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Methanol formation on Fe/Al-MFI via the oxidation of methane by nitrous oxide

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Abstract

A zeolite containing Fe and Al in the framework positions of an MFI structure was produced by hydrothermal synthesis. Subsequent thermal pretreatment caused the Fe to migrate from the lattice and become stabilized at cation-exchange sites associated with framework Al atoms. The interactions of CH_4, N_2O, and methanol with this material were investigated by IR spectroscopy and temperature-programmed reactions methods. Upon exposure of thermally pretreated Fe/Al-MFI to methanol, the Brønsted acid protons and hydroxyl groups associated with Si and Fe reacted to form surface methoxy groups. Separate infrared features were observed for methoxy species bound to Si and Fe. Exposure of Fe/Al-MFI to CH_4 and N_2O above ~ 448 K resulted in the formation of methoxy groups bound to both Fe and Si and the simultaneous loss of hydroxyl groups associated with both elements. The formation of methoxy groups was not observed on either Al-MFI or Fe-MFI, suggesting that the active sites in the oxidation of CH_4 to methoxy species by N_2O are extraframework Fe atoms associated with framework Al. The methoxy groups residing on the catalyst decomposed when the temperature was raised above 523 K and no methanol was observed in the products; however, when the methoxy groups reacted with H_2O at 523 K, these groups were rapidly hydrolyzed to form methanol. For Fe/Al-MFI, small amounts of methanol were observed when CH_4 and N_2O reacted over Fe/Al-MFI at temperatures above 523 K, but the selectivity to this product was less than 2%, the majority of the CH_4 undergoing combustion.

1. Introduction

The identification of catalysts for the partial oxidation of methane to methanol continues to be an important area of research and one that holds considerable potential for use of the large, worldwide reserves of natural gas. Studies conducted with silica-supported vanadia and molybdena have shown that methanol can be produced by using N_2O as the oxidant, rather than O_2 [1–3]. More recently, several investigators have demonstrated that Fe-ZSM-5 (an MFI structure with Al in tetrahedral framework positions and extraframework Fe) can be used to produce methanol from CH_4 and N_2O. Above ~ 523 K, Fe-ZSM-5 is known to decompose N_2O to stoichiometric amounts of N_2 and O_2 [4–14]. However, at temperatures below ~ 523 K, Panov and co-workers have demonstrated that N_2O decomposes to N_2 and atomically adsorbed oxygen bonded to the extraframework Fe [4,6,15–19]. The adsorbed oxygen formed in this way reacts with CH_4 at room temperature to form surface methoxy species [6,15,17,20–23] or with benzene to form a precursor to phenol [6,17,18,21,24,25]. While phenol can be desorbed as a stable product at temperatures > 523 K, the methoxy species decompose without the formation of methanol. Methanol can be formed, however, by hydrolyzing methoxy groups from the surface by washing the catalyst with water.

A number of methods have been investigated for incorporating Fe into ZSM-5. Postsynthetic exchange has been used to introduce Fe into extraframework positions in ZSM-5. Several studies have addressed the local structure of Fe in Fe-ZSM-5 following postsynthetic exchange. Marturano et al. [26,27], Battiston et al. [28,29], and Jia et al. [30] prepared Fe-ZSM-5 ($Fe/Al = 1$) by means of dry cation exchange using sublimed $FeCl_3$. Analysis of EXAFS mea-

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surements made on these materials led these authors to conclude that Fe is present exclusively as diferric oxo/hydroxyl-bridged species. Marturano et al. showed that the distribution of Fe in Fe-ZSM-5 is strongly dependent on the structure of the parent ZSM-5 with evidence for Fe_2O_3 particles in some samples [27]. Joyner and Stockenhuber prepared samples using various postsynthetic exchange methods, including several liquid-phase exchange methods as well as solid-state exchange with $FeCl_2$ or iron(II) carbonate [31]. Using EXAFS, they found that the final state of iron in the materials was dependent on both the preparation method and the pretreatment, with evidence of isolated Fe cations, large clusters of Fe_3O_4, as well as Fe_4O_4 nanoclusters. Using IR spectroscopy and TPR methods, Lobree et al. have reported that during solid-state exchange with $FeCl_3$, Fe^{3+} cations exchange on a one to one basis with Brønsted acid protons in addition to forming small particles of Fe_2O_3 [32]. Recent EXAFS results in our group have shown evidence for isolated Fe^{3+} cations associated with the charge-exchange sites in Fe-ZSM-5 prepared by solid-state exchange of H-ZSM-5 with $FeCl_3$ [33].

