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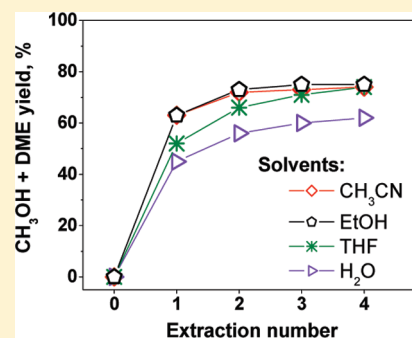
# Room-Temperature Oxidation of Methane by $\alpha$ -Oxygen and Extraction of Products from the FeZSM-5 Surface

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Supporting Information

**ABSTRACT:** Room-temperature oxidation of methane to methanol by  $\alpha$ -oxygen is of great mechanistic interest for both conventional and biomimetic oxidation catalysis. This work was carried out using new-generation FeZSM-5 samples that have the  $O_\alpha$  concentration of 100  $\mu\text{mol/g}$ . This value exceeds 3–15 times the  $O_\alpha$  concentration on the earlier studied samples, thus providing more precise quantitative measurements related to the reaction mechanism. Fourier transform infrared spectroscopy data confirmed an earlier conclusion that  $\text{CH}_4 + O_\alpha$  surface reaction proceeds by the hydrogen abstraction mechanism. This mechanism leads to hydroxy and methoxy groups residing on  $\alpha$ -sites. The methanol formation takes place by hydrolysis of  $(\text{Fe}-\text{OCH}_3)_\alpha$  groups at the step of extraction. For the first time dimethyl ether (DME) was identified in the reaction products, its amount comprising 6–7% of the methane reacted. In distinction to methanol, DME is readily extracted both by dry solvents (acetonitrile, tetrahydrofuran, ethanol) and their mixtures with water. A reliable extraction procedure was developed, which provides a 75% recovery of the methane oxidation products (methanol + DME). The missing products are shown to remain on the catalyst surface and can be quantitatively recovered in the form of  $\text{CO}_x$  at heating the sample. A mechanism involving  $\text{CH}_3^\bullet$  radicals formed in the H-abstraction step is suggested to explain the reaction stoichiometry  $\text{CH}_4:O_\alpha = 1:1.75$  and a deficit of the carbon balance at extraction.



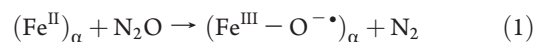
## 1. INTRODUCTION

Huge natural resources of methane and the ability of enzyme methane monooxygenases (MMO) to perform its oxidation to methanol excite the imagination of chemists and inspire new and repeated attempts to run this reaction in a catalytic way. However, for many decades this problem remains unsolved and needs a deeper insight into the mechanism of  $\text{CH}_4$  interaction with the active oxygen of catalyst.

The unique properties of MMO are related to the Fe-containing sites capable of generating extremely active oxygen species that can insert into nonactivated C–H bonds of methane under ambient conditions.<sup>1,2</sup> The attempts to create chemical analogs of MMO are hindered by inability of artificial systems to generate equally active oxygen species. Such species fail to form not only with  $\text{O}_2$  (as in the case of enzymes), but also with  $\text{H}_2\text{O}_2$  and other oxygen donors.<sup>2–4</sup>

In this connection, of great interest are FeZSM-5 zeolites. Among various iron species that can form in the system, there are very special  $(\text{Fe}^{\text{II}})_\alpha$  complexes called  $\alpha$ -sites. As shown by many authors,<sup>5–10</sup> formation of  $\alpha$ -sites occurs at high temperature treatments of FeZSM-5 (over 500 °C) due to the iron spontaneous “autoreduction”,  $\text{Fe}^{\text{III}} \rightarrow \text{Fe}^{\text{II}}$ , accompanied by the equivalent evolution of  $\text{O}_2$  into the gas phase.<sup>8</sup> According to a still not perfectly clear mechanism, a part of  $\text{Fe}^{\text{II}}$  is subjected to a strong chemical stabilization in the zeolite matrix, which makes its reoxidation by  $\text{O}_2$  thermodynamically unfavorable,<sup>11</sup> even by

heating the sample in artificial air at 700–900 °C.<sup>5,9</sup> However, these  $(\text{Fe}^{\text{II}})_\alpha$  complexes can be readily oxidized at 200–250 °C by endothermic molecules of nitrous oxide generating a highly active radical oxygen species ( $\alpha$ -oxygen,  $O_\alpha$ )



The formation of  $O_\alpha$  is a unique feature that easily distinguishes  $\alpha$ -sites from all other iron states.

