Hydrocarbon Formation from Methanol using WO₃/Al₂O₃ and Zeolite H-ZSM-5 Catalysts: Further Evidence on the Reaction Mechanism

Roger Hunter and Graham J. Hutchings

Department of Chemistry, University of the Witwatersrand, 1 Jan Smuts Avenue, Johannesburg, 2001, South Africa

Reaction of methanol with and without added hydrogen using the title catalysts gives no significant changes in the product spectrum providing strong evidence against non-bonded methylene being the active intermediate for carbon–carbon bond formation.

The conversion of methanol into hydrocarbons over the zeolite catalyst H-ZSM-5 continues to be a controversial issue, particularly the mechanism by which the initial carbon–carbon bond is formed. Originally Chang and Silvestri[1] proposed carbon–carbon bond formation to involve the insertion of methylene, formed *via* α-elimination, into the C–O bond of methanol, and recent experiments using diazomethane[2] have been suggested as supporting this proposal. An alternative proposal, independently suggested by Olah[3] using bifunctional catalysts, *e.g.* WO₃/Al₂O₃, and van den Berg[4] using H-ZSM-5 involves generation of an electrostatically bound dimethyloxonium methylide intermediate which reacts intermolecularly[5] to form the initial C–C bond. A donor–acceptor complex between dimethyl ether and the catalyst, as has been

proposed as a possible intermediate by Olah[5,6] for the WO₃/Al₂O₃ catalyst, is not possible for H-ZSM-5 since aluminium is co-ordinatively saturated. The onium-ylide mechanism as it has been termed[6] has received support from model studies involving deprotonation of trimethyloxonium salts, but ylide formation was only observed with strong bases such as 2,2,6,6-tetramethylpiperidyl-lithium.[7] More recently[8] a radical chain mechanism has been proposed based on spin-trapping of radicals in the product gases. This proposal also utilised non-bonded methylene as one of the intermediates in carbon–carbon bond formation. In this communication we present our results of co-feeding H₂ and MeOH over both the Olah WO₃/Al₂O₃ and ZSM-5 catalysts, which we consider to be strong evidence against the involvement of a

Table 1.

			Temp.	W.H.S.V.[a]	Conversion,	Hydrocarbon selectivity (% by mass)[b]							H₂,[c]	H₂/CH₄
Expt.	Reagent	Catalyst	/°C	/h⁻¹	%	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_{5+}	mole %	mole ratio
1	MeOH	WO_3/Al_2O_3	400	0.008	97.5	31.7	16.8	1.9	17.4	tr[a]	7.3	24.9	4.5	1.8
2	MeOH–H₂[d]	WO_3/Al_2O_3	400	0.008	96.3	29.0	18.2	2.8	20.5	tr	8.6	20.9	e	—
3	MeOH	WO_3/Al_2O_3	350	0.008	38.4	28.3	13.6	0.4	24.4	tr	13.3	20.0	0.7	0.7
4	MeOH–H₂[d]	WO_3/Al_2O_3	350	0.008	38.4	24.5	14.5	0.5	27.0	tr	15.2	18.3	e	—
5	MeOH	H-ZSM-5	370	0.051	100	0.3	9.9	0.1	38.0	tr	20.0	31.7	0.02	2.2
6	MeOH–H₂[d]	H-ZSM-5	370	0.051	100	0.3	11.2	0.1	35.5	tr	21.0	31.6	e	—
7	Me_2SO_4	WO_3/Al_2O_3	350	0.040	7.4	36.9	18.8	0	11.5	0	32.8	tr	0.004	0.6

[a] Weight hourly space velocity: g MeOH (g catalyst)⁻¹ h⁻¹. [b] Based only on hydrocarbon products; tr = trace. [c] Based on total exit gas analysis. [d] 9.8 mole % H₂ added to carrier gas. [e] Not determined, present in feed.
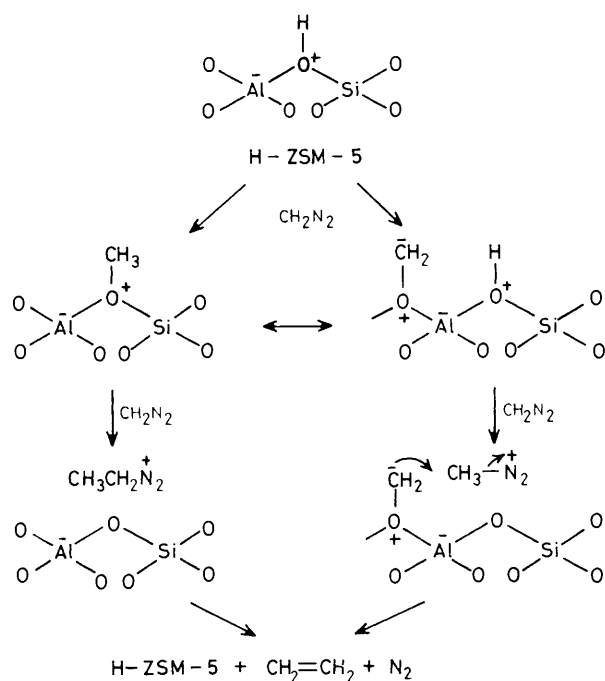
Scheme 1

free, *i.e.* non-bonded, methylene carbene intermediate as crucial in the initial C–C bond formation. In addition we present new evidence concerning the mechanism of hydrocarbon formation showing that the WO_3/Al_2O_3 catalyst demonstrates significant differences from the zeolite catalyst ZSM-5.