In the current work zeolites with the MFI structure containing differing proportions of Fe and Al in the framework were prepared by introducing Fe and/or Al into the synthesis gel prior to crystallization [13,14,34–38]. Thermal activation of such Fe/Al-MFI zeolites has been found to cause the migration of framework Fe to extraframework positions [36,38]. The migration of Fe from the framework is facilitated by the addition of steam during thermal activation [37]. Using EXAFS, XANES, EPR, and IR, measurements, Berlier et al. have shown that upon extraction from the framework, Fe is reduced from Fe^{3+} to Fe^{2+}, but can be reoxidized to Fe^{3+} by exposure to N_2O [38]. Berlier et al. have also shown that framework Al stabilizes the dispersion of extraframework Fe and have suggested that the active sites for the partial oxidation of hydrocarbons are isolated Fe atoms associated with Al [39]. EXAFS and XANES measurement in our group have shown similar results [40].

The objective of the current work is to identify the pathways by which methoxy species are produced on Fe/Al-MFI and then converted to methanol. IR spectroscopy was used to monitor the catalyst surface during exposure to CH_4 and N_2O and mass spectrometry was used to analyze the products formed during temperature-programmed reaction studies. Based on these results obtained, it is possible to suggest the elementary processes that lead to the formation of Fe-bound methoxy groups and their hydrolysis to methanol. The possibility of forming methanol under steady-state conditions was also examined.

2. Experimental

The MFI samples were prepared by the fluoride synthesis route in the following manner [41]. Ammonium fluoride, tetrapropalammonium bromide, aluminum nitrate, and water were placed in Teflon-lined bomb reactors. For Fe-MFI and Fe/Al-MFI, $FeCl_3$ was also added. The mixtures were then stirred until all solids dissolved. Ludox LS-30 was then added to each mixture and the reactors were placed in an oven at 433 K for 7 days. The resulting materials were calcined in air at 823 K for 6 h after an 8-h ramp, also in air. The MFI products were then ion-exchanged with 1 M ammonium nitrate, washed with deionized water, and dried overnight at 373 K. The samples were activated by calcining in air at 623 K and then heating in He at 1123 K for 6 h. Elemental analysis of the samples (Galbraith Laboratories) used in this work is shown in Table 1. EXAFS measurements performed on Fe-MFI and Fe/Al-MFI indicate that before activation at 1123 K in He, the Fe in both samples is located in tetrahedral positions in the MFI framework, but that after activation, the Fe migrates to extraframework positions [40]. In Fe-MFI, the extraframework Fe takes the form of Fe_2O_3 particles. In Fe/Al-MFI, the extraframework Fe consists of isolated Fe associated with framework Al.

Infrared spectra were recorded using a Nicolet Nexus 670 FT-IR equipped with an MCT-A detector. Measurements were made at a resolution of 4 cm^{-1} with a total of 64 scans per spectrum. Total gas flow rates for all experiments were 60 cm^3/min. Samples were pressed into 30 mg self-supporting pellets, and subsequently placed into an IR cell equipped with BaF_2 IR windows. Prior to each IR experiment, the sample was heated in flowing He (60 cm^3/min) from 298 to 773 K at 1 K/min. Upon reaching 773 K, the sample was pretreated for 2 h in 3.0% N_2O in He, purged in He for 1 h, and then cooled to the temperature of the experiment.

Isothermal and temperature-programmed reaction experiments were carried out in a quartz microreactor containing 100 mg of catalyst. The effluent from the reactor was monitored using a Spectra Mini-Lab Mass Spectrometer. Prior to each experiment, the sample was heated in flowing He (60 cm^3/min) from 298 to 773 K over a period of 1 h. Upon reaching 773 K, the sample was pretreated for 2 h in 3.0% N_2O in He, purged in He for 1 h, and then cooled to the temperature of the experiment.

