JOURNAL OF CATALYSIS 88, 499–504 (1984)

Ketones, Carboxylic Acids, and Esters from Conversion of Aqueous Methanol over H–ZSM-5 Zeolite

STEPHEN DEANE, KEITH WILSHIER, ROBERT WESTERN, TOM MOLE*,
AND DUNCAN SEDDON[1]

Catalysis and Surface Science Laboratory, CSIRO Division of Materials Science, University of Melbourne, Parkville 3052, and ICI Australia Ltd., Central Research Laboratories, Ascot Vale 3032, Victoria, Australia

Received December 6, 1983; revised February 28, 1984

Conversion of aqueous methanol over H-ZSM-5 zeolite in the presence of *para*-xylene (or toluene) has been effected in a batch, stirred autoclave under autogeneous pressure at 344°C. Alkanes are the main products; ketones, carboxylic acids and methyl esters are also formed. A mechanism for the organic reactions is proposed.

INTRODUCTION

Conversion of methanol to hydrocarbons over zeolite catalysts, in particular the proton form of ZSM-5 zeolite, has attracted considerable interest. Conversion involves (*1–3*):

(i) Establishment of equilibrium between methanol and dimethyl ether:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O. \quad (1)$$

(ii) Formation of light olefins:

$$nCH_3OH \rightarrow C_nH_{2n} + nH_2O \quad (2)$$

$$(\text{or } nCH_3OCH_3 \rightarrow 2C_nH_{2n} + nH_2O).$$

(iii) Formation of alkanes and benzenoid aromatics from olefins:

$$4C_nH_{2n} \rightleftharpoons 3C_nH_{2n+2} + C_nH_{2n-6}. \quad (3)$$

The mechanism of methanol conversion is not unequivocally established, but the products and other available evidence suggest that hydrogen-transfer reactions are involved only in stage (iii) of conversion (*4*). No oxygen-containing products have been reported or claimed apart from dimethyl ether, and possibly small amounts of other ethers.

The conversion of aqueous methanol has now been carried out under atypical, hydrothermal conditions and in the presence of *p*-xylene and toluene (which are known to co-catalyze conversion of aqueous methanol (*5*)). The conversion results in the formation of substantial amounts of ketones, carboxylic acids, and esters.

EXPERIMENTAL

(*a*) *ZSM-5 Zeolite*

Sample A. A gel was prepared, following the methods of Argauer and Landolt (*6*), from—(i) commercial sodium silicate (70 g; 29% SiO_2, 9.1% Na_2O), sodium hydroxide (1.3 g), and tetrapropylammonium bromide (8.8 g); and (ii) aluminum sulfate · $18H_2O$ (7.5 g), sulfuric acid (3.8 g, 98%), and water (238 g). The gel was crystallized for 24 hr at 175°C in a glass-lined steel autoclave. The resulting crystalline product was filtered, washed well with water, calcined at 500°C, and then converted to the proton form (H–ZSM-5) by treatment with dilute hydrochloric acid (0.3 *M*; 150 ml/g of zeolite) at 90–100°C overnight. The resulting zeolite contained 0.02 wt% sodium and 1.72 wt% aluminum, comprised of clusters (15–20 μm diameter) of very fine (<1 μm) crystals. Its X-ray powder pattern showed only the lines reported for ZSM-5 zeolite. Comparison of the line intensities with those of the

---

[1] Present address: Broken Hill Proprietary Co. Ltd., Melbourne Research Laboratory, 245 Wellington Road, Mulgrave, 3170, Victoria, Australia.

0021-9517/84 $3.00

TABLE 1

Products from Aqueous Methanol and p-Xylene over H–ZSM-5 Zeolite at 344°C[a]

Product	Weight[b] (g)	Product	Weight[b] (g)
Methane	0.3 (g)	Acetone	0.06 (l)
Ethylene	0.3 (g)		0.2 (a)
Ethane	0.2 (g)	Butan-2-one	0.1 (l)
Propane (+ trace propylene)	2.3 (g)		0.1 (a)
*Iso*butane (and other C_4 hydrocarbons)	1.2 (g)	3-Methylbutan-2-one	0.8 (1)
	1.0 (l)		0.4 (a)
*Iso*pentane (and other C_5 hydrocarbons)	0.5 (g)	Pentan-2-one	0.1 (l)
	2.9 (l)		Trace (a)
Hexanes[c]	2.3 (l)	3,3-Dimethylbutan-3-one	0.15 (l)
Heptanes[d]	1.9 (l)		Trace (a)
Octanes	0.3 (l)	2-Methylpentan-3-one	0.1 (l)
Nonanes	0.2 (l)	3-Methylpentan-2-one	0.2 (l)
Toluene	0.1 (l)	Methyl acetate	0.06
Ethylbenzene	0.05 (l)	Methyl propanoate	0.1
Xylenes[e]	1.2 (l)	Methyl butanoate	0.03
m/*p*-Ethyltoluenes	0.1 (l)		
1,2,4-Trimethylbenzene	0.2 (l)		
m/*p*-*n*-Propyltoluene	0.02 (l)		
1,2,4,5-Tetramethylbenzene	0.5 (l)		

[a] Methanol (60 g), water (40 g), and p-xylene (2 g) over 2 g catalyst for 9 hr.