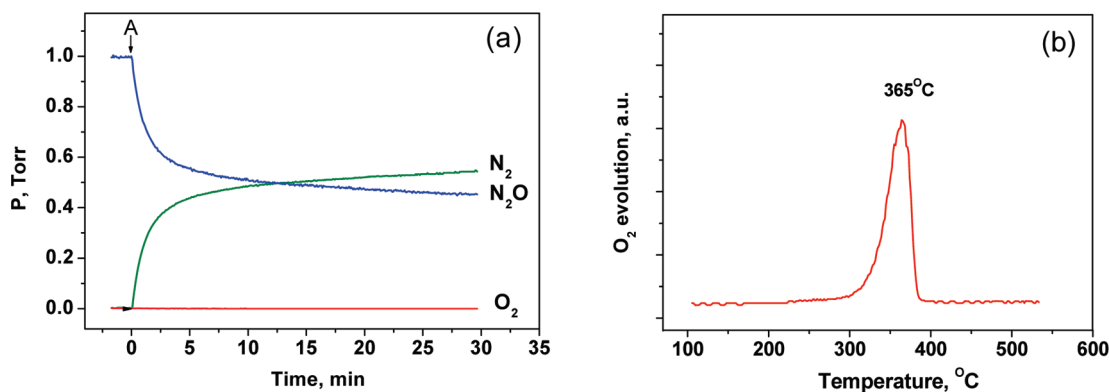
Because of the  $\text{Fe}^{\text{II}} \leftrightarrow \text{Fe}^{\text{III}}$  redox transformation and generation of  $\alpha$ -oxygen, FeZSM-5 zeolites can perform selective catalytic oxidation of benzene to phenol as well as many other oxidations.<sup>12,13</sup>

It is worth noticing that  $(\text{Fe}^{\text{III}} - \text{O}^{\bullet})_\alpha$  complexes, the formation of which by reaction 1 has been shown by Mössbauer,<sup>5,14</sup> resonant inelastic X-ray scattering (RIXS),<sup>15,16</sup> and electron paramagnetic resonance (EPR)<sup>17</sup> methods, are electronic isomers of ferryl units  $\text{Fe}^{\text{IV}}=\text{O}^{2-}$ , which are considered as the key active species in biological and biomimetic oxidations.<sup>18–20</sup> Possible parameters affecting the interconversion of  $\text{Fe}^{\text{III}} - \text{O}^{\bullet} \leftrightarrow \text{Fe}^{\text{IV}}=\text{O}^{2-}$  were analyzed by Malykhin et al.<sup>21</sup> Close electronic structures of these entities are discussed by Rosa et al.<sup>22</sup> based on quantum chemical calculations.

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**Figure 1.** Deposition of  $\alpha$ -oxygen by  $\text{N}_2\text{O}$  decomposition at 230 °C (a) and its desorption from FeZSM-5 at TP-heating (b). A = time of opening the microreactor.

Properties of  $\alpha$ -oxygen and the state of iron constituting  $\alpha$ -sites were studied in many experimental<sup>23–30</sup> and theoretical<sup>12,21,22,31–37</sup> works and discussed in several reviews.<sup>12–14</sup> Similar to the MMO active oxygen,  $\text{O}_\alpha$  has a remarkably high reactivity. At room temperature it readily performs stoichiometric oxidation of methane, benzene, and other hydrocarbons on the FeZSM-5 surface.<sup>38–43</sup> In all cases, extraction of the products reveals formation of hydroxylated compounds, which is typical of the oxidation by monooxygenases. Chemical similarity between the  $\text{O}_\alpha$  and the active oxygen of MMO is discussed by a number of authors,<sup>20–23,44–46</sup> with particular attention to this aspect by Rosa et al.<sup>22</sup> This similarity makes especially interesting to study a detailed mechanism of  $\alpha$ -oxygen interaction with methane. Recently, small amount of  $\alpha$ -oxygen was reported on the surface of CuZSM-5<sup>43–45</sup> and MnZSM-5.<sup>46</sup>

Spectral methods, in particular IR spectroscopy, are widely used for studying adsorbed species on a catalyst surface. Important information can be additionally obtained by the extraction method. This method was first used by Sobolev and co-authors to identify primary products of stoichiometric oxidation of methane<sup>38</sup> and benzene<sup>51</sup> by  $\alpha$ -oxygen at room temperature on FeZSM-5 zeolites. Later, extraction was performed by Rodkin et al.,<sup>40</sup> Knops-Gerrits et al.,<sup>42</sup> Groothaert et al.,<sup>47</sup> and Smeets et al.<sup>48</sup> when studying the oxidation of methane on FeZSM-5 and CuZSM-5. In all cases with methane, methanol was recovered as a single product of the reaction.

Quantitative measurements made previously<sup>38,52</sup> revealed an essential inconsistency in the extraction results. It was found that the amount of methanol extracted comprised only 60–75% of the methane reacted. This disbalance may be either a real fact related to some features of methane transformation on the catalyst surface or a result of inaccuracy of the extraction procedure caused by low concentration of  $\alpha$ -oxygen. Thus, in ref 38, the concentration was only 6.5  $\mu\text{mol O}_\alpha/\text{g}$ , which provided accordingly a very low product concentration in the solvent.

The present work is aimed at a detailed study of methane reaction with  $\alpha$ -oxygen and especially the product extraction from the FeZSM-5 surface. The work is prompted by our recent advances in preparing a new generation FeZSM-5 zeolites that have  $\alpha$ -oxygen concentration of 100  $\mu\text{mol O}_\alpha/\text{g}$ . This is 3–15 times higher compared to the  $\text{O}_\alpha$  concentration on the earlier studied samples. This high concentration allows one to perform more precise measurements related to the reaction mechanism as well as to develop a reliable extraction procedure, which is important for further studies in this field.

