Catalytic Application of Zeolites in the Methanol Conversion to Hydrocarbons
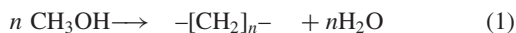
María A. Aramendía, Victoriano Borau, César Jiménez,* José M. Marinas, Rafael Roldán,
Francisco J. Romero,* and Francisco J. Urbano
*Department of Organic Chemistry, Faculty of Sciences, Córdoba University, Edificio C-3, Campus de Rabanales, Ctra. Nnal. IV,
km 396, 14014 Córdoba, Spain*

The product compositions in the methanol conversion to hydrocarbons over several zeolites are compared and discussed. Although a great number of different compounds are present, small alkanes, such as isobutane and isopentane, and poly-methylbenzenes are the major compounds over zeolites beta, mordenite and faujasite. However, zeolite ferrierite is quite selective for alkenes. Also, zeolite beta can transform acetone into hydrocarbons.

The first observation of hydrocarbon formation from methanol in molten $ZnCl_2$ was reported by LeBel in 1880, when decomposition of methanol was described to yield hexamethyl-benzene and methane.[1] In 1970s Mobil researchers found that methanol could be converted to gasoline over the intermediate-size shape-selective zeolite ZSM-5.[2] Since methanol can be produced not only from crude oil but also from natural gas and coal by currently available technology, the methanol to gasoline (MTG) process is not dependent on crude oil as a raw material.[3] This reaction yields a wide variety of products, such as alkanes, alkenes, cyclic hydrocarbons and aromatic compounds.

$$n\ CH_3OH \longrightarrow\ -[CH_2]_n-\ +nH_2O \tag{1}$$

Polyalkylated benzenes can be transformed into benzylic halides and carboxylic acid derivatives, which are important intermediates for the synthesis of polymers and discotic liquid crystals.

This paper reports results obtained in the conversion of methanol to hydrocarbons over zeolites beta, mordenite, USY and ferrierite, which are related to their structural characteristics.

The catalysts used were various zeolites purchased from Zeolyst International. The number in brackets following their names indicates the Si/Al ratio. All solids were previously activated by heating at 500 °C for 3 h. In order to avoid extensive deactivation of catalysts, all reactions were carried out in a microanalytical pulse reactor. Thus, the methanol conversion and the product composition remained constant at least up to the fifth pulse. The pulse system consisted of a gas chromatograph modified by inserting a microrreactor between the sample inlet and the analytical column. The catalyst was held by small plugs of glass wool in the 4-mm-diameter reactor tube. Helium was used as carrier gas. Experiments were conducted using a catalyst weight of 10 mg, pulse size of 0.2 μL and a flow rate of 100 mL min⁻¹. The analyses were performed on a Petrocol 100 m × 0.25 mm ID capillary column with the following program: 15 min at 40 °C and then 5 °C min⁻¹ up to 220 °C. The identity of each reaction product was determined by mass spectrometry by using a Hewlett Packard 5971A mass selective detector.

Table 1 shows the results obtained in the methanol conver-

sion over various zeolites at 400 °C. At this temperature, alkanes and aromatic compounds were the dominant products. Besides the polymethylbenzenes, some traces of ethylmethylbenzenes are present. The C_3-fraction was constituted by ethylene, propane and propene. At lower reaction temperatures, dimethyl ether was the main product in this fraction. Other compounds, not given in Table 1, specially C_5–C_7 alkanes and cycloalkanes accounted for less than 3%. Moreover, at long retention times, heavier hydrocarbons have been detected. Thus, some derivatives of naphthalene were found in trace amounts. These are important precursors for the coke formation.

Table 1. Product compositions (%wt) in the methanol conversion to hydrocarbons over several zeolites at 400 °C

Product	Beta (12.5)	Beta (37.5)	Beta (75)	MOR (45)	USY (30)
C_3-	6.1	12.9	8.1	19.2	10.8
2-Methylpropane	22.0	36.3	33.2	36.5	43.2
2-Methylbutane	6.4	13.4	9.0	8.3	17.5
2,3-Dimethylbutane	0.3	0.5	—	0.2	0.5
2-Methylpentane	1.7	3.6	4.9	1.5	4.5
3-Methylpentane	0.9	1.8	2.1	0.8	2.9
Toluene	0.7	0.5	0.8	0.5	0.8
Dimethylbenzenes	1.3	0.9	0.9	1.6	1.6
Trimethylbenzenes	3.9	3.5	1.3	4.3	3.7
Tetramethylbenzenes	12.3	10.6	7.2	9.3	5.4
Pentamethylbenzene	19.0	9.7	14.8	8.6	3.5
Hexamethylbenzene	22.3	3.1	10.8	4.6	0.8

All these catalysts have no steric restrictions since they have 12-membered ring channels, and so polymethylated benzenes are observed among the main products. Thermodynamic values for some of the reactions in the methanol conversion indicate a large driving force for methanol to form hexamethylbenzene and alkanes, as well as for further methylation of partially methylated benzenes.[4] However, penta- and hexamethylbenzene easily split off small hydrocarbons and turn into di- and trimethylbenzenes.[5] This is consistent with our observations at lower reaction temperatures. Thus, a hexa- to pentamethylbenzene ratio equal to 6.3 was obtained at 300 °C over zeolite beta, while it was only 1.2 at 400 °C. Moreover, at 300 °C the amounts of smaller aromatic compounds were practically negligible.