[b] Symbols: g = gas phase, l = nonaqueous liquid phase, a = chloroform extract of aqueous phase.

[c] 2-Methylpentane (1.7 g) and 3-methylpentane (0.3 g).

[d] Mainly 2- and 3-methylhexanes.

[e] Amounts: 1.1 g *para*-, 0.1 g *meta*- and a trace of *ortho*-isomers.

best available ZSM-5 sample indicated a >90% content of ZSM-5 zeolite.

Sample B. Sample B was prepared similarly but in an unlined autoclave and was converted to the proton form using 0.5 *M* hydrochloric acid. It consisted of smaller (5–10 μm diameter) aggregates of slightly larger crystals and had a higher (2.35 wt%) aluminum content.[2]

(*b*) *Conversion of Aqueous Methanol in the Presence of p-Xylene*

A 300-ml Magnedrive autoclave was charged with methanol (60 g), water (40 g), p-xylene (2 g), and H–ZSM-5 zeolite (Sample A, 2g). The autoclave was purged with nitrogen and then heated to 344°C for 9 hr. The autogeneous pressure was 220 bar.

The autoclave was cooled to room temperature. The gas (3 liters), nonaqueous liquid phase (14 g), and a chloroform extract of the aqueous phase were analyzed by gas chromatography and GC/mass spectrometry. The residual aqueous phase was titrated against standard sodium hydroxide solution to establish the presence of 20 mmole of (carboxylic) acids. The products identified are listed in Table 1; identifications are based on use of a Hewlett–Packard HP5995A gas chromatograph/mass spectrometer with a 50-m methylsilicone-coated quartz-capillary column.

The experiment was repeated, using 2 g toluene instead of p-xylene, and similar results were obtained (see below). In the

---

[2] Preparation of ZSM-5 zeolite of ≥2 wt% aluminum content is less reproducible than preparations of lower aluminum content, and incorporation of gel-aluminum into the lattice is incomplete. The Si/Al ratio is 15 for the gel, 25 for Sample A, and 18 for Sample B. Some etching of any borosilicate glass occurs in the preparation, with incorporation of the etched silica into the zeolite.

absence of any aromatic hydrocarbon, substantially less conversion was observed (again see below).

(*c*) *Conversion of Aqueous 2-Butanol*

2-Butanol (7.2 g), water (7.2 g), and H–ZSM-5 zeolite (Sample B, 0.35 g) were loaded into the glass liner of a small Parr bomb (45 ml capacity). The bomb was heated at 263°C for 1.5 hr, while the contents were stirred by a glass-encapsulated magnetic stirrer bar. From the cooled bomb, hydrocarbon gases (ca. 200 ml, mainly butenes), liquid organic phase (3 g, mainly olefins plus unchanged 2-butanol), and an aqueous phase (7 g, containing mainly unchanged 2-butanol) were recovered, and were analyzed by GC and GC/MS; the results are discussed below.

RESULTS AND DISCUSSION

By contrast with conversion of aqueous methanol at 1 atm pressure in the vapor phase, which is complete in contact times of ca. 1–10 sec and weight hourly space velocities of ca. 1 in a tubular microreactor at 300–340°C (*7*), conversion in the present hydrothermal experiments requires about 10 hr at temperatures $\geq$320°C. The conditions are close to the critical temperatures of the aqueous methanol (T_c = 374°C for water and 240°C for the methanol, which is, of course, converted to water and hydrocarbons as the reaction proceeds).

Some 60% of the carbon content of the methanol and *p*-xylene is accounted for by the products identified in Table 1. A little more (up to 10%) will be represented by unidentified hydrocarbons in the organic liquid phase, unidentified carboxylic acids, and ketones and esters not effectively back-extracted from the aqueous phase. The conversion is thus $\geq$70 C%. Residual methanol (and dimethyl ether), dissolved in the aqueous phase, was not assayed.

