

FROM METHANOL TO DME: COMPARISON FROM 1-D TO 3-D ZEOLITE IN THE CATALYTIC BEHAVIOUR

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ABSTRACT

In this work, a series of molecular sieves (mordenite, ZSM-12, ZSM-22, EU-1, ferrierite, ZSM-5, beta and SAPO-34) were synthesized, characterized and tested as catalysts for DME synthesis via vapour-phase methanol-dehydration reaction also benchmarking with a commercial $\gamma\text{-Al}_2\text{O}_3$. Among the several emergent industrial processes based on acid catalysis, gas-phase dimethyl ether synthesis is receiving a growing attention because DME is as reliable alternative Diesel fuel, more recently, attention was renewed as intermediate for olefins production ^[1]. Catalytic performances were assessed for different zeolite structures to investigate the role of channel systems, pore dimension and framework structure onto the catalytic behaviour and the deactivation of the different zeolite catalysts. 2-D small/medium pore structure of ferrierite seems to be a suitable *catalytic environment* for selective conversion of methanol to DME also inhibiting coke formation. On the contrary, 1-D structures with large voids lead formation of by-products (e.g. olefins) and a fast coke deposition. Coke deposition that affects the catalysts deactivation, was investigated via both TG/DTA and GC-MS techniques allowing to determine both amount and composition of carbonaceous matter deposited during the reaction. Furthermore, the analysis of acid site concentration and strength via NH_3 -TPD technique allowed to calculate turnover frequency values evaluating the efficiency of acid sites and correlating it with the observed catalytic behaviour of the investigated catalysts. Both high methanol conversion and DME yield were achieved on zeolites but catalyst stability and coke formation was strongly dependent upon the channels configuration. Large openings and/or side pockets in 1-D structures determined high carbon deposition, leading to catalyst deactivation whilst FER structure, with 2-dimensional small pore channel system, exhibited a high resistance to deactivation by inhibiting coke deposition. 3-D structures resulted in significant deposit of heavier molecules forming coke and affecting the catalytic performances. Carbon deposit phase mainly consists of poly-substituted benzenes with a substitution level depending on the channel system (size and topology). In terms of methanol conversion, DME selectivity and deactivation, FER (Si/Al=8.4) confirmed the best performances ^[2], being a reliable alternative for DME production via vapour-phase methanol dehydration. In addition, results about new direct routes for gas-phase DME synthesis via-carbon dioxide hydrogenation over multifunctional (red-ox/acid catalyst) are presented. Results showed a different behaviour of the investigated “hybrid” systems, both in terms of CO_2 conversion and product distribution. Peculiar structure-activity relationships highlighted the superior performance of CuZnZr-FER catalyst, allowing to reach the highest DME productivity value because of a superior efficiency in mass transfer due to neighbouring active sites involved in the reaction mechanism ^[3].

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