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Diphenylmethane-Mediated Transmethylation of Methylbenzenes over H-Zeolites

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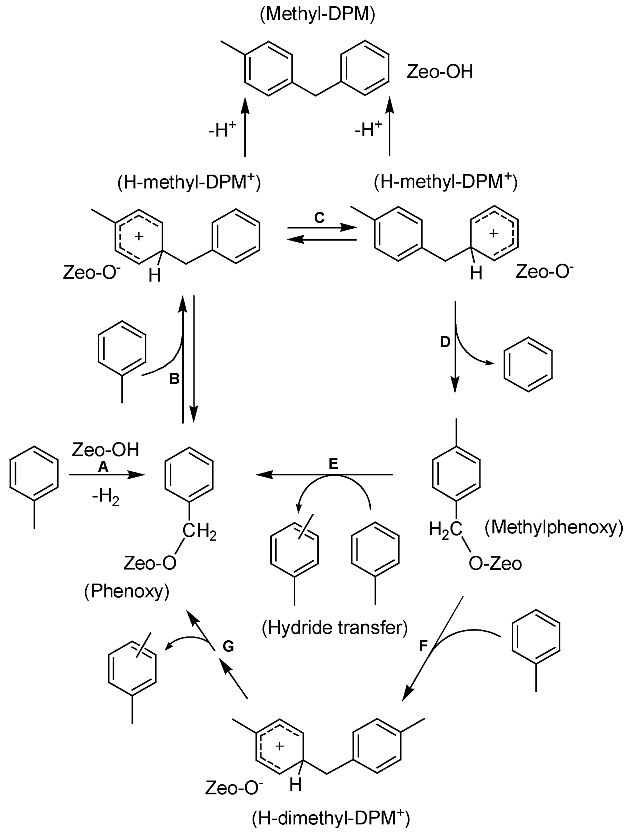
Transalkylation and isomerization of alkylated aromatic hydrocarbons are among the most important petrochemical processes. Isomerization of *m*-xylene into *p*-xylene and disproportionation of toluene into benzene and xylenes are of particular interest.[1,2] These chemical transformations were traditionally facilitated by the use of superacids or Friedel−Crafts catalysts.[1−3] Nowadays, Brönsted acidic zeolites are the exclusive catalyst choice for industrial purposes.[1] Zeolites offer substantial improvement over the traditional catalysts, in particular, with respect to product control and environmental aspects.[1,4]

The mechanism of aromatic transalkylation reactions has been the subject of considerable research effort. Most recent research has pointed toward a mechanism involving methyl-substituted *dip*henyl*m*ethanes (DPM) as reaction intermediates. Xiong et al. studied the reaction of isotopically labeled toluene over H−ZSM-5.[5] On the basis of the isotopic distribution of the products, an observed kinetic isotope effect, and a rate enhancement upon addition of traces of DPM to the reactant, the mechanistic cycle with the steps A−E outlined in Scheme 1 was proposed. The large kinetic isotope effect was suggested to be associated with the last hydride transfer (step E). Subsequent computational investigations by Clark et al., specifically related to *m*-xylene disproportionation, led to an accurate description of the energetics of steps A−E involved in Scheme 1.[6,7] It could also be inferred that the final hydride transfer (step E) has the highest barrier in the closed cycle.[6,7]

Despite their vital roles in the catalytic cycle, DPM-type compounds have never been directly detected or proved to be true reaction intermediates from experimental techniques. In this report, we provide unprecedented insights into the DPM-mediated reaction mechanism by adopting a technique originally developed by Guisnet and co-workers,[8] whereby the zeolite framework is dissolved in HF and the confined intermediates are liberated and analyzed. It has thus been possible to demonstrate the build-up of DPM species inside the zeolite pores and to follow their decomposition. Due to their inherent instability, the DPM-based intermediates are not observable at realistic reaction temperatures and rather low temperatures had to be employed.