The H–ZSM-5 zeolite is essential to the conversion. No gaseous or organic liquid phase products were observed in the absence of the zeolite.

The addition of *p*-xylene stemmed from previous observations that aromatic hydrocarbons co-catalyze conversion of aqueous methanol to olefins in the gas phase (*5, 8*). The present results confirm the beneficial effect of *p*-xylene on conversion. In the absence of *p*-xylene, gaseous products were observed, namely propane (1.4 g), butanes (1.3 g), and dimethyl ether (4.7 g). However, the organic liquid phase weighed only 3.3 g and so was not examined further. Overall the conversion of methanol to organic products (other than dimethyl ether) was $\leq$30 C%.

Conversion of aqueous methanol in the presence of 2 g of toluene instead of *p*-xylene gave results very like those obtained in the presence of the xylene, except in that the organic liquid phase (12.7 g) contained toluene (1.0 g) and xylenes (1.0 g) as the main aromatic products.[3] It is clear that the presence of toluene or *p*-xylene aids the conversion of aqueous methanol in the present experiments.

The products obtained in the present hydrothermal experiments are quite unlike those obtained using a vapor-phase reactor (*1, 2, 5*). The latter gives mainly olefins under mild conversion conditions and dominantly alkanes plus aromatics under more severe conditions. Table 1 shows the products identified in the hydrothermal experiment carried out in the presence of *p*-xylene. It can be seen that little of the product is olefinic and that there is no net formation of aromatic hydrocarbons. In decreasing order of yield the products are alkanes, ketones, and carboxylic acids and esters.

The alkanes are by far the most prominent products and are mainly simple, branched-chain alkanes—i.e., *iso*butane instead of *n*-butane, 2-methylbutane instead of *n*-pentane, etc. The ketones are simple acyclic ketones, and are mostly 2-ketones

---

[3] The gas phase contained no methane, but did contain dimethyl ether (1.2 g). The latter is not significant. Much dimethyl ether is probably lost in the aqueous phase in all the experiments.

(acetyl compounds). The esters are methyl esters of the simple monocarboxylic acids, while the individual free acids have not been identified.

The most obvious source of the observed ketones appears to be the corresponding alcohols. The present hydrothermal experiments differ from conventional methanol conversion in that the partial pressures and concentrations of water and organic products are high. This implies the presence of significant concentrations of alcohols in hydration/dehydration equilibrium with the corresponding olefins.[4]

$$C_nH_{2n} + H_2O \rightleftharpoons C_nH_{2n+1}OH \qquad (4)$$

e.g.,

$$CH_3{-}CH{=}CH_2 + H_2O \rightleftharpoons CH_3{-}CHOH{-}CH_3 \qquad (4a)$$

and

$$C_2H_5{-}CH{=}CH_2 + H_2O \rightleftharpoons C_2H_5{-}CHOH{-}CH_3 \qquad (4b)$$

Zeolites such as the proton form of ZSM-5 zeolite catalyze dehydration of alcohols to olefins at temperatures below 300°C (*3*, *4*), and so must catalyze the establishment of equilibrium (*4*).

The formation of branched-chain alkanes and aromatics in normal methanol conversion probably involves the abstraction of hydride anions from unsaturated hydrocarbons by tertiary carbenium ions.[5] Thus reaction (3) would involve such steps as

$$\left.\begin{array}{c} C_nH_{2n+1}^{+} \\ \text{tertiary carbenium ion} \\ C_mH_{2m} \\ \text{olefin} \end{array}\right\} \rightarrow \left\{\begin{array}{c} C_nH_{2n+2} \\ \text{branched-chain alkane} \\ C_mH_{2m-1}^{+} \\ \text{unsaturated carbenium ion} \end{array}\right. \qquad (5)$$

Analogous reaction (6) seems reasonable and would allow conversion of a tertiary carbenium ion and a secondary alcohol to a branched-chain alkane and a protonated ketone. Reaction (6) provides a means whereby an olefin can react with a secondary alcohol to give an alkane and a ketone.

$$\left.\begin{array}{c} C_nH_{2n+1}^{+} \\ \text{tertiary carbenium ion} \\ \text{R-CHOH-R}' \\ \text{secondary alcohol} \end{array}\right\} \rightarrow \left\{\begin{array}{c} C_nH_{2n+2} \\ \text{branched-chain alkane} \\ \text{R-}\overset{+}{\text{C}}\text{OH-R}' \\ \text{protonated ketone} \end{array}\right. \qquad (6)$$

The feasibility of reaction (6) was tested by reacting aqueous 2-butanol over H-ZSM-5 zeolite under hydrothermal conditions at a lower temperature (263°C) and for a shorter time ($1\frac{1}{2}$ hr) than in the methanol conversion experiments.