Table 1
Sample elemental analysis

Sample	Si (wt%)	Al (wt%)	Fe (wt%)	Si/Al	Fe/Al
Al-MFI	43.68	0.63	–	67	–
Fe/Al-MFI	42.79	0.49	0.38	84	0.38
Fe-MFI	43.94	–	0.94	–	–

3. Results and discussion

Prior to investigating the interactions of N_2O and CH_4, the interactions of CH_3OH with Al-MFI and Fe/Al-MFI were carried out. It has been reported previously that upon interaction of methanol with silica and zeolites having an MFI structure, methanol reacts with various hydroxyl groups, replacing these groups with surface methoxy groups [42–45]. Fig. 1 shows IR spectra taken after exposure of Al-MFI and Fe/Al-MFI to 5000 ppm methanol in He and subsequent purge in He at 528 K (background spectra correspond to Al-MFI and Fe/Al-MFI recorded at 528 K under He). For Al-MFI, pairs of bands are observed in the CH-stretching region at 2980 and 2868 cm^{-1} and at 2957 and 2854 cm^{-1}. The bands at 2980 and 2868 cm^{-1} can be assigned to asymmetric and symmetric C–H stretches of methoxy groups produced by the reaction of methanol with Brønsted acid centers [46,47],

$$CH_3OH + {\equiv}Si\text{–}O(H)\text{–}Al{\equiv} \rightarrow {\equiv}Si\text{–}O(CH_3)\text{–}Al{\equiv} + H_2O, \tag{1}$$

whereas the bands at 2957 and 2854 can be assigned to asymmetric and symmetric CH stretches of methoxy groups produced by the reaction of methanol with silanol groups [43,45–48],

$$CH_3OH + {\equiv}Si\text{–}OH \rightarrow {\equiv}Si\text{–}OCH_3 + H_2O. \tag{2}$$

Four negative bands are observed in the OH-stretching region between 3500 and 3800 cm^{-1}. The loss of band intensity after methanol exposure is due to the loss of hydroxyl groups. The band at 3740 cm^{-1} is assigned to O–H-stretching vibrations of silanol groups terminating the zeolite lattice [47] and the band at 3720 cm^{-1} is attributed to silanol groups associated with internal defects [47]. The band at 3655 cm^{-1} can be assigned to hydroxyl groups on extraframework Al [45–47] and the band at 3600 cm^{-1} is attributed to Brønsted acid OH stretches at framework Al positions [45–47].

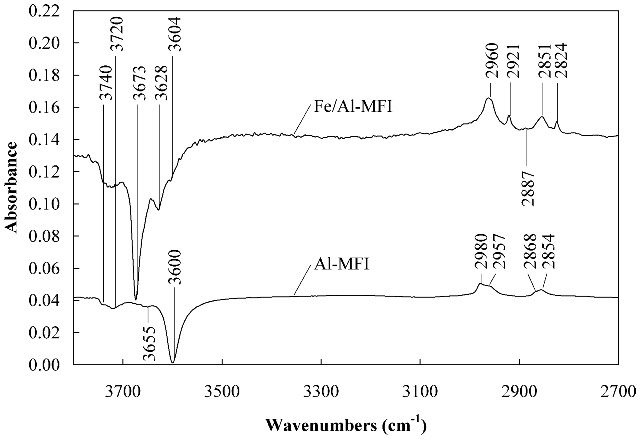


Fig. 1. IR spectra of exposure of Al-MFI and Fe/Al-MFI to methanol at 528 K.

For Fe/Al-MFI, the pair of bands due to $\equiv SiOCH_3$ are visible at 2960 and 2851 cm^{-1}. New bands not seen on Al-MFI are observed at 2921 and 2824 cm^{-1}. As these bands are not seen after exposure of Al-MFI to methanol, the pair of bands at 2921 and 2824 cm^{-1} are assigned to the asymmetric and symmetric CH stretches of Fe-bound methoxy groups. Kameoka et al. have made a similar assignment for these bands on Fe-BEA [49]. An additional small band is apparent at 2887 cm^{-1} that may be due to formate (see discussion below). Negative bands are seen at 3730, 3673, 3628, and 3604 cm^{-1}. The band at 3730 cm^{-1} is likely a superposition of the bands at 3740 and 3720 cm^{-1} for OH stretches associated with external and internal silanol groups, respectively. The band at 3673 cm^{-1} is assigned to hydroxyl groups bonded to extraframework Fe, based on similar bands on FeOOH due to OH coordinated Fe [50,51]. The band at 3628 cm^{-1} has previously been assigned to Brønsted acid OH stretches at framework Fe positions, $\equiv Si\text{–}O(H)\text{–}Fe\equiv$ [34,36–38]. However, IR spectra of FeOOH display an IR band at 3624 cm^{-1} due to OH groups coordinated to one Fe ion [50], and, hence, the band at 3628 cm^{-1} may also be due to OH groups bonded to extraframework Fe. Since the ratio of the intensities for the bands at 3673 and 3628 cm^{-1} remains constant as the total intensities of these bands change, it is proposed that these bands correspond to the asymmetric and symmetric stretches of two hydroxyl groups associated with one Fe center ($Fe(OH)_2$). The band at 3604 cm^{-1} is due to Brønsted acid OH stretches at framework Al positions. It is noted that the bands due to $\equiv SiOCH_3$ groups (2960 and 2851 cm^{-1}) are considerably more intense for Fe/Al-MFI than those for Al-MFI. This may be a consequence of the higher concentration of silanol groups at internal defect sites created by the migration of Fe from the framework during thermal pretreatment of the zeolite. It is also noted that the intensities of the negative OH bands are much greater than those of the corresponding methoxy CH bands. A similar observation has been reported previously for the interaction of methanol with ZSM-5 [46].

