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A novel direct catalytic production of *p*-xylene from isobutanol

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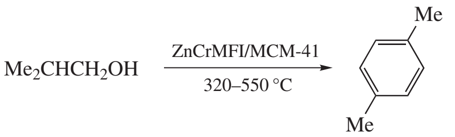
A new one-step production of *p*-xylene (along with other liquid hydrocarbons) from isobutanol is catalyzed by zinc and chromium promoted micro-mesoporous MFI/MCM-41 composite (synthesized by hydrothermal-microwave method). The use of isobutanol of biogenic origin is in accordance with the principles of 'green chemistry'.



Expanding the feedstock for petrochemical products using renewable raw materials of plant origin is a strategic task. The production of petrochemicals from aliphatic alcohols of biogenic nature, specifically from isobutanol, has attracted increasing attention of scientists.[1]

Gevo Company (USA) implemented one-step production of isobutanol by fermentation of sugars with a capacity of 4.5 million liters per year. Produced isobutanol is converted to isobutylene and then to fuel components.[1,2] It is expected that part of this isobutanol will be processed into *p*-xylene to produce terephthalic acid and polyethylene terephthalate.[1,3].

There is only a few publications describing the transformation of isobutanol over MFI zeolites (ZSM-5).[4–6] Methanol and other aliphatic alcohols, including isobutanol, were converted to a gasoline fraction over ZSM-5 zeolite;[6] however, the composition of the product was not specified.

We have previously shown[7] that isobutanol can be effectively converted to hydrocarbons in the presence of a micro-mesoporous composite catalyst MFI/MCM-41 synthesized by hydrothermal-microwave dual templating method. At 400 °C, the product mainly contains liquid hydrocarbons in 61 wt% yield. The yield of xylenes does not exceed 3 wt%, with *m*-xylene predominating among them. The patent[8] describes the preparation of *p*-xylene from aliphatic C_1–C_4 alcohols, mainly methanol, on ZSM-5 zeolites; however, the yield of *p*-xylene was lower than 2 wt%.

Here, we report for the first time on a new one-step process to produce *p*-xylene from isobutanol over micro-mesoporous composite MFI/MCM-41 promoted with zinc and chromium oxides, which is further designated as ZnCrMFI/MCM-41. Zinc and chromium (1 wt% each) were incorporated by impregnation into the composite MFI/MCM-41, which in turn was synthesized using microwave irradiation.[9] The yield of liquid hydrocarbons was determined as a percentage of the theoretical one. Isobutanol conversion was 100% in all experiments. Details of MFI/MCM-41 synthesis and catalytic tests are given in Online Supplementary Materials. XRD (Figure S1, S2), SEM (Figure S3) and TEM data (Figure S4) demonstrate that the phase composition of synthesized catalysts corresponds to MFI/MCM-41 structure, while Zn and Cr species are too small to be detected by XRD.

Comparison of the isobutanol conversion over non-promoted MFI/MCM-41 and ZnCrMFI/MCM-41 is shown in Figure 1. When the temperature is raised from 450 to 500 °C, the total yield of liquid hydrocarbons over MFI/MCM-41 [Figure 1(*a*)] grows from 22 to 38 wt%, and the yield of aromatic hydrocarbons increases from 14 to 24 wt%. The total yield of liquid hydrocarbons on the ZnCrMFI/MCM-41 catalyst [Figure 1(*b*)] reaches 67 wt% at 320 °C. As the temperature increases to 550 °C, the total yield of liquid hydrocarbons decreases gradually to 34 wt%. At the same time, the yield of aromatic hydrocarbons grows from 7 wt% at 320 °C to 26 wt% at 400 °C. Further increase in the temperature to 550 °C practically does not affect the yield of aromatic hydrocarbons, which reaches 26–29 wt%.

The change in the yield and composition of xylenes as a function of temperature is shown in Figure 2. In the presence of non-promoted catalyst MFI/MCM-41 [Figure 2(*a*)] both a maximum total yield of xylenes (6 wt%) and a maximum yield of *p*-xylene (3 wt%) is achieved at 450 °C. An increase in temperature to 500 °C leads to a decrease in these values.