## 2. EXPERIMENTAL SECTION

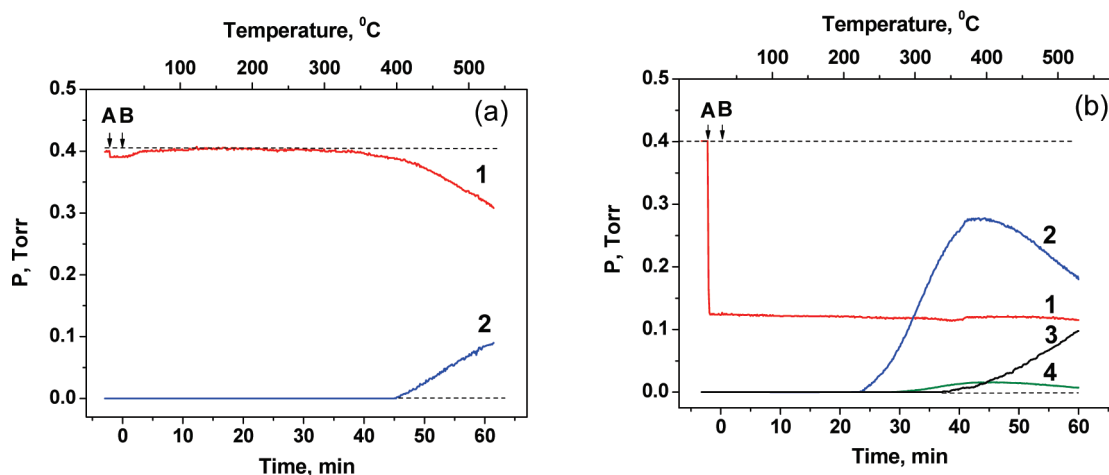
The FeZSM-5 catalyst was prepared by impregnation of the parent HZSM-5 zeolite (Si/Al = 25;  $C_{\text{Na}} < 0.01$  wt %) with a  $\text{FeCl}_3$  solution.<sup>5</sup> To obtain a high concentration of  $\alpha$ -sites ( $C_\alpha$ ); the sample calcined in air at 550 °C was additionally heated in vacuum at 900 °C. The value of  $C_\alpha$  was determined from the maximum amount of  $\alpha$ -oxygen that can be deposited on the sample by reaction 1. At  $C_\alpha$  calculation, one  $\text{O}_\alpha$  atom is assumed to occupy one  $\alpha$ -site. The activated sample has the iron concentration  $C_{\text{Fe}} = 2.0$  wt % Fe (Fe/Al = 0.53) and  $C_\alpha = 6.0 \times 10^{19}$  site/g (100  $\mu\text{mol/g}$ ).

Deposition of  $\alpha$ -oxygen and its reaction with methane were carried out in a vacuum static setup described elsewhere.<sup>8</sup> The setup was equipped with absolute pressure gauges (0.002–100 Torr) and a mass spectrometer PPT Residual Gas Analyzer (MKS Instruments). The FeZSM-5 sample was loaded into a quartz microreactor (6.5  $\text{cm}^3$ ) and subjected to a standard pretreatment that included alternate heating at 550 °C in vacuum and in oxygen at 2 Torr pressure. Such pretreatment provides careful removal of water and organic impurities from the surface as well as ensures complete oxidation of the iron which can be oxidized by  $\text{O}_2$  and therefore is not composing the  $\alpha$ -sites. The latter circumstance is essential for correct measurement of the  $\alpha$ -oxygen amount.

The  $\text{O}_\alpha$  deposition was performed by FeZSM-5 treatment with  $\text{N}_2\text{O}$  at 230 °C with the initial pressure 1 Torr. As Figure 1a shows, at these conditions the decomposition of  $\text{N}_2\text{O}$  takes place to follow exactly eq 1. The oxygen generated from  $\text{N}_2\text{O}$  remains adsorbed on the  $\alpha$ -sites while equivalent amount of  $\text{N}_2$  evolves into the gas phase. A temperature-programmed heating (Figure 1b) shows that  $\alpha$ -oxygen is stable up to ca. 300 °C and then desorbs into the gas phase as a single  $\text{O}_2$  peak at 365 °C. No  $\text{O}_2$  peak appears if the treatment is done with dioxygen instead of  $\text{N}_2\text{O}$ .

The measurements of  $\alpha$ -oxygen amount are described elsewhere.<sup>53,54</sup> In this work we used mainly two methods based on the amount of  $\text{N}_2\text{O}$  decomposed (eq 1) and the equilibrium composition of dioxygen at isotopic exchange  $^{18}\text{O}_2/^{16}\text{O}_\alpha$  performed at 100 °C. Both methods give close results and avoid destruction of  $\alpha$ -oxygen, which can be used in further experiments with methane.