Fig. 2 shows IR spectra collected during the heating of Fe/Al-MFI from 298 to 768 K at 1 K/min in the presence

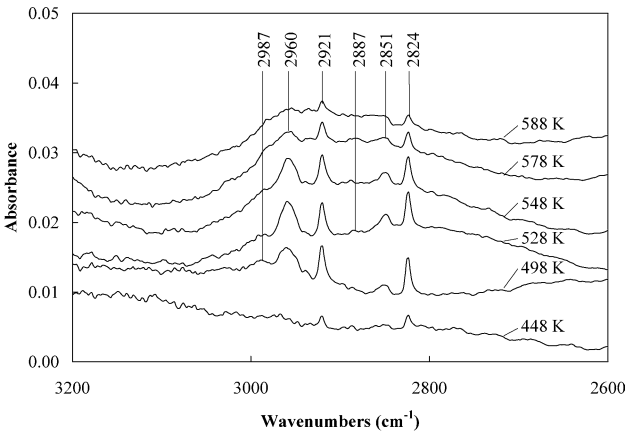


Fig. 2. IR spectra of exposure of Fe/Al-MFI to CH_4 and N_2O.

of 15,000 ppm N_2O and 15,000 ppm CH_4 in He flowing over the catalyst (in a separate experiment a set of background spectra was taken of the sample in 15,000 ppm CH_4 in He while heating from 298 to 768 K, resulting in difference spectra consisting of only surface species and gas-phase N_2O). At approximately 448 K the pair of bands assigned to methoxy groups on Fe (2921 and 2824 cm^{-1}) become apparent in the C–H-stretching region of the spectrum. These bands increase in intensity up to a temperature of about 548 K and then begin to decrease in intensity at higher temperatures. Around 498 K, the pair of bands attributed to silicon-bound methoxy ($\equiv$Si–OCH_3) (2960 and 2851 cm^{-1}) becomes apparent. These bands also decrease in intensity above 548 K. A weak pair of bands at 2987 and 2887 cm^{-1} appear by 528 K. These bands are similar to those reported for formate groups on alumina [52]. By 588 K these bands have decreased in intensity. In contrast to what is observed for thermally pretreated Fe/Al-MFI, no methoxy species were observed upon exposure of Al-MFI or thermally pretreated Fe-MFI to a mixture of N_2O and CH_4. The absence of such features for Al-MFI clearly indicates that Fe sites are the active centers for the oxidation of CH_4 by N_2O. EXAFS results on the materials used in the present study indicate that Fe/Al-MFI Fe is predominately in the form of isolated Fe associated with framework Al after activation [40]. By contrast, the Fe in thermally pretreated Fe-MFI was found to exist predominately in the form of small Fe_3O_4 clusters. It is, therefore, evident that framework Al is necessary to anchor Fe, preventing Fe from aggregating to form particles of iron oxide. Taken together, the observations obtained for Al-MFI, Fe-MFI, and Fe/Al-MFI indicate that methoxy species are formed only on extraframework Fe cations produced by thermal pretreatment of Fe/Al-MFI.

