethylbenzene is still a major catalytic event. A statistical ^{13}C label distribution in disproportionation via dealkylation/alkylation of ethylbenzene accommodating the label in β-position is shown in Scheme 5.

As shown in this scheme, such a reaction pathway would yield a signal ratio of A/B = 0.333. Therefore, nonbranching



Statistically ---> A:B=0.333

SCHEME 5

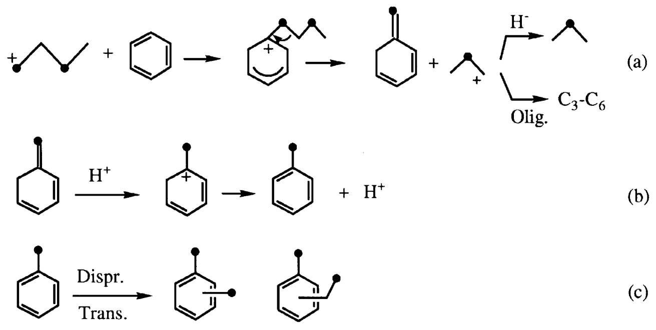
rearrangement of ethylbenzene (Scheme 3) coupled with disproportionation via dealkylation/alkylation steps (Scheme 5) may account for the strong intensity of the signal B at these late stages of this reaction process.

Toluene/Xylenes formation. Over and above, toluene/xylenes are formed at this reaction stage. On HMOR, extensive secondary reactions of ethylene have been previously suggested (4, 5) to lead to toluene/xylenes formation. If this was so, one would expect the ^{13}C label to alternate positions in xylene isomers as shown in Scheme 6. Of course, such a distribution would produce signals in both the aromatic as well as the aliphatic regions of the spectrum. The absence of signals in the aromatic region strongly suggests that xylenes do not form by extensive secondary reactions of ethylene.

The results of this work suggest the reaction pathway pictured in Scheme 7, where a primary oligomer such as butyl carbenium ion may attack the aromatic ring and then undergo cracking at the side chain to form a highly reactive cyclotriene. The last may be protonated and then deprotonated to form toluene which in turn could form xylenes or ethyltoluene via disproportionation/transalkylation reactions. Interestingly, the ^{13}C label is now remained in the side chain and does not move to the aromatic ring.

Ethylbenzene on Pt–HMOR

The first reaction stages—Effect of Pt. The early stages of the reaction of ethylbenzene on Pt–HMOR (200–300°C) resemble those of HMOR (Schemes 1 and 3). Hence, disproportionation via Scheme 1 coupled with the nonbranching rearrangement of ethylbenzene (Scheme 3) constitute the first stages of this catalytic process. Moreover, ethylbenzene starts interacting with Pt, whereas the intermediacy of diphenylethane structure in disproportionation reactions (Scheme 1) is now spectroscopically confirmed. Ethane is also observed at these early reaction stages resulting from ethylene hydrogenation on Pt sites (Scheme 8). A comparison of the spectrum at 300°C with the corresponding one of HMOR catalyst indicates that Pt promotes ethylbenzene dealkylation and at the same time suppresses ethylbenzene alkylation by rapid hydrogenation of the highly reactive ethylene. In this way, disproportionation via dealkylation/alkylation steps in very much limited.

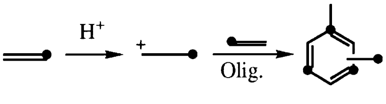


SCHEME 7

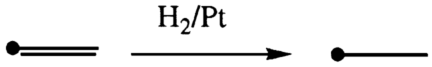
This observation adds to the argument that the ^{13}C label transfer to the β-position and thus the signal at 15.2 ppm is not derived from dealkylation/alkylation steps. As shown in the spectrum of 300°C (Pt–HMOR), while alkylation of ethylbenzene is very much suppressed by rapid hydrogenation of ethylene, the intensity of the line at 15.2 ppm arising from ^{13}C label transfer to the β-position is still very strong. Therefore, nonbranching rearrangement of ethylbenzene as shown in Scheme 3 is proved once more to be a functioning reaction pathway in both HMOR and Pt–HMOR catalysts.

Xylenes formation. In the next reaction stages (350–400°C), the increasing interaction of organic species with Pt coupled with coke formation lead to an extensive loss of signal intensity as well as a substantial line-broadening of the detected resonances. At these stages, ethane is a major product formed by dealkylation/hydrogenation steps. A number of C_1–C_6 hydrocarbon products are also produced most probably by hydrocracking of the highly reactive cycloalkenes (2), intermediates in ethylbenzene skeletal isomerisation to xylenes (Scheme 9a).

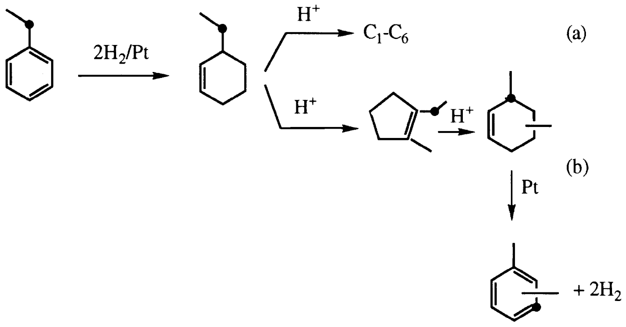
It has long been proposed (2) that ethylbenzene may be isomerised to xylenes via the intermediacy of cycloalkenes formed by partial hydrogenation of ethylbenzene, as shown in Scheme 9. It becomes clear that in such an isomerization route the ^{13}C label is expected to move from the side chain to the aromatic ring (Scheme 9b). Thus, one would expect to observe resonances in the aromatic region of the spectrum. The NMR spectra corresponding to these late reaction stages do exhibit lines assigned to methyl groups of xylene isomers, but due to line-broadening and loss in signal intensity, the aromatic region of the spectrum becomes



SCHEME 6



SCHEME 8



SCHEME 9

completely featureless. Hence, no indication as to this particular fashion of isomerization is acquired in this investigation.