FTIR diffuse reflection spectra were taken in a quartz cell with an ultrahigh vacuum shut-off cock. To perform pretreatments of the sample identical to those used in other experiments, the cell was connected to the vacuum setup in place of the working



**Figure 2.** RT reaction of methane with FeZSM-5 surface before (a) and after (b)  $\alpha$ -oxygen deposition followed by TP-heating of the sample. A: the time of microreactor opening; B: the time of heating onset. (1)  $\text{CH}_4$ ; (2)  $\text{CO}$ ; (3)  $\text{CO}_2$ ; (4)  $\text{H}_2$ .

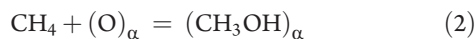
reactor. This method provided an adequate comparison of IR data with the results of adsorption measurements. IR spectra were recorded using a Shimadzu FTIR 8300 Fourier spectrometer at a resolution  $4\text{ cm}^{-1}$  with 100 scans per spectrum. A specially devised holder can precisely fix the cell relative to the beam, which allowed obtaining well reproducible results.

In this work, special attention was paid to the development of reliable extraction procedure. For extraction, a FeZSM-5 sample (commonly 0.2 g, 0.25–0.5 mm fraction) after the  $\text{CH}_4 + \text{O}_\alpha$  reaction was transferred from the vacuum setup to a vial (Supelco, 2 mL) with a minimum contact of zeolite with the atmosphere. After filling with a solvent (commonly 1.5 mL), the vial was hermetically sealed and placed for a specified time in a rotator, which turned it over in the “head up–head down” manner at 30 rpm to provide good mixing. Then the vial was placed in a centrifuge for 1 min to separate the solvent from the catalyst particles, which may hinder a subsequent chromatographic analysis. For complete recovery of the reaction products, the extraction procedure was repeated several times with a new portion of solvent.

Gas chromatography (GC) analysis of extracted products was performed with a Kristall 2000 M instrument equipped with an automatic liquid sampler and a capillary column HP Plot U designed for analysis of low-boiling oxygen-containing organic substances. To provide reliable measurements of small methanol concentrations (main operating range is 0.5–15  $\mu\text{mol/mL}$ , 20–600 ppm), we preliminarily plotted two detailed calibration dependences (absolute and relative with an internal standard) in the concentration range of 0.25–25  $\mu\text{mol/mL}$ . Both dependences are linear and start from the origin of coordinates (Supporting Information, Figure 1).

### 3. RESULTS

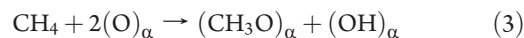
As it was noted above, in all preceding works methanol was the only product extracted from the catalyst surface after methane reaction with  $\alpha$ -oxygen. Therefore, it was assumed<sup>38,45,48</sup> that this is a single-step reaction leading directly to the adsorbed methanol



Later some facts were discovered that did not agree with this assumption. In particular, Dubkov et al.<sup>43</sup> reported that the ratio

of the  $\text{CH}_4$  amount reacted to the amount of  $\alpha$ -oxygen deposited was 1:1.8, which is much higher than 1:1, as eq 2 implies. To explain this disagreement, the authors hypothesized that in the course of reaction a part of  $\text{O}_\alpha$  is blocked in the zeolite micropores by the formed molecules of methanol and becomes inaccessible to methane. But special experiments did not confirm this hypothesis.

The use of IR spectroscopy significantly clarified this issue. It was found that methane reaction with  $\text{O}_\alpha$  proceeds by dissociative route leading to the formation of methoxy and hydroxy groups<sup>41,55,56</sup>



It means that methanol forms due to hydrolysis of methoxy groups taking place at the extraction step



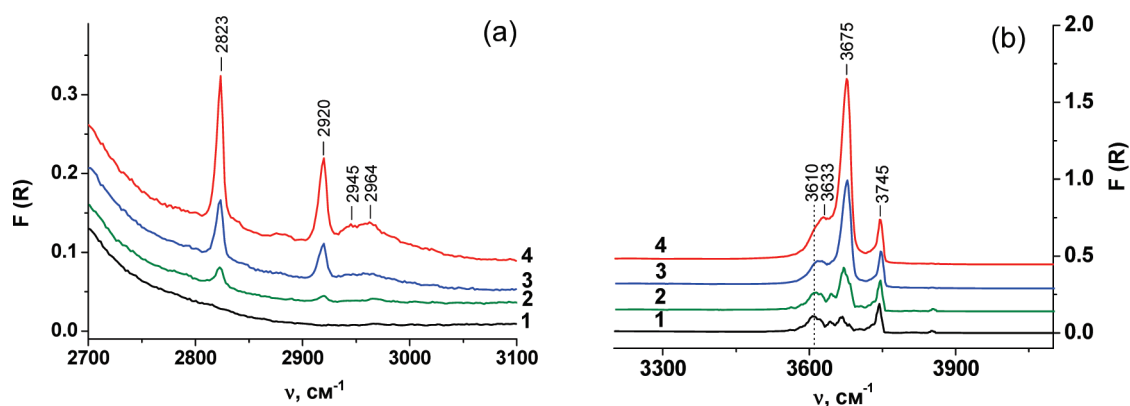
The hydrolysis process of Fe-OCH<sub>3</sub> was registered with IR spectra by Wood et al.<sup>55</sup>

However, the mechanism represented by eqs 3 and 4 implies the stoichiometry  $\text{CH}_4:\text{O}_\alpha = 1:2$ , which also does not fit completely the experimental value 1:1.8. One may assume that the reaction proceeds by a mixed route. That is, in addition to the main dissociative route, 20–30% of methane reacts by eq 2, which leads directly to methanol and provides the overall stoichiometry 1:1.8. Elucidation of this mechanistic detail is among the aims of our work.

