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Mechanistic peculiarities of the N_2O reduction by CH_4 over Fe-silicalite

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Abstract

Transient isotopic studies in the temporal analysis of products (TAP) reactor evidenced the importance of the lifetime of oxygen species generated upon N_2O decomposition on extraframework iron sites of Fe-silicalite for methane oxidation at 723 K. Fe-silicalite effectively activates CH_4 when N_2O and CH_4 are pulsed together in the reactor. However, these oxygen species gradually become inactive for methane oxidation as the time delay between the N_2O and CH_4 pulses is increased from 0 to 2 s.

Keywords: N_2O reduction; Iron silicalite; Oxygen species; Lifetime; CH_4 oxidation; Mechanism; TAP reactor

1. Introduction

N_2O mitigation is a topic of current interest due to the adverse consequences of this harmful gas in our atmosphere. Iron-containing zeolites present unique features for selective catalytic reduction (SCR) of N_2O at low temperatures (<700 K) in the presence of various reducing agents [1–8]. In contrast to the vast number of studies comparing catalytic performance of various Fe-zeolites and reductants for N_2O reduction, only few fundamental studies assessing the intrinsic mechanism of N_2O reduction have been published. Kunimori and co-workers [9–11] reported that methane is effectively oxidized by N_2O over Fe-beta when both reactants were fed together in the catalytic reactor. Contrarily, the reaction of CH_4 with the N_2O-pretreated catalyst showed very low activity. Two different oxygen species originated from N_2O were suggested to explain this finding: highly reactive (nascent) oxygen species and non-reactive (thermally accommodated) oxygen species. By varying the time delays between the N_2O and C_3H_8 pulses, the importance of the lifetime of oxygen species for N_2O–C_3H_8 interactions over Fe-silicalite was recently evidenced in our mechanistic studies using the temporal analysis of products (TAP) reactor [12,13]. Highly reactive oxygen species originated from N_2O lost their activity for C_3H_8 oxidation when N_2O and C_3H_8 were fed separately. In contrast, the oxidation of CO by N_2O did not depend on the lifetime of the oxygen species [13].

In view of the dependence of the reaction mechanism on the nature of the reducing agent, it is appropriate to extrapolate our previous TAP studies with C_3H_8 and CO to CH_4. In this paper, we have investigated the mechanism of reduction of N_2O by $^{13}CH_4$ over Fe-silicalite at 723 K in the TAP reactor. Particular attention is given to the influence of the lifetime of oxygen species deposited by N_2O over extraframework iron sites of Fe-silicalite on methane oxidation. It is also important to prove whether the matrix (beta in [9–11] or MFI in the present study) influences the N_2O–CH_4 interactions over iron-containing zeolites.

2. Experimental

2.1. Catalyst

Details on the hydrothermal synthesis and characterization of isomorphously substituted Fe-silicalite have been described elsewhere [4,14]. Characterization of the steam-activated Fe-silicalite (Si/Al ~ ∞ and 0.68 wt.% Fe) indicated a rather uniform distribution of iron species dominated by isolated Fe^{3+} ions in extraframework positions. A certain fraction of oligonuclear iron-oxo species in the zeolite channels was also

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identified, while clustering into large iron oxide particles was prevented.

2.2. Transient studies

Transient experiments were performed in the temporal analysis of products (TAP) reactor, a pulse technique with a time resolution sub-millisecond. The TAP-2 reactor system has been described in detail elsewhere [15]. The catalyst (50 mg, 250–355 μm) was packed between two layers of quartz spheres of the same size fraction in the quartz fixed-bad micro-reactor (6 mm i.d.). Prior to the experiments, Fe-silicalite was pretreated in flowing He (30 ml STP min^{-1}) at 773 K and atmospheric pressure for 2 h. The pretreated sample was then exposed to vacuum (10^{-5} Pa) and pulse experiments were subsequently performed. Feed components were dosed by means of two high-speed pulse valves. Pulse size of reactive components was ca. 5×10^{14} molecules. This pulse size corresponds to the Knudsen diffusion regime, where the interaction of molecules in the gas phase is minimized. Accordingly, purely heterogeneous reaction steps are considered. The reaction of N_2O and $^{13}CH_4$ was investigated at 723 K by means of pump–probe experiments. Mixtures of N_2O:Xe = 1:1 (pump) and $^{13}CH_4$:Ne = 1:1 (probe) were sequentially pulsed in the micro-reactor applying times delays (Δt) between the two mixtures in the range of 0–2 s. Experiments at $\Delta t = 0$ s correspond to simultaneous pulsing of both mixtures.

