

Supplementary Information

Quantitative ^{67}Zn , ^{27}Al and ^1H MAS NMR spectroscopy for the characterization of Zn species in ZSM-5 catalysts

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Synthesis of ZnO/H-ZSM-5 Zeolite

A piece of metal ^{67}Zn (0.0129 g; 0.1921 mmol) in a glazed porcelain evaporating dish was poured over by 5 drops of conc. HCOOH (0.0752 g; 1.6348 mmol), 2 drops conc. HNO_3 (0.0263 g; 0.4178 mmol) and 0.1117 g (6.2 mmol) of water. The dish with the reagents was placed into an empty desiccator for 1.5 days. After that, the dish with the obtained clear solution was placed into the oven heated up to 90 °C for 4 hours to evaporate the solution up to dry salts. Then, the dish was placed into the oven and heated up to 190 °C for 16 hours. The cooled dish was weighed, and it was found that the weight of the dried solids was 0.0154 g. This value is very close to that what would be expected for ZnO if it formed (the expected value: 0.0159 g). The solids in the dish were dissolved by the aqueous solution comprised of 3 drops of conc. HCOOH (0.0490 g; 1.065 mmol) and 0.99 g of water. The dish with the solution was held in the empty desiccator for 1 day to assure the full dissolving. After that, the solution was diluted with 0.5 g of water, and the dish was placed into the oven heated up to 60 °C for about 1 h to evaporate the excess of formic acid. The obtained aqueous solution of zinc formate (1.1799 g; no smell of formic acid) was mixed with the freshly calcined at 420 °C powder of H-ZSM-5 (0.3331g; Si/Al=13). The dish with the zeolitic suspension was held in the empty desiccator for 1 day in order to equilibrate the ion-exchange process in the

suspension. Then, the desiccator was opened, a porcelain bowl charged with 4A adsorbent was placed into it, and the desiccator was closed again. After 16 hours the dish with the dried zeolitic cake was taken out from the desiccator, the cake (0.3840 g) was gently, but thoroughly, powdered and mixed with the help of a glass spatula. The dish with the sample was placed into an electric muffle. Calcination was performed in the following regime: temperature ramping rate was 2 °C/min from 20 up to 450 °C with intermediate isothermal steps at 150 and 230 °C for 1 h in each; at 450 °C the sample was kept for 6 h. After finishing the calcination procedure, the dish was put into the desiccator to cool down. Finally, the dish with the sample was weighed to determine the weight of the sample. It was found to be 0.3427 g. This value is very close to the sum of the weights of zinc and H-ZSM-5 powder, taken for the preparation (0.3460 g). In other words, it is very close to that what may be expected in the case of full ion exchange of zeolitic protons for zinc ions. The concentration of Zn in the product determined by elemental analysis is 3.86 wt%.