10% WO_3/Al_2O_3, prepared according to the method of Olah[5] and H-ZSM-5 were separately treated in a fixed bed microreactor with methanol which was fed to the reactor with a dry argon carrier gas. Catalysts were dried at 450 °C for 2 h in a dry carrier gas *in situ* in the reactor before use and products were analysed using gas chromatography. The reaction of methanol over the catalyst WO_3/Al_2O_3 (see Table 1, expts. 1, 3) shows that the major hydrocarbon product is typically methane, as has been noted previously by Olah,[5] but in addition comparable yields of hydrogen are also observed. By

contrast methane and hydrogen yields are always low at conversion >1% with the zeolite catalyst (typical data are shown in expt. 5). To test if the methane is formed with both catalysts *via* reaction of an intermediate with hydrogen the same reactions were carried out in the presence of added hydrogen (expts. 2, 4, 6) resulting in no increase in the yield of methane in any of the experiments. These results strongly indicate that a free methylene intermediate is not involved since an increase in methane yield would have been expected based on the known reaction between methylene and hydrogen.[9]

We have recently provided evidence[10] to suggest that a plausible mechanism of carbon–carbon bond formation initially involves a surface-bonded methyloxonium ion which is deprotonated to generate a surface-bonded methylide, isoelectronic with a surface-bonded carbene. Clearly neither of these intermediates would be expected to react with hydrogen to generate methane, although methane formation, not obviously accounted for by a radical mechanism, could be explained by hydride reduction of the methyloxonium ion by methanol.[11] Furthermore, as Olah has pointed out[6] in a recent communication, with regard to diazomethane conversion over ZSM-5, although there is no known analogy for the insertion of singlet methylene into methyloxonium ions there is precedence for the alkylation of diazomethane by an incipient methyl cation. We consider this to be consistent with our proposal that initial carbon–carbon bond formation involves a C_1 *bonded* intermediate. In the case of diazomethane conversion either a surface-bonded methylide could demethylate protonated diazomethane or diazomethane could demethylate a surface-bonded methyloxonium ion (see Scheme 1).

Finally to examine whether the WO_3/Al_2O_3 system, which Olah has extrapolated as having the same initial mechanism as ZSM-5,[6] could convert a reactant which we have considered[10] cannot form a trimethyloxonium ion, we reacted dimethyl sulphate over the WO_3/Al_2O_3 catalyst (expt. 7). The results show that a low conversion was effected but one which reflected a similar product distribution as found previously for methanol. We consider this to be strong evidence against carbon–carbon bond formation involving a trimethyloxonium ion intermediate with the WO_3/Al_2O_3 catalyst. The results of our experiments using H₂ co-feeding present clear evidence that non-bonded methylene is not a viable intermediate with either of the catalysts examined. Moreover the results obtained concerning the significant differences in the methane and hydrogen yields for WO_3/Al_2O_3 and H-ZSM-5 show that

mechanistic studies cannot be extrapolated with any certainty from one system to another as has recently been assumed.[6]

References

1 C. D. Chang and A. J. Silvestri, *J. Catal.*, 1977, **47**, 249.
2 C. S. Lee and M. M. Wu, *J. Chem. Soc., Chem. Commun.*, 1985, 250.
3 G. A. Olah, *Pure Appl. Chem.*, 1981, **53**, 201.
4 J. P. van den Berg, J. P. Wolthuizen, and J. H. C. van Hoof, in 'Proc. 5th Int. Conf. Zeolites,' ed. L. V. C. Rees, Heyden, London, 1980, p. 649.
5 G. A. Olah, H. Doggweiler, J. D. Felberg, S. Frohlich, M. J. Grdina, R. Karpeles, T. Keumi, S. Inaba, W. M. Ip, K. Lammertsma, G. Salem, and D. Tabor, *J. Am. Chem. Soc.*, 1984, **106**, 2143.
6 G. A. Olah, G. K. S. Prakash, R. W. Ellis, and J. A. Olah, *J. Chem. Soc., Chem. Commun.*, 1986, 9.
7 P. Rimmelin, H. Taghavi, and J. Sommer, *J. Chem. Soc., Chem. Commun.*, 1984, 1210.
8 J. K. A. Clarke, R. Darcy, B. F. Hegarty, E. O'Donoghue, V. Amir-Ebrahimi, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1986, 425.
9 W. Kirmse, in 'Carbene Chemistry,' Academic Press, New York, 1971.
10 R. Hunter and G. J. Hutchings, *J. Chem. Soc., Chem. Commun.*, 1985, 1643; 1986, 1006.
11 G. J. Hutchings, M. V. M. Hall, F. Gottschalk, and R. Hunter, *J. Chem. Soc., Faraday Trans 1*, 1987, **83**, 571.