The reactants Ne (4.5), Xe (4.0), N_2O (2.0), and $^{13}CH_4$ (99 at.% ^{13}C, Aldrich) were used without additional purification. A quadrupole mass spectrometer (HAL RC 301 Hiden Analytical) was used for quantitative analysis of reactants and reaction products. The transient responses at the reactor outlet were monitored at the following atomic mass units (AMUs): 132 (Xe), 45 ($^{13}CO_2$), 44 (N_2O, CO_2), 32 (O_2), 30 (N_2O), 29 (^{13}CO), 28 (N_2, CO, N_2O, CO_2), 20 (Ne), 18 (H_2O), 17 ($^{13}CH_4$, H_2O), and 16 ($^{13}CH_4$, O_2). In the experiments, 10 pulses were recorded and averaged for each AMU in order to improve the signal-to-noise ratio. The variations in feed components and reaction products were determined from the respective AMUs using standard fragmentation patterns and sensitivity factors.

3. Results and discussion

Sequential pulse experiments with N_2O and $^{13}CH_4$ were carried out in the TAP reactor in order to analyze whether the lifetime of oxygen species deposited on the catalyst upon N_2O decomposition influences the oxidation of methane. In this operation mode, a pulse of nitrous oxide (pump) is followed by a pulse of the hydrocarbon (probe) after a certain time delay (Δt) ranging from 0 to 2 s. Isotopically labeled $^{13}CH_4$ and non-labeled $^{14}N_2O$ were used to uncouple the analysis of N_2O–CO_2 and N_2–CO in mass spectrometry. The use of the most abundant isotope for methane, i.e. $^{12}CH_4$, makes it impossible due to the identical main AMUs of $^{14}N_2O$ and $^{12}CO_2$ (44) as well as $^{14}N_2O$, $^{14}N_2$ and ^{12}CO (28).

^{13}CO and $^{13}CO_2$ were the only carbon-containing products detected by MS analysis at the reactor outlet when N_2O and $^{13}CH_4$ were sequentially pulsed over Fe-silicalite. This is valid for all the time delays between the nitrous oxide and methane pulses. Fig. 1 shows typical transient responses of N_2O, $^{13}CH_4$, N_2, ^{13}CO, and $^{13}CO_2$, when N_2O and $^{13}CH_4$ were simultaneously pulsed ($\Delta t = 0$ s). The transient responses of N_2O and $^{13}CH_4$ have the sharpest shape as a consequence of their consumption. Since N_2 is formed from N_2O, its transient response is broader and slightly shifted to longer times as compared to that of nitrous oxide. The products of $^{13}CH_4$ oxidation, i.e. ^{13}CO and $^{13}CO_2$ appear at similar time as N_2. However, their transient responses are considerably broader than that of nitrogen. This indicates a relatively strong interaction of $^{13}CO_x$ with Fe-silicalite, as reported in our previous paper for N_2O–^{13}CO interactions [13].

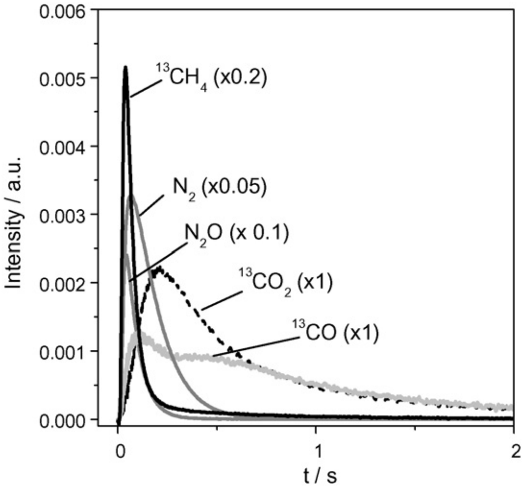

Fig. 1. Transient responses of N_2O, $^{13}CH_4$, N_2, ^{13}CO, and $^{13}CO_2$ upon simultaneous pulsing of N_2O and $^{13}CH_4$ over Fe-silicalite at 723 K. Pulse size of N_2O and $^{13}CH_4$: ca. 5×10^{14} molecules.