The gas phase contained mainly mixed straight-chain butenes, but also a little *n*-butane and propylene. The organic liquid phase contained mainly a complex mixture of olefins and unchanged 2-butanol, but also some alkanes. The aqueous phase contained mainly 2-butanol. However, *iso*propanol was also found in the aqueous phase (estimated 3 C% yield w.r.t. the 2-butanol

---

[4] Vapor-phase thermodynamic data (assuming nonideal gas behavior) for the system *iso*propanol/*n*-propanol/propylene + water indicate a roughly 20/1 ratio of propylene/*iso*propanol under the conditions of aqueous methanol conversion; *iso*propanol is favored rather than *n*-propanol.

[5] For discussion of hydride abstraction reactions over ZSM-5 zeolite see Refs. (*4*, *9*, *10*).

reactant), as was acetone (est. 0.1 C% yield w.r.t. 2-butanol). 2-Butanone was found in both the organic and aqueous liquid phases and its yield was estimated as 0.3% with respect to the reactant. Overall 2-butanol conversion was about 50%.

These 2-butanol results can be understood as follows. The 2-butanol undergoes dehydration (the reverse of reaction (4)), and the resulting butenes undergo conversion to other olefins *via* oligomerization/cracking reactions. Equilibrium (7) is readily established over H-ZSM-5 zeolite in a gas-phase reactor below 300°C (*3, 11, 12*).

$$\tfrac{1}{3}C_3H_6 \rightleftharpoons \tfrac{1}{4}C_4H_8 \rightleftharpoons \tfrac{1}{5}C_5H_{10}, \text{ etc.} \quad (7)$$

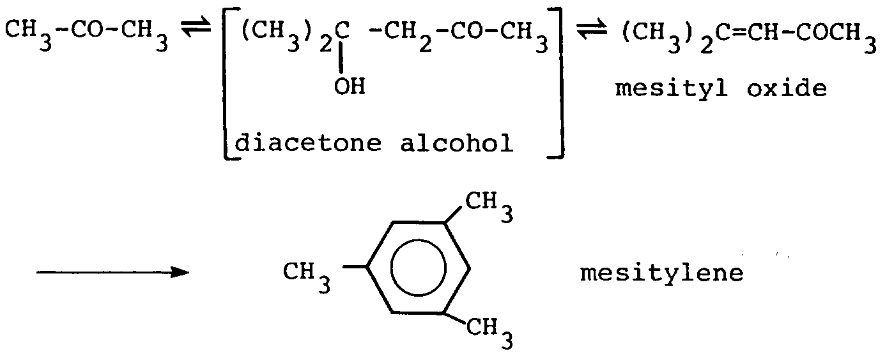
The various olefins would be expected to hydrate to corresponding alcohols, hence the presence of *iso*propanol.

Reaction (6) between 2-butanol and protonated olefins gives the observed 2-butanone and alkanes. Similarly reaction between *iso*propanol and protonated olefins gives the observed acetone and alkanes.[6]

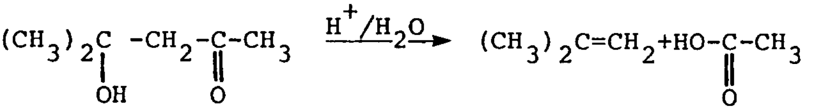
Carboxylic acids and esters might be formed *via* primary alcohols (e.g., propylene → 1-propanol → propanal → propionic acid), by analogy with reaction (6). However, carboxylic acids may also be formed from the ketone products, as is explained below.

Acid-catalyzed condensation (see below) of acetone to mesityl oxide (and ultimately to mesitylene) is well known. By contrast, condensation over ZSM-5 zeolite under mild conditions (24% conversion at 329°C) gives *iso*butene as the main product (*14*). We have also observed (*13*) that aqueous acetone gives *iso*butene (and acetic acid) with high selectivity over ZSM-5 zeolite at 200–250°C. The *iso*butene is presumably formed by hydrolysis of diacetone alcohol (see below).

Hydrolysis of α,β-unsaturated ketones and β-hydroxy ketones to carboxylic acids and olefins is probably general. It was reported to occur over phosphoric acid/silica at 265°C by McAllister *et al.* in 1940 (*15*).[7]



(8)



$$(CH_3)_2\underset{\substack{|\\OH}}{C}-CH_2-\underset{\substack{\|\\O}}{C}-CH_3 \xrightarrow{H^+/H_2O} (CH_3)_2C=CH_2+HO-\underset{\substack{\|\\O}}{C}-CH_3 \quad (9)$$

Various ketones may give various branched-chain olefins and carboxylic acids by reactions similar to (8) and (9). The branched-chain olefins would be expected to give tertiary carbenium ions and thus (by hydride abstraction) branched-chain al-

---

[6] Various micro-reactor studies (*13*) of the conversion of aqueous C_{3-4} alcohols at ≤300°C have given low yields of acetone, 2-butanone, and 3-methyl-2-butanone.