Scheme 1



Toluene was reacted[9] from gas phase over a sample of H−ZSM-5[10] (250 mg) in a fixed bed microreactor at 150 °C. At this temperature, no gas phase products were detected. After 16 h on stream, the reaction was quenched by removing the catalyst from the reactor and cooling it to room temperature. The catalyst was then divided into seven 25 mg batches (I−VII). Batch I was dissolved in 15% HF without any further treatment. The liberated organic material was extracted from the water phase with CCl_4 (CCl_4 wash of the zeolite without HF treatment did not lead to any detectable products) and analyzed with GC−MS (Figure 1). The barely discernible peak 1 has a mass spectrum and retention time corresponding to *p*/*m*-xylene. Hydrocarbons lower than C_8 could not be analyzed due to inevitable detector saturation by toluene and the CCl_4 solvent. Peak 2 represents benzaldehyde superimposed on a less intense signal from trimethylbenzene (notice the axis break). As no oxygen-containing species are present in the feed, benzaldehyde has been formed from some C_7 precursor, such as chemisorbed toluene (phenoxy, Scheme 1), during the HF dissolution. This was corroborated by an experiment where toluene was adsorbed on the zeolite at room temperature and subsequently dissolved in HF. After the CCl_4 extraction, benzaldehyde was detected, whereas other products were totally absent. The compound giving rise to peak 3 has a molecular mass of 148, equivalent to a $C_{11}H_{16}$ hydrocarbon, but the retention time does not match that of pentamethylbenzene. The NIST98 database consistently suggests this compound to be diethylmethylbenzene, but the exact positions of the ring substituents are uncertain. Peaks 4a−c represent isomers of methylated indene and naphthalene derivatives. The compounds represented by peaks 5 and 6 are most interesting, as they correspond to DPM species. Peak 5 is identified as methyl−DPM (Scheme 1), whereas peaks 6a−b are matched with isomers of

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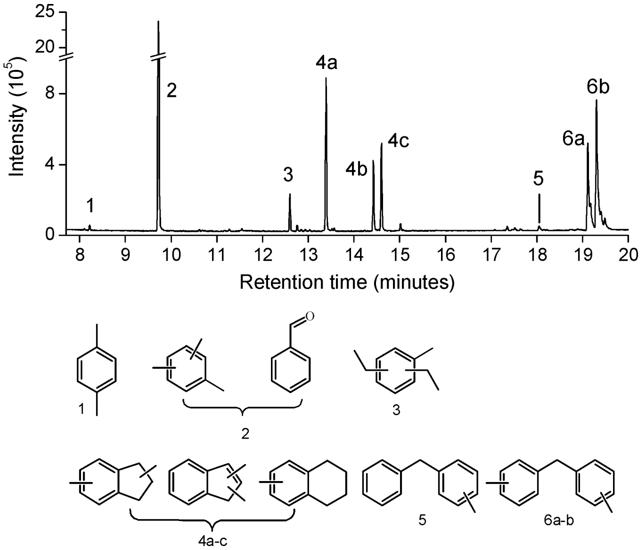

Figure 1. Total ion chromatogram details (GC−MS) of the CCl_4 extract of H−ZSM-5 (batch I) dissolved in HF. Prior to dissolution, the catalyst was exposed to toluene for 16 h at 150 °C. The peak numbering corresponds to the compounds given in the lower part of the figure.