Fig. 3 shows IR spectra recorded at 528 K during exposure of Fe/Al-MFI to 15,000 ppm N_2O and 15,000 ppm CH_4 over a period of 200 min (the background spectrum corresponds to Fe/Al-MFI at 528 K in 15,000 ppm CH_4 in He). The bands at 2238 and 2207 cm^{-1} are assigned to gas-phase N_2O. After 10 min of exposure to N_2O/CH_4, the pair of bands assigned to methoxy groups on Fe, located at 2921 and 2824 cm^{-1}, are detected. After 20 min of exposure, the pairs of methoxy bands at 2960 and 2851 cm^{-1} due to silicon-bound methoxy groups appear, as well as the pair of bands at 2987 and 2887 cm^{-1}. These latter two bands and the large band at 1586 cm^{-1} are attributed to formate groups, based on the similarity of their positions to those for formate groups observed on alumina [52]. Kameoka et al. report that formate on Fe displays a band at 2969 cm^{-1}, somewhat lower than the band observed in the present work at 2987 cm^{-1} [49]. Taken together it is likely that the bands at 2987, 2887, and 1586 correspond to formate groups associated with Al and/or Fe sites. The presence of formate groups associated with the siliceous part of the zeolite is not expected, since such groups do not form on silica [53]. Additionally, a series of bands are observed at lower energies, corresponding to 1473, 1460, 1434, 1413, and 1391 cm^{-1}. These bands are in the region of the spectrum anticipated for methoxy CH-bending vibrations [44]. As these methoxy bands grow in intensity, a series of negative bands form in the OH-stretching region of the spectrum. These features are located at 3740, 3673, and 3628 cm^{-1}, corresponding to silanol groups, extraframework Fe, and extraframework Fe or Brønsted acid OH stretches (i.e., $\equiv$Si–O(H)–Fe$\equiv$).

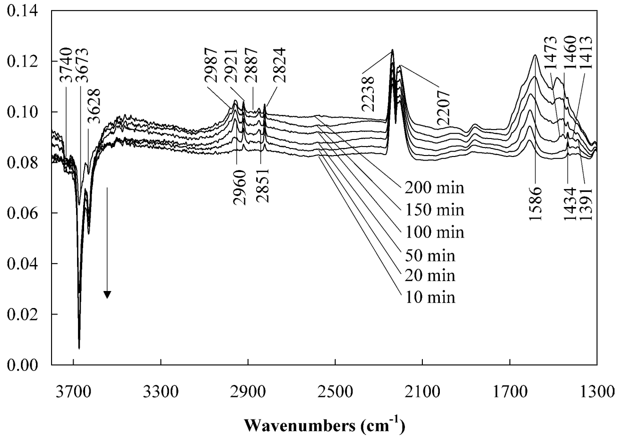
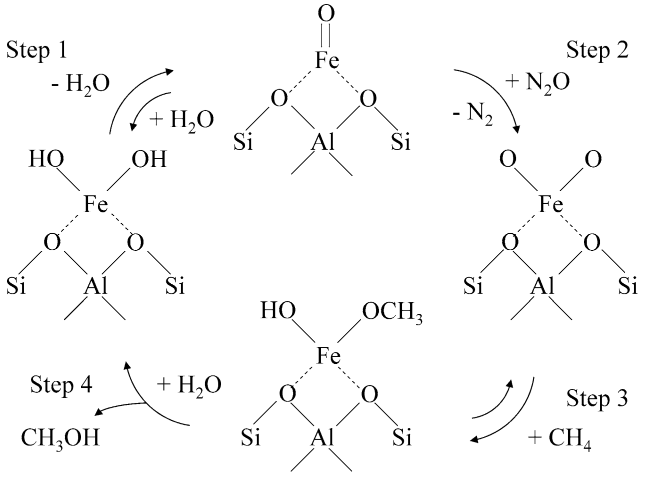


Fig. 3. IR spectra of exposure of Fe/Al-MFI to CH_4 and N_2O at 528 K.

The results presented in Fig. 3 are similar to those reported by Kameoka et al. [49] and by Panov et al. [17]. Kameoka et al. showed that upon passage of a mixture of CH_4 and N_2O over Fe-BEA, bands appeared at 2919 and 2826 cm^{-1} that they assigned to Fe-bound methoxy groups. These authors also noted the disappearance of a band at 3683 cm^{-1} that they assigned to Fe–OH groups. Panov et al. have described experiments in which surface oxygen was loaded onto a sample of Fe/Al-MFI thermally pretreated in N_2O decomposition, after which the sample was cooled to room temperature and then exposed to CH_4. Four IR bands were observed in the CH-stretching region of the spectrum at 2964, 2945, 2919, and 2823 cm^{-1}. The authors assigned the bands at 2919 and 2964 cm^{-1} to asymmetric C–H-stretching vibrations of methoxy groups, the band at 2945 cm^{-1} to an overtone deformation vibration of methoxy groups, and the band at 2823 cm^{-1} to a symmetric C–H-stretching vibration of methoxy groups. No assignment was made for the sites on which these methoxy groups reside. Panov et al. also reported the appearance of positive bands in the OH region at 3674 and 3635 cm^{-1}.

