The nature of the active oxidant in biomimetic oxidation of methane over Fe—ZSM-5 zeolite

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Capability of iron-containing non-heme Fe_2O enzyme, methane monooxygenase (MMO), to perform selective oxidation of methane to methanol puts the biomimetic oxidation of methane in the group of the most important problems of catalysis.[1] It has been recently shown[2] that methane can be oxidized at room temperature upon interaction with an active oxidant formed on the surface of the Fe—ZSM-5 zeolite treated by N_2O. Experimental data[3] and quantum-chemical calculations[4] indicate that the surface iron complexes on Fe—ZSM-5 are binuclear; hence, taking into account the capability of Fe—ZSM-5 to oxidize methane selectively at room temperature, it can be assumed to be an adequate model of MMO. It was of interest to determine the nature of the active oxidant of this model. Active intermediates of the catalytic cycle with MMO have been recently characterized by stop-flow and frozen matrix techniques.[5]

We found that according to the data of the Mössbauer spectroscopy, the active oxidant, which is formed during treatment of Fe—ZSM-5 by nitrogen monooxide and is capable of oxidizing methane at room temperature, is a binuclear complex of Fe^{III}, unlike MMO, in which a binuclear complex of Fe^{IV} is the active oxidant. The samples of Fe—ZSM-5 containing 0.24 wt. % ^{57}Fe were obtained and treated by N_2O according to the known procedure.[6]

It follows from Table 1 that although the parameters of the Mössbauer spectra of the oxidized and reduced Fe—ZSM-5 are close to the corresponding parameters of MMO, substantial differences between the active oxidants both in the MMO and in the model are observed. A comparison of the parameters of the Mössbauer spectra of the initial MMO and of the active intermediate Q allowed one to conclude[5] that Fe^{IV} is present in the active intermediate Q. In our case, a similar comparison shows that the active oxidant is the Fe^{III} complex. The results obtained indicate also the formation of two forms of the active oxidant, (1) and (2), or a nonequivalence of the ligand surroundings for the Fe(1) and Fe(2) atoms occurring in the same complex. The nature of the residual Fe^{II} is not clear yet.

Table 1. Comparison of the parameters of the Mössbauer spectra of Fe—ZSM-5 and MMO at 90 K

Sample	State Fe	δ /mm s^{-1}	ΔE_Q /mm s^{-1}	Fraction (%)(±5)
Initial	Fe^{III}	0.55	1.04	24
Fe—ZSM-5	Fe^{II}	1.37	3.11	76
Active oxidant (AO),	$Fe^{III}(1)$	0.39	0.78	30
Fe—ZSM-5 + [O]	$Fe^{III}(2)$	0.45	1.70	41
	Fe^{II}	1.28	2.58	29
AO + CH_4	Fe^{III}	0.57	1.55	75
	Fe^{II}	1.06	3.31	25
Oxidized MMO[7]	Fe^{III}	0.50	1.05	
Reduced MMO[7]	Fe^{II}	1.30	3.014	
Active intermediate Q[5]	Fe^{IV}	0.17	0.53	

According to our data, a complex of an O atom with a binuclear center Fe_2O[8] may be the active oxidant. On the basis of calculations, the authors[9] suppose that this center has the structure of a peroxocomplex. As follows from the Mössbauer spectra, the active oxidant transforms to a complex with methanol during the reaction with methane and this complex eliminates methanol slowly, thus forming the oxidized Fe—ZSM-5. Thus, the reaction mechanism can involve the following steps:

$$Fe_2^{II} \xrightarrow{N_2O} Fe_2^{III}O \xrightarrow{N_2O} Fe_2^{III}O(O) \longrightarrow$$

$$\xrightarrow{CH_4} Fe_2^{III}O(MeOH) \longrightarrow Fe_2^{III}O$$

We believe that the difference from MMO is due to the different ligand surroundings of the Fe_2O center.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1583—1584, June, 1996.

1066-5285/96/4506-1509 $15.00 © 1996 Plenum Publishing Corporation

The authors express their gratitude to Academician A. E. Shilov for assistance and useful remarks.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 94-03-08529) and INTAS (Grant 93-315).

References

1. A. A. Shteinman, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1011 [*Russ. Chem. Bull.*, 1995, **44**, 975 (Engl. Transl.)].
2. V. I. Sobolev, K. A. Dubkov, O. V. Panna, and G. I. Panov, *Catalysis Today*, 1995, **24**, 251.
3. G. I. Panov, V. I. Sobolev, K. A. Dubkov, V. N. Parmon, N. S. Ovanesyan, A. E. Shilov, and A. A. Shteinman, *J. Am. Chem. Soc.*, 1996, in press.
4. M. Yu. Filatov, A. G. Pelmenschikov, and G. M. Zhidomirov, *J. Mol. Catal.*, 1993, **80**, 243.
5. S. K. Lee, B. G. Fox, W. A. Froland, J. D. Lipscomb, and E. Muenck, *J. Am. Chem. Soc.*, 1993, **115**, 6450.
6. G. I. Panov, V. I. Sobolev, and A. S. Kharitonov, *J. Mol. Cat.*, 1990, **61**, 85.
7. J. G. Dewitt, J. G. Bentsen, A. C. Rosenzweig, B. Hedman, J. Green, S. Pilkington, G. C. Papaefthymiou, H. Dalton, K. O. Hodgson, and S. J. Lippard, *J. Am. Chem. Soc.*, 1991, **113**, 9219.
8. A. A. Shteinman, *FEBS Lett.*, 1995, **362**, 5.
9. A. V. Arbusnikov and G. M. Zhidomirov, *Catal. Lett.*, 1996, in press.

Received February22, 1995