Fig. 2 compares the degrees of N_2O and $^{13}CH_4$ conversion at 723 K for various time delays between the pulsed gases. The

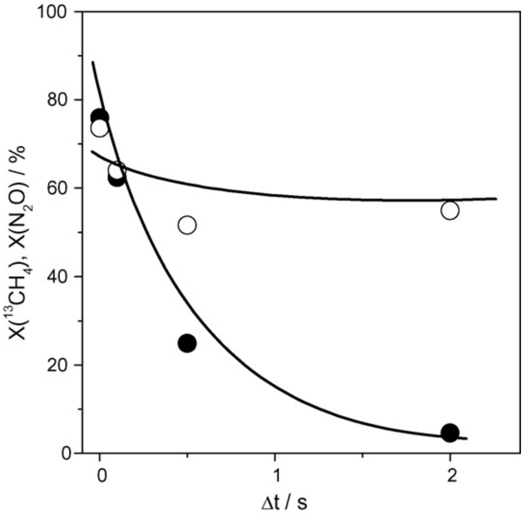

Fig. 2. Conversion of (●) $^{13}CH_4$ and (○) N_2O as a function of the time delay (Δt) between the pulses of N_2O and $^{13}CH_4$ at 723 K. Pulse size as in caption of Fig. 1.

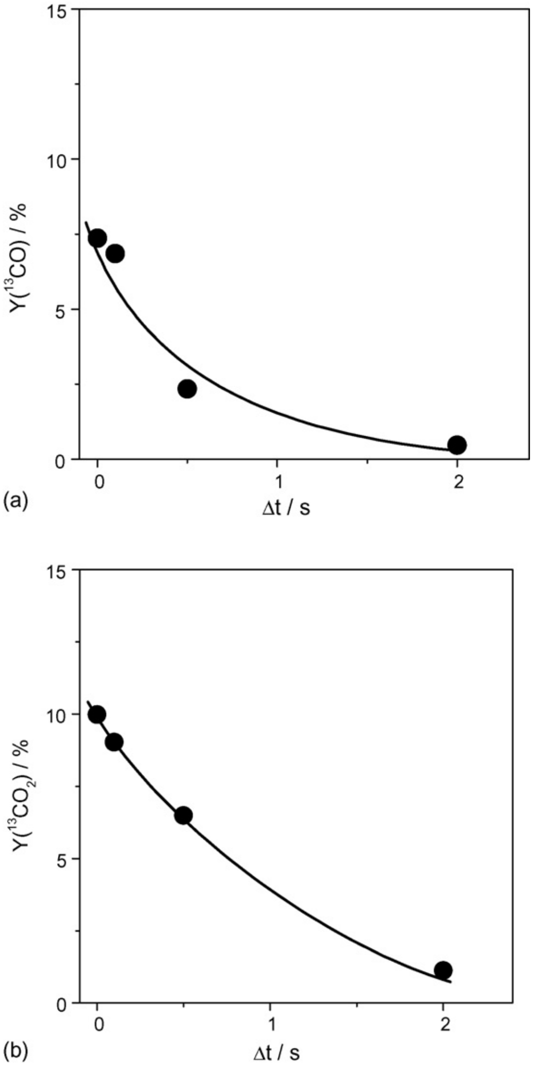

Fig. 3. Yield of (a) ^{13}CO and (b) $^{13}CO_2$ vs. time delay (Δt) between N_2O and $^{13}CH_4$ pulses at 723 K. Pulse size as in caption of Fig. 1.

