

Hydrocarbon Formation from Methylating Agents over the Zeolite Catalyst H-ZSM-5 and its Conjugate Base: Evidence against the Trimethyloxonium Ion–Ylide Mechanism

Roger Hunter and Graham J. Hutchings

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

Reaction of methylating agents over the zeolite catalyst H-ZSM-5 and the sodium form of the conjugate base is shown to give hydrocarbons; ethylene formation from Me_2SO_4 over Na-ZSM-5 is strong evidence against involvement of trimethyloxonium ion ylides in C–C bond formation.

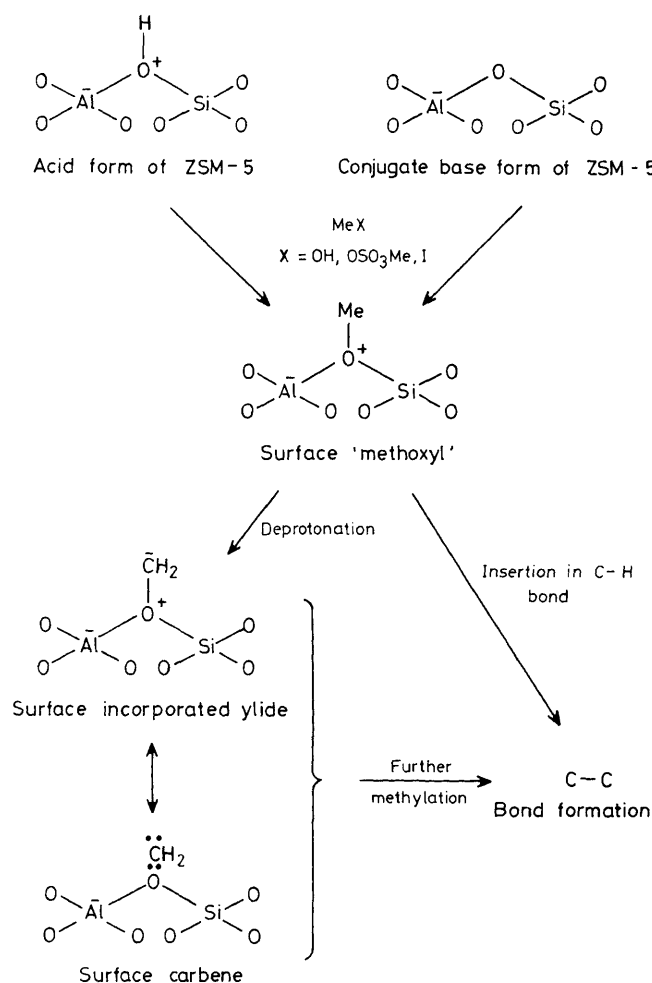
In the conversion of methanol into hydrocarbons using H-ZSM-5 zeolite¹ and other catalysts,² an agreement on the mechanism of the carbon–carbon bond formation step has yet to be reached. Experimental evidence to date points towards either an oxonium ion ylide^{3,4} or a surface bound carbene species^{1,5} to be the most likely intermediates. In a recent

communication⁶ we reported that $\text{LiAl}(\text{OPri})_4$ as a model compound for the conjugate base of H-ZSM-5 is far more nucleophilic than basic towards a range of methylating agents including trimethyloxonium ion. In this communication we report on the reaction of a series of methylating agents over H-ZSM-5 as well as over the sodium form of its conjugate base

Table 1.

Catalyst	Methylating agent	W.H.S.V.	T, °C	Time on line, min	Total conversion, %	Product selectivity, mole %			
						CH ₄	C ₂ H ₄	C ₃ H ₆	≥ C ₄
H-ZSM-5	MeOH	0.15	250	15	7.1	4.0	3.9	4.1	92.0
		0.15	250	60	16.7	1.1	14.1	5.6	79.2
		0.15	250	100	22.6	0.9	24.3	6.3	68.5
H-ZSM-5	Me ₂ SO ₄	0.075	250	15	0.12	81.5	18.5	0	0
		0.075	250	60	3.3	20.5	44.9	28.2	6.4
		0.075	250	100	12.9	2.5	28.9	11.2	57.4
		0.075	250	230	21.2	1.5	45.2	15.1	38.2
H-ZSM-5	MeI ^a	0.8	250	60	0.02	66.1	33.9	0	0
		0.8	250	100	0.13	7.0	44.1	32.5	16.4
Na-ZSM-5	MeOH ^b	0.075	300	200	0.001	64.4	35.6	0	0
Na-ZSM-5	Me ₂ SO ₄	0.075	250	90	0.06	52.4	47.6	0	0
		0.075	300	130	2.0	48.1	51.9	Trace	0
Na-ZSM-5	MeI	0.1	250	15	0.05	66.0	34.0	0	0
		0.1	300	90	0.07	70.0	30.0	0	0

^a No conversion observed after 15 min. ^b No conversion observed for 160 min at 250 °C.



and show that strong acid sites are not essential for hydrocarbon formation with good methylating agents.

