The effect of Fe site location in Fe-MFI zeolite catalysts on the performance of conversion of methane to methanol with H_2O_2

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Abstract: The conversion of methane to methanol over Fe-containing zeolite catalysts under mild conditions has been investigated. To clarify the impact of the distribution and the state of the Fe species in the MFI-type zeolite, Fe-containing zeolite catalysts were prepared by hydrothermal synthesis method using OSDA with or without Na cations. Different catalytic properties were illuminated depending on the Fe state and acidic properties. We found that sulfolane was a good solvent in terms of the improvement in the production of methanol and its stability during the reaction.

Keywords: Methane oxidation, Fe-MFI, sulfolane

1. Introduction

Significant interest exists in the development of direct routes for the conversion of methane to value-added products. Recently, Fe-containing MFI-type zeolites were used in the oxidation of methane to methanol with H_2O_2 in an environmentally benign process at only 50 °C [1]. However, some factors that influence the catalytic performance have not fully been investigated. We have established a method for controlling the Al distribution in the MFI framework [2]; correspondingly, the Fe site and state will be affected by the presence of Na cations. Hence, the effects of the location of Fe site in the MFI zeolite on the catalytic performance in the oxidation of methane to methanol were investigated.

2. Experimental

Fe-MFI zeolite catalysts were synthesized using TPA with or without Na cation according to the literature just change the Al source as Fe source in the synthesis gel [2]. The H-type zeolites were obtained from NH_4^+-type after calcination at 823 K for 5 h. Final products were designated as FMT*x* for TPA without Na, FMTN*x* for TPA with Na cation, where *x* means the Si/Fe ratio in the synthesis gel.

The catalytic reaction was performed in a Teflon-lined stainless-steel autoclave (100 ml). In a typical reaction, 3 MPa methane was poured into 10 ml sulfolane, 30 mmol H_2O_2 and 50 mg of catalyst. The reaction mixture was heated at 50 ºC and magnetically stirred at approximately 1000 rpm for 2 h.

3. Results and discussion

The XRD patterns of the catalysts indicated that all the catalysts retained the MFI structure. By the UV-vis spectra of the catalysts, two characteristic oxygen-to-metal charge-transfer bands around 211 and 245 nm, which are related to Fe^{3+} at isolated tetrahedral framework sites. Calcination results in extensive migration of tetrahedral Fe species from the framework to extra framework positions: oligomeric iron oxide clusters, larger Fe_2O_3-like aggregates, and bulk Fe_2O_3 can be distinguished [3].

The reaction results are shown in Table 1. First, FMT catalysts achieved higher liquid products and H_2O_2 conversion than FMTN catalysts at different Si/Fe ratios although FMT catalysts contained lower Fe content compared with FMTN ones. Interestingly, CH_3OH yield was influenced by the Fe distribution. Sitting of Fe atoms at narrow space led to a high performance. Meanwhile, high Si/Fe ratio enhanced the products yield. The selectivity of methanol for both FMT and FMTN catalysts are maintained above 56 %.

To clarify the reason for the different catalytic performance, Fe state was investigated by NO-adsorbed FT-IR technique. Figure 1(a) shows the NO-adsorbed FT-IR spectra of FMT25 and FMTN25 catalysts. According to the literature [4], only isolated and oligomer cluster iron species on the extra framework possess the ability of NO adsorption. The bands at around 1918 and 1812 cm^{-1} can be attributed to

$Fe^{2+}(NO)_3$ complexes. $Fe^{2+}(NO)$ complexes formed on the isolated Fe are reasonable for the catalysts at 1867 cm^{-1}. The bands at 1763 cm^{-1} are assigned to $Fe^{2+}(NO)_2$ species [5]. There is significant difference in the four main bands between the two samples. Thus, we would conclude that presence of Na cations or not in the synthesis gel might be a key for the Fe distribution and state, leading to different catalytic performance in the CH_4 conversion. Besides, the acidity is another significant factor to reflect the Fe site. Figure 1(b) shows the NH_3-TPD spectra of FMT and FMTN catalysts. The peaks intensity of FMTN are stronger than that of FMT under different Si/Fe ratios for both *l*-peak and *h*-peak, indicating that the Fe content in the framework of FMTN is higher than that of FMT.