**3.1. Reaction of  $\text{CH}_4$  with  $\alpha$ -Oxygen.** **3.1.1. Reaction Stoichiometry.** To determine the reaction stoichiometry in comparison with the earlier results, we run two comparative experiments on a room-temperature methane interaction with the zeolite (Figure 2). In the first experiment, methane interacts with the zeolite after its standard pretreatment (no  $\alpha$ -oxygen on the surface), whereas in the second experiment it reacts after deposition of  $\alpha$ -oxygen (100  $\mu\text{mol O}_\alpha/\text{g}$ ). One may see that without  $\alpha$ -oxygen (Figure 2a) the zeolite is inert toward methane. After opening the reactor (time A), only a weak reversible adsorption of  $\text{CH}_4$  is observed. With slight heating, methane desorbs completely and restores the initial pressure.

A different picture is observed in the case of  $\text{O}_\alpha$  (Figure 2b). After the reactor opening, strong irreversible consumption of





**Figure 3.** IR spectra of FeZSM-5 in CH (a) and OH (b) vibration regions after RT reaction of methane with different amount of  $\alpha$ -oxygen: (1) no  $O_\alpha$  (sample upon standard pretreatment); (2) 20  $\mu\text{mol } O_\alpha/\text{g}$ ; (3) 50  $\mu\text{mol } O_\alpha/\text{g}$ ; (4) 100  $\mu\text{mol } O_\alpha/\text{g}$ .

methane takes place, pointing to the chemical reaction  $\text{CH}_4 + O_\alpha$  proceeding rapidly at room temperature. This leads to quite a different behavior of the sample at its subsequent temperature programmed heating. Without  $\alpha$ -oxygen (Figure 2a), the system shows no change up to 350–400  $^\circ\text{C}$ , and only further heating gives rise to some CO evolution due to methane oxidation by surface oxygen of the sample. In the case of  $\alpha$ -oxygen (Figure 2b), an intensive evolution of CO starts already at 220  $^\circ\text{C}$ , with its partial oxidation to  $\text{CO}_2$ . No other carbon-containing products are detected in the gas phase. In the latter experiment,  $\text{CO}_x$  formation is not a result of methane oxidation (its pressure remains constant) but obviously caused by degradation of the surface products formed by  $\text{CH}_4$  reaction with  $\alpha$ -oxygen. The total amount of  $\text{CO} + \text{CO}_2$  corresponds to the amount of reacted methane.

From the pressure drop in the given reaction volume of the setup (715  $\text{cm}^3$ ) shown in Figure 2b one can calculate the amount of methane reacted with  $O_\alpha$ . Repeated measurements gave a stoichiometric ratio  $\text{CH}_4:O_\alpha = 1:1.75 \pm 0.05$ . Earlier, this ratio was measured by Dubkov et al.<sup>43</sup> With the sample having  $C_\alpha = 1.8 \times 10^{19}$  site/g (30  $\mu\text{mol}/\text{g}$ ) they obtained virtually the same value,  $\text{CH}_4:O_\alpha = 1.8$ . This coincidence seems somewhat surprising since one may expect the ratio to depend on the  $\alpha$ -site concentration. However, in the  $C_\alpha$  range studied this dependence is probably not pronounced.

**3.1.2. IR DATA.** Figure 3 shows IR spectra of the sample after methane reaction with different amounts of  $\alpha$ -oxygen preliminarily deposited on the FeZSM-5 surface. For the bare sample (no  $O_\alpha$  spectrum 1), no absorption bands are observed in the CH stretching region (2700–3100  $\text{cm}^{-1}$ ). In the region of OH stretches, there are bands typical of the proper hydroxy groups of the zeolite: terminal silanol groups  $\text{Si}-\text{OH}$  (3745  $\text{cm}^{-1}$ ) and bridging groups  $\text{Si}-\text{OH}-\text{Al}$  (3610  $\text{cm}^{-1}$ ). There is also a band at 3670  $\text{cm}^{-1}$ , which is usually assigned to OH groups on extralattice Al atoms.<sup>55</sup> Neither  $\text{CH}_4$  adsorption on the  $O_\alpha$ -free surface nor the deposition of  $\alpha$ -oxygen change the spectrum (not shown).