MeOH, Me₂SO₄, and MeI were individually reacted using a dry nitrogen carrier gas firstly over H-ZSM-5 zeolite followed

by the sodium form of its conjugate base. The weight hourly space velocity (W.H.S.V.) was kept to around 0.1 g.g⁻¹ h⁻¹ (except for MeI/H-ZSM-5 = 0.8), achieved by regulating the temperature of each methylating agent before introduction over the catalyst. Prior to each run the catalyst was always scrupulously dried at 400 °C with dry N₂ carrier gas for several hours in order to eliminate all traces of water. Samples were analysed by gas chromatography.

MeSO₃F (Magic Methyl) proved too reactive under these conditions decomposing in the chamber as evidenced by a blank run. Blank experiments in the absence of catalysts for the other three methylating agents did not produce any hydrocarbons.

The results obtained with the two catalysts are summarised in Table 1. With the acidic H-ZSM-5 the temperature of the catalyst was kept at 250 °C and time on line varied from 100 min for MeOH and MeI to 230 min for Me₂SO₄. The most reactive of the three as expected was MeOH with a total conversion into hydrocarbons of 22.6 mole % after 100 min. Me₂SO₄ proved to be a very good reactant too with a conversion of 12.9 mole % after 100 min while MeI proved to be much less reactive with a conversion of only 0.13 mole % after 100 min albeit at a higher W.H.S.V. Any MeOH produced as a by-product with Me₂SO₄ would be insignificant compared with the concentration of Me₂SO₄ around it. Another noticeable feature with H-ZSM-5 was that relative conversion into higher hydrocarbons (>C₂) followed the same trend as reactivity *i.e.* MeOH > Me₂SO₄ > MeI suggesting that some propene at least is the product of methylation of ethene.

These results suggest that hydrophilicity of the reagent (on account of the very large difference between Me₂SO₄ and MeI based on methylating ability above) may be an important feature for entry into the internal catalyst channels. They are also consistent with the order of ease of formation and methylating ability of the protonated form of each reagent. Moreover since the oxygens of Me₂SO₄ are far less nucleophilic than the oxygen of MeOH it is unlikely that under these conditions Me₂SO₄ could form an oxonium ion, an essential feature of the oxonium ion-ylide mechanism as proposed by van der Berg.

With the sodium form of the conjugate base of the zeolite we also obtained results consistent with a methylation mechanism. This time Me₂SO₄ proved to be several orders of

magnitude more reactive than MeOH. Even MeI gave a higher conversion into hydrocarbons (0.07 mole % after 90 min/300 °C) which in all cases were a mixture of methane and ethene (trace of propene with Me₂SO₄ after 130 min/300 °C). The striking feature of these results is that oxonium ion formation is impossible under these basic conditions.

In the light of these results we suggest that methylation of the conjugate base to give what Ono⁷ calls a surface 'methoxyl' may well be the important first step in carbon-carbon bond formation (Scheme 1). Deprotonation to give a surface incorporated ylide⁸ identical to the Mobil surface carbene species and consistent with the deuterium exchange evidence reported by Mole,⁹ or insertion of the surface bound methyl into the C-H bond of methanol or dimethyl ether⁷ are the likeliest possibilities for the actual C-C bond formation step from this intermediate.

Received, 22nd July 1985; Com. 1061

References

- 1 C. D. Chang and A. J. Silvestri, *J. Catal.*, 1977, **47**, 249.
- 2 G. A. Olah, H. Doggweiler, J. D. Felbeg, S. Frohlich, M. J. Grdina, R. Karpeles, T. Kevmi, S. Laba, W. M. Ip, K. Lam-mertsma, G. Salem, and D. C. Tabar, *J. Am. Chem. Soc.*, 1984, **106**, 2143.
- 3 J. P. van den Berg, J. P. Wolthuizen, and J. H. C. van Hoof, Proceedings of the 5th Conference on Zeolites, Naples, Italy, 1980, p. 649.
- 4 G. A. Olah, *Pure Appl. Chem.*, 1981, **53**, 201.
- 5 C. S. Lee and M. M. Wu, *J. Chem. Soc., Chem. Commun.*, 1985, 250.
- 6 R. Hunter and G. J. Hutchings, *J. Chem. Soc., Chem. Commun.*, 1985, 886.
- 7 Y. Ono and T. Mori, *J. Chem. Soc., Faraday Trans. 1*, 1981, 77, 2209.
- 8 Deprotonation of trimethyl oxonium ion by BF₄⁻ has recently been reported, C. Engelen, J. Wolthuizen, and J. van Hooff, *J. Chem. Soc., Chem. Commun.*, 1985, 300.
- 9 T. Mole, *J. Catal.*, 1983, **84**, 423.