highest methane conversion was achieved, when N_2O and $^{13}CH_4$ were pulsed simultaneously. The conversion of $^{13}CH_4$ decreases from ca. 80% to ca. 10% upon increasing the time delay between N_2O and $^{13}CH_4$ pulses from 0 to 2 s. The same behavior was observed for the yields of $^{13}CO_2$ and ^{13}CO as shown in Fig. 3. In contrast to methane conversion, N_2O conversion is practically not influenced by the time delay between N_2O and $^{13}CH_4$ pulses (Fig. 2). Thus it is clear that N_2O and $^{13}CH_4$ conversions are uncoupled when the N_2O and $^{13}CH_4$ pulses are separated in time. This means than N_2O decomposes providing active oxygen species but methane oxidation by the formed atomic oxygen species is impeded. It has to be emphasized that gas-phase oxygen was never observed at the applied time delays. This makes it possible to conclude that the decreased $^{13}CH_4$ conversion in Fig. 2 and the respective decrease in $^{13}CO_x$ formation in Fig. 3 cannot be ascribed to a decrease in the concentration of reactive oxygen species due to O_2 desorption, but rather due to a transformation of highly reactive (short-lived) oxygen species to less reactive (long-lived) oxygen. In excellent agreement, the importance of the lifetime of oxygen species for N_2O–CH_4 interactions over Fe-beta has been also highlighted by the group of Kunimori and co-workers [10,11]. Thus it can be concluded that the lifetime effect of oxygen species on hydrocarbon oxidation is not determined by the type of zeolite matrix (BEA versus MFI). The latter authors have proposed two types of oxygen species originated from N_2O activation over Fe-beta during SCR with CH_4: (i) nascent oxygen transient species, which are highly reactive and efficiently activate methane at $T > 473$ K, and (ii) thermally accommodated oxygen, which led to very low activities even at 623 K. Apparently, the former oxygen populates the catalyst surface when N_2O and CH_4 were fed together, while the latter oxygen was mainly present when CH_4 was fed over N_2O-pretreated catalyst. The results in Figs. 2 and 3 draw a clear parallelism with our previous findings related to N_2O–C_3H_8 interactions over Fe-silicalite [12,13], revealing the importance of the lifetime of reactive oxygen species deposited by N_2O for the hydrocarbon oxidation. As suggested in these papers, highly reactive species (O*) formed from N_2O (Eq. (1)) are gradually transformed into less reactive (OΔ) ones (Eq. (2)). Based on the appearance of $^{13}CO_x$ upon separated pulsing of N_2O and $^{13}CH_4$ ($\Delta t > 0$ s in Fig. 3), it can be suggested that the highly reactive oxygen species activates methane according to the well-accepted scavenging mechanism (Eq. (3)). The group of Kunimori proposed methoxide and/or formate groups as intermediate species in CO_x formation [9–11]:

$$N_2O + * \rightarrow N_2 + O* \tag{1}$$

$$O* + \Delta \rightarrow O\Delta + * \tag{2}$$

$$HC + O* \rightarrow CO_x + H_2O + * \tag{3}$$

It is important to note that the ratio of $^{13}CO/^{13}CO_2$ decreases slightly from 0.75 to 0.5 upon increasing the time delay between N_2O and $^{13}CH_4$ pulses from 0 to 2 s. This means that the $^{13}CO_2$ production overcomes the ^{13}CO production with the time delay. From the stoichiometry of ^{13}CO and $^{13}CO_2$ production from $^{13}CH_4$ (Eqs. (4) and (5)) more oxygen species are needed for $^{13}CO_2$ formation as compared to ^{13}CO formation:

$$^{13}CH_4 + 3O* \rightarrow {}^{13}CO + 2H_2O + * \tag{4}$$

$$^{13}CH_4 + 4O* \rightarrow {}^{13}CO_2 + 2H_2O + * \tag{5}$$

Taking into account Eqs. (4) and (5) and the ratio of $^{13}CO_2/^{13}CO$ at various time delays, it can be concluded that the reactivity of oxygen species is of key importance for $^{13}CO_x$ production, more than the actual concentration of adsorbed oxygen. If the latter would play a prominent role, an increase in the $^{13}CO/^{13}CO_2$ ratio with increasing in the time delay would have been observed. Thus, our results support that the decreased $^{13}CO_x$ formation in Fig. 3 is due to a transformation of highly reactive oxygen species into less reactive ones.

4. Conclusion

Our transient isotopic investigation in the TAP reactor has revealed that the classical scavenging mechanism properly describes the reduction of N_2O with CH_4 over Fe-silicalite. According to this, the C–H bond of the alkane is activated by oxygen species deposited on the catalysts upon N_2O decomposition. Oxygen species show notable activity for hydrocarbon oxidation only when N_2O and CH_4 are pulsed together. Delaying the hydrocarbon pulse with respect to the N_2O pulse causes a gradual decrease of the reductant conversion as a consequence of the relatively rapid transformation of highly reactive oxygen species into unreactive ones, which appear to be stabilized in the zeolite matrix.

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