The reaction  $\text{CH}_4 + O_\alpha$  gives rise to new bands in both regions (spectra 2–4). Intensity of these bands grows with the increasing amount of  $\alpha$ -oxygen and attains a maximum at its maximum value of 100  $\mu\text{mol } O_\alpha/\text{g}$ . Absorption bands in the CH region (two intensive and two weak) are caused by methoxy groups  $\text{Fe}-\text{OCH}_3$ . To follow the authors,<sup>41</sup> we assign 2823  $\text{cm}^{-1}$  to symmetric C–H stretches, 2920 and 2964  $\text{cm}^{-1}$  to asymmetric stretches, and 2945  $\text{cm}^{-1}$  to the overtone of deformation

**Table 1.** Extraction by Dry Solvents

solvent	methanol		DME	
	$\mu\text{mol}/\text{g}$	yield, %	$\mu\text{mol}/\text{g}$	yield, %
THF	1	2	1.5	6
acetonitrile	0.5	1	1.5	6
ethanol	23	45	1.3	5

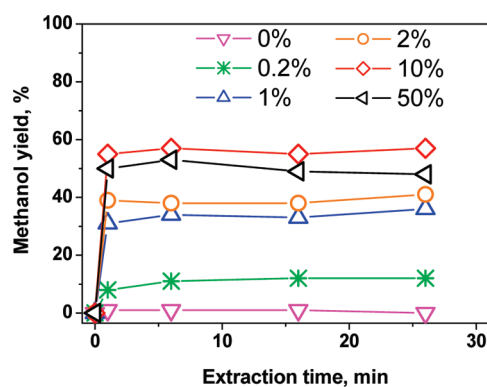
vibrations. A close assignment was given by Wood et al.<sup>55</sup> and Kameoka et al.<sup>56</sup> (These authors observed formation of  $\text{Fe}-\text{OCH}_3$  groups upon  $\text{CH}_4$  reaction with  $\text{N}_2\text{O}$  over FeZSM-5 and FeBEA zeolites at 150–255  $^\circ\text{C}$ .) By contrast with our expectation, the spectra in Figure 3 show no signals typical of adsorbed methanol that should be presented by two intensive bands at 2850 and 2955  $\text{cm}^{-1}$  (Figure 2 of Supporting Information).

In the OH stretching region, the methane reaction leads to an intensive band at 3675  $\text{cm}^{-1}$  with a shoulder at 3633  $\text{cm}^{-1}$ . Two types of the  $(\text{Fe}-\text{OH})_\alpha$  groups may relate with the two type  $\alpha$ -sites differing in iron coordination as shown by Mössbauer data.<sup>5</sup> The assignment of these bands to the  $(\text{Fe}-\text{OH})_\alpha$  groups was supported by the isotope shifts resulting from the replacement of  $^{16}\text{O}_\alpha$  by  $^{18}\text{O}_\alpha$ .<sup>57</sup>

**3.2. Product Extraction.** One of the problems concerning methanol extraction from the FeZSM-5 surface is the carbon disbalance. As was noted above, the amount of methanol recovered in the earlier works constituted only 60–75% of the consumed methane. A possible reason is low efficiency of the extractant being used. Following the authors,<sup>38</sup> all subsequent works<sup>42,47–49,52</sup> performed the extraction by a mixture of acetonitrile and water in 1:1 ratio without proper substantiation of this choice.

In the present work, we compared some solvents and their mixtures with water to determine their efficiency as extractants. Net water and three organic solvents of 99.9+% purity were compared: acetonitrile (Kriochrom), tetrahydrofuran (Vekton), and ethanol additionally dried by distillation over sodium metal.

**3.2.1. Extraction by Dry Solvents.** Since transformation of methoxy groups to methanol requires hydrolysis by water, one may expect that extraction by dry solvents should fail to yield methanol. Results of dry extraction are presented in Table 1. Indeed, one can see that in the case of tetrahydrofuran (THF) and acetonitrile, methanol is virtually absent. A minor  $\text{CH}_3\text{OH}$  yield (1–2% of the reacted methane) may be related with small

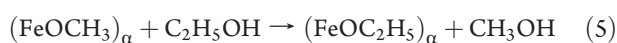


**Figure 4.** Effect of water content in acetonitrile (vol %) and extraction time on the methanol yield.

**Table 2.** Extraction by Water-Containing Solvents and Water

solvent	product	products yield (%) in the corresponding extraction cycle				total yield, %
		1	2	3	4	
acetonitrile	DME	6	0	0	0	6
	methanol	57	12	1	0	70
ethanol	DME	5	1	0	0	6
	methanol	59	9	2	0	70
THF	DME	6	1	0	0	7
	methanol	46	13	5	3	67
water	DME	2	1	0	0	3
	methanol	43	10	4	2	59

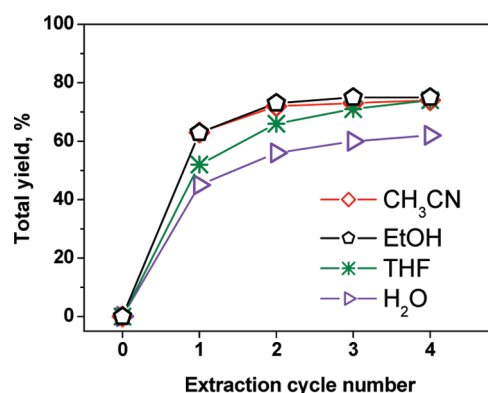
water admixtures in the solvents. Ethanol shows a rather different result providing a 45% yield of methanol, which cannot be explained by water admixture. Here methanol most probably forms due to substitution of methoxy groups by ethoxy groups



Quite a surprising result of Table 1 is dimethyl ether (DME), which is discovered for the first time in the reaction products. Its amount is independent of the solvent identity and in all cases comprises 5–6% of the reacted methane amount.