CONCLUSION

The results of this work provide spectroscopic evidence as to the reaction mechanisms operating in these catalytic processes. Over catalysts HMOR and Pt–HMOR, the reaction commences with the formation of diethylbenzenes retaining the label at the α-position of the side chain.This observation coupled with simple statistical calculations, strongly suggests that disproportionation, at these early stages, proceeds via the intermediacy of diphenylethane structure. The ^{13}C label transfer to β-position, observed at later stages of this reaction over both HMOR and Pt–HMOR catalysts, is accounted for by the nonbranching rearrangement of ethylbenzene entailing the intermediacy of a two-electron–three-center bond. Over HMOR catalyst, disproportionation via dealkylation/alkylation reactions accompanied by secondary reactions of ethylene leading to a variety of C_3–C_6 hydrocarbon products becomes apparent at later reaction stages. At the same time, the ^{13}C label transfer to the β-position via the nonbranching rearrangement of ethylbenzene appears to be a predominant process. Over Pt–HMOR catalyst, dealkylation of ethylbenzene followed by hydrogenation of the highly reactive ethylene to ethane is very much promoted by Pt, whereas alkylation of ethylbenzene is suppressed. In the meantime, xylenes as well as a variety of C_1–C_6 hydrocarbon products are formed. Hydrocracking of the highly reactive cycloalkenes, intermediates in ethylbenzene to xylene isomerization, may account for the formation of C_1–C_6 hydrocarbon products over Pt–HMOR.

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REFERENCES

1. Karge, H. G., Ladebeck, J., Sarbak, Z., and Hatada, K., *Zeolites* **2**, 94 (1982).
2. Olson, D. H., and Haag, W. O., *ACS Symp. Series* **240**, 275–307 (1984).
3. Amelse, J. A., *Stud. Surface Sci. Catal.* **38**, 165 (1988).
4. Silva, J. M., Ribeiro, M. F., Ramôa Ribeiro, R., Benazi, E., and Guisnet, M., *J. Catal.* **125**, 1 (1995).
5. Silva, J. M., Ribeiro, M. F., Ramôa Ribeiro, R., Benazi, E., and Guisnet, M., *J. Catal.* **125**, 15 (1995).
6. Anderson, M. W., and Klinowski, J., *Nature* **339**, 200 (1989).
7. Anderson, M. W., and Klinowski, J., *J. Am. Chem. Soc.* **112**, 10 (1990).
8. Datema, K. P., Nowak, A. K., Houckgeest, J., van, B., and Wielers, A. F. H., *Catal. Lett.* **11**, 267 (1991).
9. Aronson, M. T., Gorte, R. J., Farneth, W. E., and White, D., *J. Am. Chem. Soc.* **111**, 2052 (1989).
10. Haw, J. F., Richardson, B. R., Oshiro, S., Lazo, N. D., and Speed, J. A., *J. Am. Chem. Soc.* **111**, 2052 (1989).
11. Richardson, B. R., Lazo, N. D., Schettler, P. D., White, J. L., and Haw, J. F., *J. Am. Chem. Soc.* **112**, 2886 (1990).
12. Lazo, N. D., Richardson, B. R., Schettler, P. D., White, J. L., Munson, E. J., and Haw, J. F., *J. Phys. Chem.* **95**, 9420 (1990).
13. Munson, E. J., Kheir, A. A., Lazo, N. D., and Haw, J. F., *J. Phys. Chem.* **96**, 740 (1992).
14. Murray, D. K., Chang, J. W., and Haw, J. F., *J. Am. Chem. Soc.* **115**, 4732 (1993).
15. Nowak, A. K., Wilson, A. E., Roberts, K., and Datema, K. P., *J. Catal.* **144**, 495 (1993).
16. Philippou, A., and Anderson, M. W., *J. Am. Chem. Soc.* **116**, 5774 (1994).
17. Ivanova, I. I., and Derouane, E. G., *Stud. Surf. Sci. Catal.* **85**, 357 (1994).
18. Philippou, A., and Anderson, M. W., *J. Catal.* **158**, 385 (1996).
19. Van den Berg, J. P., Wolthuizen, J. P., Clague, A. D. H., Hays, G. R., Huis, R., and van Hoof, J. H. C., *J. Catal.* **80**, 130 (1983).
20. Lange, J.-P., and Gutsze, A., *Appl. Catal.* **45**, 345 (1988).
21. Karge, H. G., Darmstadt, H., Gutsze, A., Vieth, H. M., and Buntkowsky, G., *Stud. Surface Sci. Catal.* **84**, 1465 (1994).
22. Olah, G. A., *J. Am. Chem. Soc.* **94**, 808 (1972).
23. Daage, M., and Fajula, F., *J. Catal.* **81**, 405 (1993).