dimethyl−DPM. Inside the zeolite, these DPM derivatives are likely to be in their protonated form.[6] According to Scheme 1, H-methyl−DPM$^+$ results from the reaction between a phenoxy group and a toluene molecule from the gas phase (step B). After an intramolecular proton migration (step C), H-methyl−DPM$^+$ may split off benzene and leave a xylene fragment bonded to the zeolite lattice as a methylphenoxy group (step D). The methylphenoxy species may then abstract a hydride from another methyl-substituted aromatic, such as toluene, forming xylene that can enter the gas phase. This route is not feasible at 150 °C, as xylenes hardly can be detected, neither in the gas phase nor among the confined compounds. For *m*-xylene disproportionation, computational methods have predicted this final hydride transfer to have the highest barrier in the cycle.[7] An alternative route for the methylphenoxy species, which proceeds via a lower barrier,[7] is the formation of H-dimethyl−DPM$^+$ upon reaction with toluene (step F). The feasibility of this reaction at 150 °C is underlined by the prominence of peaks 6a−b in Figure 1 and has never been suggested for methylbenzene transmethylations. Also, the present data clearly show that step E has the highest barrier among the reaction steps B, C, D, and F. As we will see below, H-dimethyl−DPMs$^+$ do decompose under a concomitant evolution of xylene at elevated temperature.

On the basis of the present results, and contrary to early speculations,[11] we have proved that DPM derivatives indeed can be formed in the ZSM-5 channels when toluene is reacted. To clarify the role of these species as true reaction intermediates, we heated separately the H-dimethyl−DPM$^+$ containing batches II−VII to 200 °C in a stream of N_2 for times ranging from 5 to 120 min. To follow the evolution of the organics confined within the zeolite at increasing flushing times, each of the flushed batches were subjected to exactly the same HF dissolution procedure as batch I. The thus obtained chromatograms are presented in Figure 2 (only the segments covering the xylene− and dimethyl−DPM signals are shown). Peaks 6a−b in Figure 2, representing the dimethyl−DPM isomers, decrease in intensity at increasing flushing times. The dimethyl−DPM species are evidently highly unstable and decompose at 200 °C. Peak 1 in the figure presents the evolution of the xylene concentration in the pores of the zeolite during the flushing. At increasing flushing times, the xylene signal increases in intensity, levels off, and start to decline—strongly suggesting a link to dimethyl−DPMs. One possible route for xylene formation from dimethyl−DPM is step F (reverse) followed by step E. Another option can be the direct decomposition of dimethyl−DPM (step G), implying that the dimethyl−DPMs are vital reaction intermediates rather than the manifestation of a reversible side reaction (step F). Presently, no definitive conclusion may be drawn on the relevance of step G.

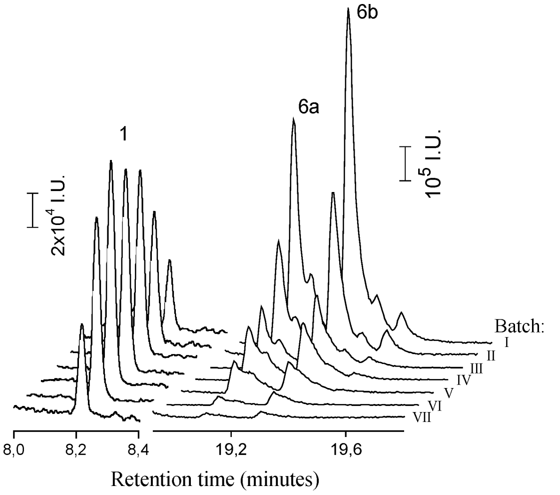

Figure 2. Chromatogram details (GC−MS) of the CCl_4 extract from batches I−VII. Only the segments covering the xylene and dimethyl−DPM peaks are displayed. Prior to HF dissolution, the catalyst was exposed to toluene for 16 h at 150 °C. Batches II−VII were subsequently flushed at 200 °C for increasing times ranging from 5 min (batch II) to 120 min (batch VII).

In summary, we can state that, despite their bulkiness, (di)-methylated DPM species may indeed be formed at high concentrations in the ZSM-5 channels when toluene is reacted. The dimethyl−DPM species are unstable when present in the zeolite voids and decompose under a concomitant evolution of xylene at 200 °C.

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(10) The H−ZSM-5 was synthesized according to standard procedures using TPABr as template. The Si/Al ratio is 45, and the crystal size is 5 μm.
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