On the promoted ZnCrMFI/MCM-41 catalyst [Figure 2(*b*)] at 450 °C, the total yield of xylenes reaches 9 wt%, yield of *p*-xylene being 7 wt%. This result is much better than that achieved on an unmodified catalyst MFI/MCM-41. The content of *p*-xylene in the mixture of isomers is 78%, and its content in the liquid

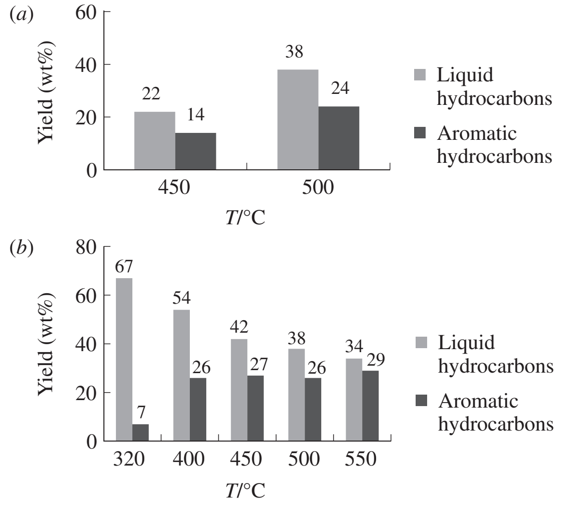


Figure 1 Yields of liquid hydrocarbons and sum of aromatic hydrocarbons obtained from isobutanol on (*a*) MFI/MCM-41 and (*b*) ZnCrMFI/MCM-41 at various temperatures (isobutanol weight hour space velocity 2.3 h^{-1}, time on stream 2 h).

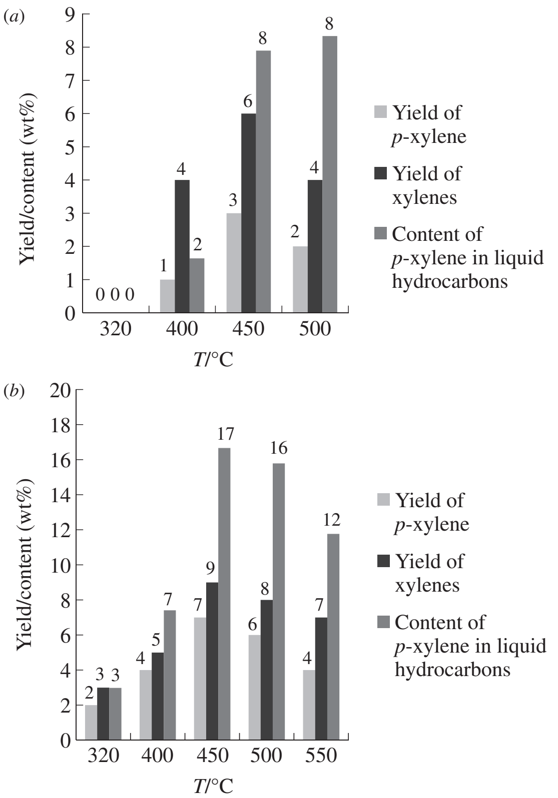


Figure 2 Yield of xylenes and content of *p*-xylene in liquid hydrocarbon products of isobutanol conversion on (*a*) MFI/MCM-41 and (*b*) ZnCrMFI/MCM-41 at various temperatures (isobutanol weight hour space velocity 2.3 h^{-1}, time on stream 2 h).

hydrocarbons obtained is 17 wt%. Further increase in temperature does not provide the increase in *p*-xylene yield.

Thus, we have developed a new one-step method for *p*-xylene production from isobutanol. Promoted with zinc and chromium micro-mesoporous MFI/MCM-41 composite catalyzes the isobutanol conversion to liquid hydrocarbons with a high content of *p*-xylene. The content of *p*-xylene in the products of catalytic reforming[10,11] (the main source of *p*-xylene) does not exceed 5 wt%. The content of *p*-xylene among the products of isobutanol conversion over catalyst developed by us, reaches 17 wt%. The advantage of the process is a high isomeric purity of the resulting *p*-xylene, whose content in the mixture of isomers reaches 78%. The use of isobutanol of biogenic origin in the process is in accordance with the principles of ‘green chemistry’. Our results demonstrate that introduction of Zn and Cr in MFI/MCM-41 composite enhances selectivity towards *p*-xylene formation. The reasons of such phenomenon need further investigation. However, we can assume that zinc and chromium ions affect not only the structure of the catalyst, since we have previously shown that these ions change the nature of the Brønsted (B) and Lewis (L) acid sites of the MFI zeolite.[12] According to the data obtained in the aromatization of alkanes,[13,14] the L-centers of the zeolite contribute to the primary formation of olefin intermediates, and the B-centers are responsible for obtaining aromatics. Therefore, Zn and Cr ions influence the nature of B- and L-centers of MFI zeolite incorporated in mesoporous MCM-41 silicate that presumably determines the *p*-xylene selectivity.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.07.002.

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