The concurrent disappearance of OH groups associated with extraframework Fe and silicon sites and the appearance of methoxy groups associated with Fe and Si can be explained on the basis of the reaction scheme shown in Fig. 4. In Step 1 of this scheme, Fe associated with two hydroxyl groups, $Z[Fe(OH)_2]$, looses water to form Z[Fe=O]. The existence of $Z[Fe(OH)_2]$ is supported by EXAFS studies of Fe-ZSM-5 and Fe/Al-MFI [33,40], and by the IR studies reported here. Both experimental and theoretical studies suggest that $Z[Fe(OH)_2]$ must first undergo dehydration to form Z[Fe=O] before N_2O decomposition can occur [54–56]. Experimental studies also demonstrate that only a fraction of



$$CH_3OH + Z[Fe(OH)_2] \rightarrow H_2O + Z[Fe(OCH_3)(OH)]$$
$$CH_3OH + \equiv Si\text{-}OH \rightarrow H_2O + \equiv Si\text{-}OCH_3$$

Fig. 4. Reaction sequence for the formation of methoxy species on Fe and Si sites during the oxidation of CH_4 by N_2O.

the Fe in Fe-ZSM-5 or Fe/Al-MFI is active for N_2O decomposition. Work done with the sample of Fe/Al-MFI used in the present study shows that only 10% of the total Fe is active, suggesting that dehydration is an activated process, and that not all sites undergo dehydration to the same extent [54]. In Step 2, N_2O reacts with Z[Fe=O] to release N_2 and form Z[OFeO]. We have recently shown that this reaction occurs with an activation energy of 16.8 kcal/mol [55]. Quantum chemical calculations demonstrate that the product of this reaction, Z[OFeO], is stable [57]. CH_4 then reacts with Z[OFeO] in Step 3 to produce a methoxy species and a hydroxyl species on the Fe center. Water formed via the combustion of CH_4 (see below) readily hydrolyzes the methoxy groups from the surface of the catalyst, Step 4. Methanol produced in Step 4 can then migrate to both nonactive Fe sites, $Z[Fe(OH)_2]$, and ≡Si–OH groups to produce $Z[Fe(OH)(OCH_3)]$ and $\equiv Si–OCH_3$. The simultaneous formation of methoxy groups and the loss of hydroxyl groups at the nonactive Fe centers is consistent with the IR observations reported in Fig. 3. The catalytic cycle represented by Steps 1–4 is identical to those described by Liang et al. [57].

Fig. 5 shows the gas composition observed during the temperature-programmed reaction of a mixture containing 15,000 ppm N_2O and 15,000 ppm CH_4. Above 491 K, the concentration of N_2O begins to decrease and N_2 and CO are formed concurrently. H_2 is also detected above 537 K, and water, above 630 K (not shown). Above 577 K small amounts of methanol are also detected. The amount of methanol increases up to 675 K, and then decreases at higher temperatures.

In order to study the decomposition of methoxy groups, two experiments were performed in which the sample was exposed to methanol at 528 K to produce surface methoxy groups, purged in He to remove any weakly bound methanol, and then heated from 528 to 773 K in either He or 15,000 ppm N_2O. Heating in He produced small amounts of CO, H_2, and H_2O over the temperature range of 587 to 773 K (not shown). By contrast, when the catalyst is heated in He containing N_2O (Fig. 6), a burst of CO is detected together with some water (not shown). Concomitant with the burst of CO, there is a decrease in the concentration of N_2O, and a burst of N_2. It is notable that the moles of N_2 and CO formed are virtually identical. These observations suggest that surface methoxy groups are oxidized by N_2O, in the following manner:

$$CH_3O–Fe + N_2O \rightarrow Fe–OH + CO + N_2 + H_2. \tag{3}$$

No further oxidation of methoxy groups was detected above 566 K and only the stoichiometric decomposition of N_2O to N_2 and O_2 was observed above 650 K. The latter results are identical to those reported for N_2O decomposition over the sample of Fe/Al-MFI used in the present study [54].

