Methane peroxide oxidation over Fe-containing MFI: effect of the catalyst texture and surface properties

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Abstract: The selectivity of Fe-MFI catalysts to partial peroxide oxidation of methane to methanol and formic acid was studied depending on their topology (Nanocrystals, Microcrystals, and bulk Commercial) and activation with oxalic acid. The increase in TOF and selectivity to formic acid, as well as a sharp decrease in the selectivity to CO_2 over all the activated catalysts were accounted for by an increase in the total acidity of the catalysts and the number of oligomeric Fe oxo-clusters. Different pathways to the formation of methanol/CO_2 (via free radical mechanism) and formic acid (via heterogeneous route) over Fe-MFI catalysts were suggested.

Keywords:, Fe-ZSM-5, Fe-silicalite, Formic acid, Methanol

1. Introduction (11-point boldface)

The chemical activation of methane is a fundamental chemical problem of vital importance [1] because of the abundant resources of methane on the planet, the possibility of its continuous recovery as a result of the global nature's cycle of carbon (ca. 109 ton per year) [2] and stability of the methane molecules. Fe- and Cu-MFI zeolites were shown earlier to catalyze the peroxide oxidation of light paraffins [3] and recently methane to methanol at a high enough selectivity under mild conditions (50 °C) [4-6].

The present study was aimed at revealing the influence of Fe-MFI catalysts properties on the selectivity to partial peroxide oxidation of methane to methanol and formic acid.

2. Experimental

The catalysts of different topology (Fe-silicalite Nanocrystals, Fe-silicalite Microcrystals [8,9], Commercial H-ZSM-5-30 [9], Figure 1) are studied before and after activation of the catalytically active sites with an oxalic acid solution [8,9].

Catalysts were characterized by XRD, ICP-OES, SEM, TEM, N_2 adsorption, UV-vis DR, TPD of ammonia. Methane was oxidized at 50 °C and 30 bar in a 450 mL autoclave under vigorous stirring. The weighed catalyst was 2.7 $g \cdot L^{-1}$, H_2O_2 concentration was 1 M.

3. Results and discussion

CO and CO_2 were detected as the products of the gas phase reaction. Methanol was detected by GC and formic acid by HPLC in the aqueous phase. By using ^1H and 13C NMR the following products were detected in the reaction solutions: methanol, formic acid, formaldehyde hydrate, and methyl hydroperoxide. Main products appeared to be methanol, formic acid and CO_2 (Table 1).

The catalyst activity and selectivity to the main reaction products are determined by three key factors: the external surface area/crystallite size, concentration of Brönsted acid sites, and concentration/size of Fe oxide clusters. TOF of methane oxidation increases in the series: Nanocrystals < Microcrystals << Commercial. The selectivity to methanol depends mainly of the crystallite size and increases in the same series.

Activation of all the catalysts with oxalic acid causes a decrease in the selectivity of the methane oxidation to CO_2 and methanol. At the same time, the selectivity to formic acid increased, probably due to an increase in the quantity of oligomeric Fe oxide clusters and α-Fe_2O_3-like particles (UV-vis DR data).

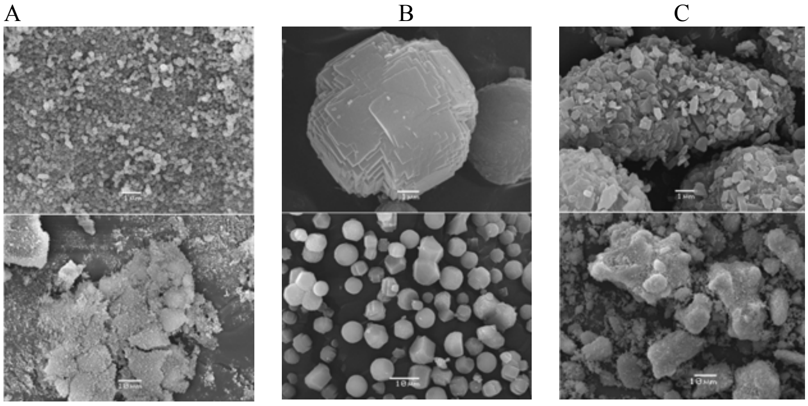

Figure 1. SEM images of Fe–silicalite Nanocrystals (A), Fe-silicalite Microcrystals (B) and Commercial Fe-ZSM-5 (C) at different magnifications.

Table 1. Methane peroxide oxidation over Fe-containing catalysts (50°C, 30 bar, 30 min, 1 M H_2O_2, 2.7 $g \cdot L^{-1}$ catalyst, pH_{init} 3.5).

Entry	Catalyst	H_2O_2		CH_4		TOF (H_2O_2)/ TOF (CH_4)	Selectivity, %				pH_{final}	Fe leaching,	
		Conversion, %	TOF, h^{-1}	Conversion, %	TOF, h^{-1}		MeOH	HCOOH	CO	CO_2		mg L^{-1}	%
1	Nanocrystals	12	356	0,14	22	16.2	14	41	1.6	44	3.1	0.1	0.28
2	Nanocrystals *activated*	12	425	0.22	39	9.2	12	65	0.7	23	2.9	0.1	0.31
3	Microcrystals	9	289	0.16	25	11.6	16	64	0.9	19	3.0	0.1	0.26
4	Microcrystals *activated*	13	435	0.30	46	9.5	12	72	0.6	13	2.9	0.1	0.26
5	Commercial	15	950	0.42	140	6.6	36	26	0.6	37	3.0	0.2	1.14
6	Commercial *activated*	20	1403	1.02	338	4.2	10	84	0.9	5,1	2.8	0.4	2.28
7	Blank experiment	0	0	0	0	-	0	0	0	0	3.5	0	0
8	Leaching test after Entry 6	0	0	0	0	-	0	0	0	0	2.7	0.4	0
9	$Fe(NO_3)_3$	10	683	0.02	6	68.3	0	0	1	99	1.9	-	-

4. Conclusions

Our inspection of correlations of the selectivity with the above discussed factors allowed an assumption to be formulated concerning different pathways to the formation of methanol/CO_2 and formic acid from methane over Fe-MFI catalysts. In the presence of the Commercial catalyst the selectivity to formic acid appeared to be quite high (up to 84%) and the selectivity of the hydrogen peroxide involving into the methane oxidation – quite comparable (till 75%) with the bypath- decomposition of the hydrogen peroxide itself. It generates optimism in possibility to synthesize Fe-containing catalysts with the preferential oxidation of light alkanes with H_2O_2 in mild condition.

Acknowledgements

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