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Selective oxidation of methane to methanol on a FeZSM-5 surface

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Abstract

Methane is selectively oxidized to methanol at room temperature over the interaction with α-form of the surface oxygen produced on FeZSM-5 zeolite by N_2O decomposition.

1. Introduction

Numerous efforts to accomplish a partial oxidation of methane have encountered the problem of a low reaction selectivity. This problem relates to the fact that under hard conditions which are necessary for CH_4 activation, the partial oxidation products are much more reactive than methane and easily subjected to a further transformation. To overcome this problem, nature gave up the idea to activate CH_4. Instead, it resorted to a unique ability of Fe-containing enzyme–methane monooxygenase, to activate O_2 and to produce highly reactive atomic oxygen species. They are capable of oxidizing non-activated CH_4 molecules at room temperature to yield methanol [1].

In view of this consideration, CH_4 interaction with the α-oxygen form produced by N_2O decomposition on FeZSM-5 surface is of great interest. α-Oxygen has been shown to exhibit a very high reactivity which also enables it to interact with methane at room temperature [2]. The product of this reaction was not identified. Spectroscopic techniques (IR, NMR) proved not to be sensitive enough, while attempts to isolate the product by its desorption upon heating brought about its secondary transformations. In the present study we use for this purpose a new approach based on the product extraction from FeZSM-5 surface followed by its chromatographic analysis [3].

2. Experimental

Experiments were carried out in a vacuum static unit equipped with an on-line mass spectrometer. ZSM-5 zeolite with $SiO_2/Al_2O_3 = 100$ and containing 0.30 wt.-% Fe_2O_3 was used as a catalyst. α-Oxygen form was loaded by N_2O decomposition at 240°C according to the reaction [2].

Interaction with methane was carried out at room temperature. Then, the sample was taken from the reactor and subjected to the extraction procedure using water or water solution of acetonitrile as a solvent. A gas chromatograph provided with FID was used for the product analysis.

3. Results and discussion

After CH_4 interaction with α-oxygen a temperature-programmed heating of the FeZSM-5 sam-

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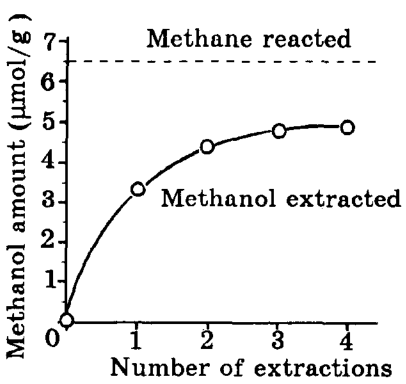

Fig. 1.

ple results in CO evolution into the gas phase. An identical CO thermodesorption spectrum was obtained in a control experiment while heating the sample containing an equivalent amount of preadsorbed CH_3OH. It assumes methanol is the most probable primary reaction product. This assumption was entirely confirmed by the extraction which discovered CH_3OH to be the only product removed from surface.

Fig. 1 shows the amount of methane involved in the reaction with α-oxygen (6.5 µmol/g) as well as the amount of methanol extracted. After 4-fold extraction the amount of methanol is equal to 5.0 µmol/g which is responsible for nearly 80% of the methane consumption. A small loss of product during the extraction and analysis procedures is a possible reason for this disagreement while the actual methanol amount most likely corresponds to the following reaction:

$$CH_4 + (O)_\alpha = (CH_3OH)_\alpha$$

4. Acknowledgement

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5. References

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