Fig. 7 demonstrates the effect of water on surface methoxy groups on Fe/Al-MFI. Fe/Al-MFI was first exposed to N_2O and CH_4 for 1 h at 528 K, after which a spectrum was recorded while the sample was still under N_2O/CH_4 (the

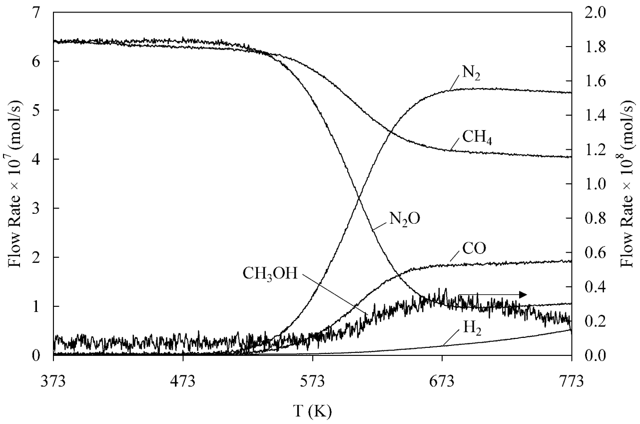


Fig. 5. Temperature-programmed reaction of CH_4 and N_2O over Fe/Al-MFI monitored by mass spectrometry.

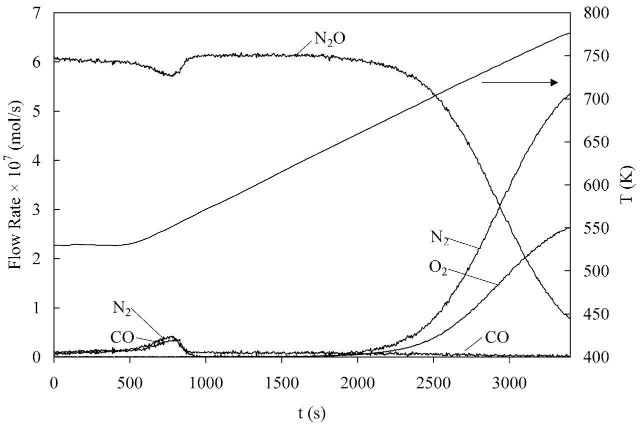


Fig. 6. Temperature-programmed reaction of N_2O with surface methoxy species on Fe/Al-MFI formed during exposure of Fe/Al-MFI to methanol at 528 K.

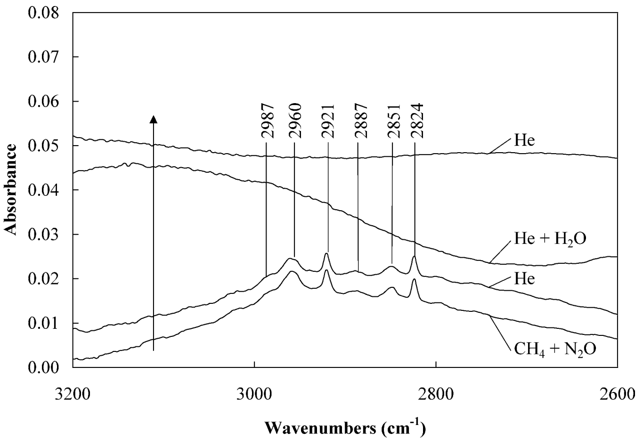


Fig. 7. IR spectra of Fe/Al-MFI after exposure to CH_4 and N_2O, dry He, He, and 25,000 ppm H_2O, and finally dry He at 528 K.

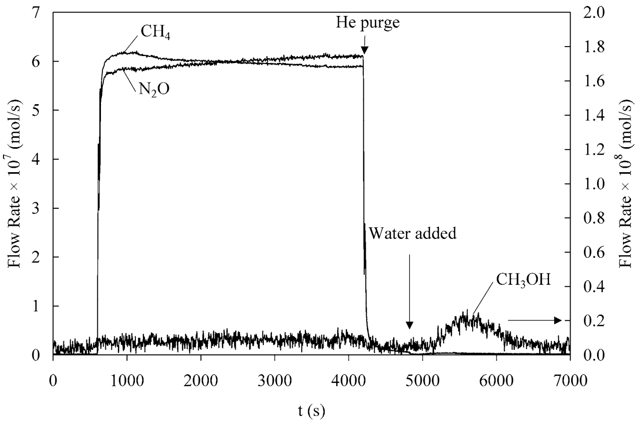


Fig. 8. Exposure of Fe/Al-MFI to CH_4 and N_2O to produce surface methoxy species, followed by a He purge, and then exposure to He and 25,000 ppm H_2O. All experiments were conducted at 528 K.