**3.2.2. Extraction in the Presence of Water.** To find an optimal concentration of water, we tested mixtures of acetonitrile with different water content. The effect of extraction time on the products yield was also studied. It is seen (Figure 4) that the extraction process is fast and terminates in several minutes. Beside methanol and DME, no other products were detected in the extract. Similar to the dry extraction, the DME yield is 5–6% and does not depend on the water content. For this reason, in Figure 4 we depicted only the data for methanol, to show more clear effect of water.

Even a small addition of water strongly enhances the methanol extraction, providing a 10% yield at 0.2 vol % H<sub>2</sub>O. As water content increases, so does the CH<sub>3</sub>OH yield, which exceeds 50% at 10% H<sub>2</sub>O. This corresponds to the maximum amount of methanol that can be recovered in one extraction cycle. A further water addition does not increase the extraction efficiency. As a large H<sub>2</sub>O amount hinders precise measuring of DME, in



**Figure 5.** Effect of extraction cycle numbers on total yield of DME and methanol extracted by water and water-containing solvents.

subsequent experiments we use water content 10 vol % and extraction time 10 min.

Under such extraction conditions, we performed an experiment with deuterated methane CD<sub>4</sub> (98.5%) instead of CH<sub>4</sub>. Analysis of the resulting extract by GS-MS revealed the product methanol of CD<sub>3</sub>OH composition.

We studied also how the number of extraction cycles affects the amount of products recovered by different water-containing solvents: acetonitrile, THF, and ethanol. Results for four extraction cycles are presented in Table 2 and Figure 5 along with the data for net water.

One can see that the first extraction cycle recovers the main amount of products: almost the entire DME and the major part of methanol. A noticeable amount of methanol is still recovered in the second cycle. In the case of acetonitrile and ethanol, this cycle virtually completes the process. THF and water are less efficient. With these solvents, a minor amount of methanol is observed in the third and even fourth cycles. The ultimate total yield of DME and methanol for organic solvents comprises 74–76%. In the case of water, the yield is 62%.

## 4. DISCUSSION

**4.1. Carbon Balance.** The above results show that we failed to achieve complete extraction of the reaction products. Although the high O<sub>α</sub> concentration allowed us to discover DME in addition to CH<sub>3</sub>OH, its amount was insufficient for the full carbon balance of the reaction. The total yield of CH<sub>3</sub>OH and DME comprised only 75%. Attempts to perform the extraction at elevated temperature as well as those with the addition of formic acid (to catalyze hydrolysis of Fe-OCH<sub>3</sub> groups) did not improve the result.

We also tried the extraction by supercritical CO<sub>2</sub> (description of these experiments is omitted here). However, this solvent also did not provide a complete balance. Extraction by dry CO<sub>2</sub> recovered only a small quantity of DME, and water addition led to methanol approximately in the same amount as in the case of organic solvents.

High accuracy of our measurements seems to leave the only one explanation of the observed carbon deficit: a missing part of the reaction products remains on the catalyst surface. To verify this hypothesis, we carried out the following experiment, which completely confirmed this assumption.

After four extraction cycles by net water (not to contaminate the surface by solvent's carbon), the sample was placed in the

vacuum setup. First it was evacuated at 50 °C. Then the reaction volume was closed, and the sample was slowly heated to 550 °C in the presence of a trap cooled by liquid nitrogen. At heating, CO evolved to the gas phase in the amount equivalent to 7% of the methane consumed. Main part of the product was found after thawing the trap: it was CO<sub>2</sub> in the amount responsible for another 30% of the CH<sub>4</sub> reacted. So, taken together with ~60% yield of the CH<sub>3</sub>OH extracted by water, this amount of CO<sub>x</sub> provides for the first time a virtually complete carbon balance of the reaction CH<sub>4</sub> + O<sub>α</sub>.

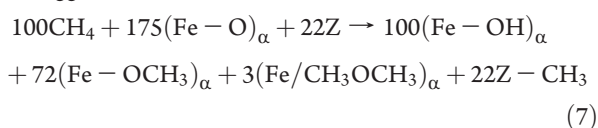
**4.2. Reaction Mechanism.** Although DME is responsible only for a minor part of the methane reacted (~6%), its origin is of considerable interest. First we hypothesized that DME forms due to a conventional dehydration process of the extracted methanol, which can be catalyzed by acid sites of the zeolite



However, the following experiment did not support the hypothesis. After the standard pretreatment, the catalyst sample was placed in a vial filled with 1.5 mL solvent (acetonitrile +10 vol % H<sub>2</sub>O). Then, 0.2 mL of methanol was added to the solvent by a microsyringe to provide methanol concentration close to its concentration in the extraction experiment. After rotation and centrifuging, the solution was periodically taken for GC analysis. Even after 24 h, no DME was found.