Table 1. Composition and reaction results of Fe-MFI zeolite catalysts.

Catalyst	**Si/Fe**		**Product Amount (μmol)**			**Product Selectivity (%)** [a]			**H_2O_2**	**H_2O_2**
	In gel	**ICP**	**MeOH**	**HCOOH**	**HCOH**	**MeOH**	**HCOOH**	**HCOH**	**Conv. (%)**[b]	**Eff. (%)**[c]
FMT25	25	41	301.0	14.2	219.8	56	3	41	11.2	19.0
FMT50	50	95	266.3	29.8	82.7	70	8	22	7.3	18.5
FMTN25	25	29	279.3	19.2	186.6	58	4	38	11.1	16.3
FMTN50	50	59	115.7	26.8	63.2	56	13	31	5.8	13.8

[a] Each product selectivity= (moles of each product)/(moles of total liquid products).

[b] H_2O_2 conversion = (moles of H_2O_2 after reaction)/(initial moles of H_2O_2).

[c] H_2O_2 efficiency = (moles of total liquid products)/(moles of H_2O_2 conversion).

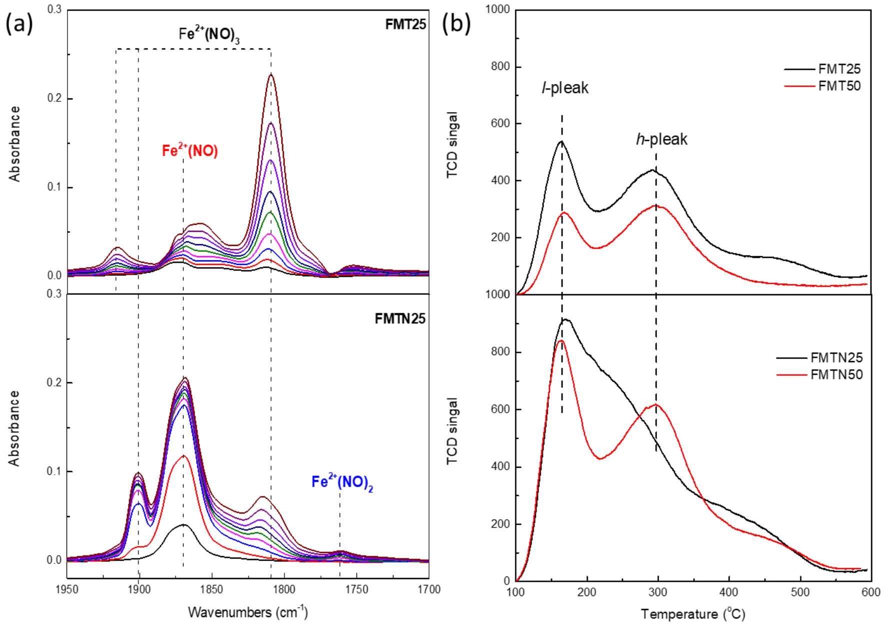

Figure 1. (a) NO-adsorbed FT-IR spectra of FMT25 and TMTN25 catalysts, conditions: evacuated at 773 K for 2 h, adsorption temp. = 298 K, P_{NO} = 5-1000 Pa. (b) NH_3-TPD spectra of FMT and FMTN zeolite catalysts.

4. Conclusions

The catalysts of Fe-MFI with or without Na cations in the synthesis gel achieved different performance in hydroxylation of methane to methanol. It is most likely to be affected by the Fe site location. Similar to the distribution of Al in MFI zeolite, iron is possible gathered around in the intersection of the framework for as-made type FMT catalysts, after calcination, iron in the framework migrate to extra framework close to the intersection which is more conducive to the formation of active iron species.

References

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