background spectrum corresponds to Fe/Al-MFI at 528 K in 15,000 ppm CH_4). Similar to the results shown in Fig. 3, surface methoxy bands are observed to form at 2960 and 2851 cm^{-1}, due to silicon-bound methoxy groups, and at 2921 and 2824 cm^{-1}, due to Fe-bound methoxy groups. Weak bands are also seen at 2987 and 2887 cm^{-1}. The sample was then purged in He and another spectrum was recorded (the background spectrum corresponds to Fe/Al-MFI at 528 K in He). Purging the gas phase had no effect on the intensity of the methoxy bands. The sample was then exposed to 25,000 ppm H_2O in He. During this period, the surface methoxy bands disappeared (the background spectrum corresponds to Fe/Al-MFI at 528 K in He). A spectrum was next recorded after the sample was purged in dry He to show that H_2O does not obscure the methoxy bands (the background spectrum corresponds to Fe/Al-MFI at 528 K in He). The sequence of steps described above was repeated several times after the sample had been thoroughly dried to confirm that exposure of the sample to water vapor did not alter its ability to form methoxy groups.

Complementary to the IR experiment shown in Fig. 7, an experiment was performed using mass spectrometry to monitor the gas-phase products during the exposure of Fe/Al-MFI to 25,000 ppm H_2O in He following the formation of methoxy surface species. As shown in Fig. 8, the sample was first exposed to N_2O/CH_4 for 1 h, during which surface methoxy groups were formed on the surface, in a manner similar to that occurring during the IR experiments. The catalyst was then purged in dry He to remove any weakly bound surface species and exposed to a flow of 25,000 ppm H_2O in He. Immediately upon exposure to H_2O, small amounts of methanol were detected in the gas phase. The total amount of methanol formed was 0.25 mol methanol/mol Fe. As noted earlier, during a study of N_2O decomposition on the sample of Fe/Al-MFI used in this investigation we showed that only 10% of the total Fe in the sample is active for N_2O decomposition [54]. The ratio of methanol to active Fe is therefore, $CH_3OH/Fe_{active} = 2.5$. What this implies is that the Fe on which N_2O decomposes is catalytically active for the formation of methanol. The observation of 0.25 mol methanol/mol Fe is consistent with the observation that methoxy groups migrate to sites other than the active iron sites. By integrating the band at 2960 cm^{-1} corresponding to silicon-bound methoxy and the band at 2921 corresponding to Fe-bound methoxy after 60 min of exposure to CH_4/N_2O as shown in Fig. 3, a ratio of 2.3 is obtained, indicating that about twice as much methoxy resides on the Si sites as on the Fe sites. Both the high thermal stability of iron-bound methoxy groups and their facile hydrolysis to form methanol is supported by quantum chemical calculations [57]. For example, these studies show that the activation barrier to form adsorbed CH_2O from $Fe(OCH_3)(OH)$ is 39.3 kcal/mol but the activation barrier for the reaction of H_2O with $Fe(OCH_3)(OH)$ to form CH_3OH is only 6.2 kcal/mol.

4. Conclusions

The interactions of CH_4, N_2O, and methanol with activated Fe/Al-MFI were investigated by IR spectroscopy and temperature-programmed reactions in order to study the processes involved in the direct oxidation of CH_4 to methanol by N_2O. Exposure of Fe/Al-MFI to methanol resulted in the replacement of Fe hydroxyl groups by Fe-bound methoxy species and the appearance of methoxy groups bound to Si and Al, resulting from the reaction of methanol with ≡Si–OH and ≡Al–OH groups. When Fe was not present, e.g., for Al-MFI, only the latter types of methoxy groups were observed. Fe/Al-MFI was active above ~ 448 K for the direct oxidation of CH_4 by N_2O to form surface methoxy species, similar to those seen after exposure of the sample to methanol. However, no surface methoxy group formation was observed on Al-MFI and thermally pretreated Fe-MFI, suggesting that the active sites in the oxidation of CH_4 to methoxy species by N_2O are extraframework Fe species associated with framework Al. Above 580 K, small concentrations of methanol are observed in the gas phase for the case of Fe/Al-MFI, as well as CO, H_2, and H_2O. Surface methoxy groups decompose to CO upon heating in He or N_2O. However, when H_2O is introduced at reaction temperatures, surface methoxy species hydrolyze rapidly to form methanol. Passage of a mixture of CH_4 and N_2O over Fe/Al-MFI resulted in the formation of methanol above ~ 523 K, but the selectivity to this product was only about 2%, and most of the CH_4 was combusted.

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