Another type of experiment related to a DME origin was conducted in the vacuum setup. After standard pretreatment of the sample, we performed adsorption of various amounts of methanol vapors (100 and 500 μmol/g) on the FeZSM-5 surface. The subsequent extraction yields neither DME nor other compounds except for initial methanol. We think the above results are quite convincing arguments for concluding that DME formation takes place immediately in the course of CH<sub>4</sub> + O<sub>α</sub> surface reaction.

Taking together all experimental data presented in the work including a stoichiometric ratio CH<sub>4</sub>:O<sub>α</sub> = 1:1.75 obtained from amounts of methane and α-oxygen reacted at room temperature, the following reaction scheme seen in Table 3 can be suggested



In the first step, the H atom is abstracted from CH<sub>4</sub> to form a hydroxy group residing on the α-site and a methyl radical CH<sub>3</sub>•. As it is reviewed by Mayer et al.,<sup>58</sup> such a step is widely accepted in various fields of oxidation chemistry. Next, three steps describe reactions of CH<sub>3</sub>• radicals. The main part (75%) of the radicals reacts with O<sub>α</sub> (step 2) to produce methoxy groups (Fe–OCH<sub>3</sub>)<sub>α</sub> which are observed in the IR spectra due to their C–H vibrations.

**Table 3. Reaction Scheme**

step 1	CH <sub>4</sub> + (Fe–O•) <sub>α</sub> → (Fe–OH) <sub>α</sub> + CH <sub>3</sub> •	100
step 2	CH <sub>3</sub> • + (Fe–O•) <sub>α</sub> → (Fe–OCH <sub>3</sub> ) <sub>α</sub>	75
step 3	CH <sub>3</sub> • + (Fe–OCH <sub>3</sub> ) <sub>α</sub> → (Fe/CH <sub>3</sub> OCH <sub>3</sub> ) <sub>α</sub>	3
step 4	CH <sub>3</sub> • + Z → Z–CH <sub>3</sub>	22

Another 3% reacts with methoxy groups (step 3) to yield DME adsorbed on α-sites. According to the extraction results, its amount is responsible for 6% of the methane reacted. The remaining 22% of methyl radicals are assumed to react with some Z sites of the zeolite catalyst to produce Z–CH<sub>3</sub> groups. These groups are not observed as an individual IR peak in the C–H region. The latter fact may be explained either by decreased polarity of C–H bonds in the groups or (if Z includes the oxygen atom) their IR signals may be undistinguishable from those of the (Fe–OCH<sub>3</sub>)<sub>α</sub>. If Z–CH<sub>3</sub> groups are not hydrolyzed, they should remain on the surface leading to a 22% carbon deficit at extraction. Within the measurement accuracy, this value coincides with the experimental deficit of 25%.

Remarkably, the mechanistic transformations presented by the reaction scheme assume surface mobility of CH<sub>3</sub>• radicals at room temperature. However, recombination of CH<sub>3</sub>• species does not take place at these conditions, since neither ethane nor ethylene are found in the reaction products.

## 5. CONCLUSION

A FeZSM-5 catalyst with a high concentration of α-oxygen (100 μmol/g) was synthesized. The use of this catalyst as well as improved experimental procedures allowed us to elaborate results of preceding studies on the room-temperature methane oxidation by α-oxygen. It was shown for the first time that the reaction gives not only methanol, which is the main product extracted from the catalyst surface, but also DME, which amount comprises 6–7% of the methane reacted. It is noteworthy that DME is a result of the surface reaction CH<sub>4</sub> + O<sub>α</sub> rather than a product of conventional dehydration process of the methanol extracted.

In agreement with earlier studies, the IR data confirm the oxidation of CH<sub>4</sub> to occur via the hydrogen abstraction mechanism leading to the formation of hydroxy and methoxy groups.

A detailed study was conducted to find an efficient solvent and proper extraction conditions for recovery of the reaction products from the FeZSM-5 surface. If diffusion limitation is avoided, the extraction proceeds quickly and terminates in several minutes. Acetonitrile and THF with 10 vol % water can be recommended as efficient solvents.

In spite of all our efforts we did not achieve a complete extraction of the reaction products. The total amount of extracted methanol and DME comprises 75% of the methane reacted. The missing products were shown to remain on the surface and, upon heating the sample, can be removed in the gas phase as CO<sub>x</sub>, which amount completes for the first time a 100% carbon mass balance.

A mechanism of CH<sub>4</sub> oxidation by α-oxygen is suggested to explain both the observed overall reaction stoichiometry and the deficit of the carbon balance at extraction.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** GC methanol calibration dependences, IR spectra of methanol adsorbed on the FeZSM-5 surface. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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