[7] A referee kindly drew our attention to this work.

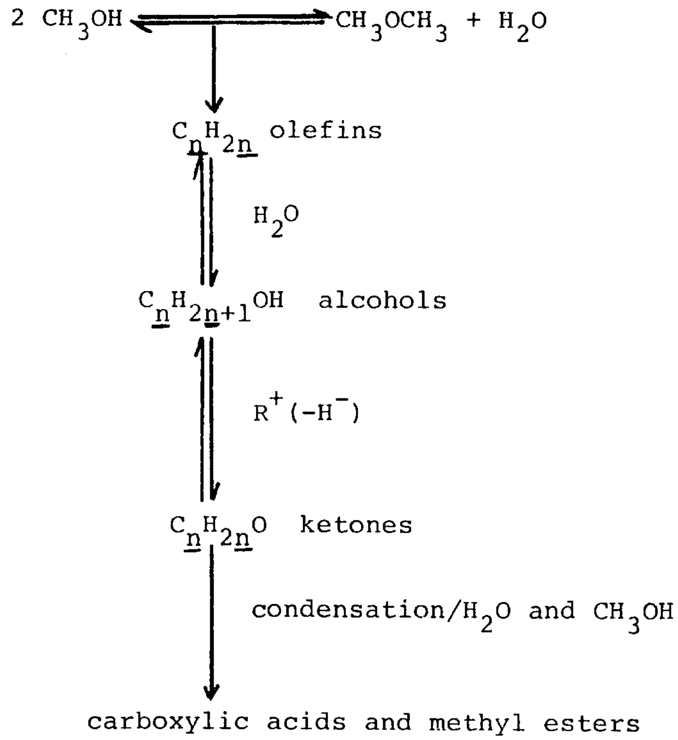


FIG. 1. Hydrothermal formation of oxygenated products from aqueous methanol over ZSM-5 zeolite.

kanes, and the carboxylic acids should be partially converted to methyl esters in an aqueous methanol medium (methanolysis of diacetone alcohol and similar ketone-condensation products, might also give methyl esters more directly).

Thus the carboxylic acids and methyl esters can be regarded as secondary products formed from ketones. The proposed overall reaction scheme is shown in Fig. 1.

ACKNOWLEDGMENTS

This work was carried out under the sponsorship of the National Energy Research, Development and Demonstration Council of Australia. The authors thank ICI Australia for permission to publish this work and Dr. J. R. Anderson for advice and encouragement.

REFERENCES

1. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).
2. Chang, C. D., *Catal. Rev.-Sci. Eng.* **25,** 1 (1983).
3. Anderson, J. R., Mole, T., and Christov, V., *J. Catal.* **61,** 477 (1980).
4. Mole, T., *J. Catal.* **84,** 423 (1983).
5. Mole, T., Whiteside, J. A., and Seddon, D., *J. Catal.* **82,** 261 (1983).
6. Argauer, R. J., and Landolt, J. R., U.S. Patent 3,702,886 (1972).
7. Mole, T., and Whiteside, J. A., *J. Catal.* **75,** 284 (1982).
8. Mole, T., Bett, G., and Seddon, D., *J. Catal.,* **84,** 435 (1983).
9. Haag, W. O., Lago, R. M., and Rodewald, P. G., *J. Mol. Catal.* **17,** 161 (1982).
10. Dejaifve, P., Vedrine, J. C., Bolis, V., and Derouane, E. G., *J. Catal.* **63,** 331 (1980).
11. Garwood, W. E., *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.* **27,** 563 (1982).
12. Garwood, W. E., *in* "Intrazeolite Chemistry" (G. D. Stucky and F. G. Dwyer, Eds.), ACS Symposium Series No. 218, p. 383. Amer. Chem. Soc., Washington, D.C., 1983.
13. Mole, T., unpublished work.
14. Chang, C. D., Lang, W. H., and Bell, W. K., *in* "Catalysis of Organic Reactions" (W. R. Moser, Ed.), p. 73. Dekker, New York, 1981.
15. McAllister, S. H., Bailey, W. A., and Bouton, C. M., *J. Amer. Chem. Soc.* **62,** 3210 (1940).