The aromatic distribution on different zeolites has been explained in terms of their pore size and kinetic reasons. The diffusion coefficient of hexamethylbenzene is very small, about four orders of magnitude smaller than that of the 1,2,3,4-tetramethylbenzene, even if both molecules have the same critical diameter (8.6 Å).[6] If the diffusion is very slow, the molecules will be retained in the pores for a long time, where they will stay until

demethylated or broken. Thus, a lower selectivity towards hexamethylbenzene would be expected for mordenite in comparison with zeolite beta. Transition-state selectivity would also follow the same trend. However, this could not explain the small amount of hexamethylbenzene when zeolite USY is used as catalyst.

A determining factor in the selectivity of the different catalysts must be the coking. According to equation 1, methanol is converted in alkenes which might disproportionate into alkanes, arenes and coke. A high alkane to arene ratio is indicative of coking and the large pores of zeolite USY could favour this process. This makes very difficult to establish structure-activity relationships because product distribution varies with time on stream and reactions conditions. In fact, some authors have not reported the formation of polymethylbenzenes over zeolite beta.[7]

Ferrierite was also used as catalyst in the methanol conversion. It has 10-membered ring channels and lower acidity as compared to the others.[8] This catalyst is very selective towards olefins, particularly C_5 alkenes, which are the main products (Figure 1). Its catalytic behaviour is quite different from that of the zeolite ZSM-5 which yields substantial amounts of alkanes and aromatics compounds.[4] Probably transition-state selectivity plays a major role in the product distribution by avoiding the cyclization of alkenes to aromatic compounds. Also, the prevalence of alkenes involves relatively slow hydride transfer processes, which are responsible for their disproportionation into alkanes and aromatic compounds.[9] These processes are decisive for the transformation of methanol to hydrocarbons. An experiment where ethanol alone was passed over beta(12.5) at 400 °C under the same conditions revealed that it was converted into ethene and only small amounts of aromatic compounds (from toluene to tetramethylbenzenes) were formed (less than 10%). However, acetone can be transformed into hydrocarbons under similar conditions (Figure 2). In this case, toluene and dimethylbenzenes, which account for 10 and 12.4%, respectively, are the most abundant aromatic compounds. Also, the fraction of naphthalene derivatives is not negligible.
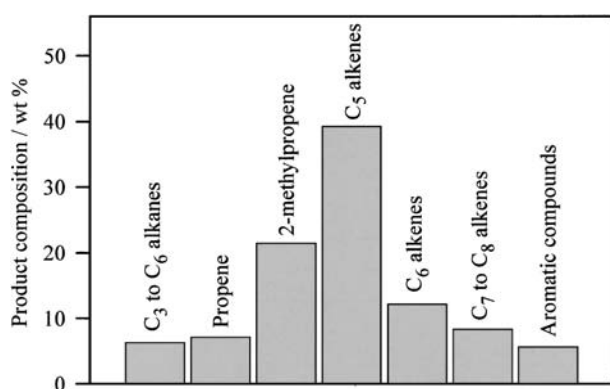

Figure 1. Product composition in the methanol conversion to hydrocarbons over zeolite ferrierite(27.5) at 400 °C.

Although the hydrocarbon product distribution is governed by interconversion reactions, our results suggest that it is strongly
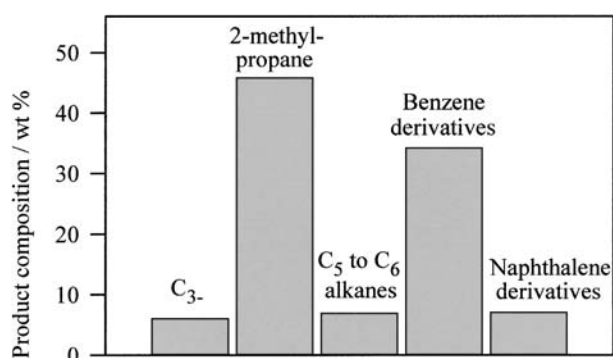

Figure 2. Product composition in the acetone conversion to hydrocarbons over zeolite beta(12.5) at 400 °C.

influenced by the structure of the zeolite through steric restrictions and by secondary processes such as the hydrogen transfer activity and coking. These factors largely depend on the reactant since methanol and acetone behave very differently from ethene. Our results are consistent with the formation of methylene species, either by intramolecular dehydration of methanol or by decomposition of acetone through an intermediate ketene or acetaldehyde.[10] All polymethylated alkanes would be formed by : CH_2 insertion into C–H or C–C bonds. Steric constraints and so the shape-selectivity of the zeolites favor this reaction on the extremes of the growing chains and control their branching. Subsequent cyclization and aromatization reactions would give rise to the rest of the products detected. Further investigations are needed to elucidate these contributions and the mechanism of this complex transformation.

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