

# Mechanistic peculiarities of the N<sub>2</sub>O reduction by CH<sub>4</sub> over Fe-silicalite

Evgenii V. Kondratenko<sup>a,\*</sup>, Javier Pérez-Ramírez<sup>b,\*</sup>

<sup>a</sup> Leibniz-Institute für Katalyse e. V. an der Universität Rostock, Aussenstelle Berlin, Richard-Willstätter-Str. 12, D-12489 Berlin, Germany

<sup>b</sup> Laboratory for Heterogeneous Catalysis, Catalan Institution for Research and Advanced Studies (ICREA) and Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, E-43007 Tarragona, Spain

Available online 11 September 2006

## Abstract

Transient isotopic studies in the temporal analysis of products (TAP) reactor evidenced the importance of the lifetime of oxygen species generated upon N<sub>2</sub>O decomposition on extraframework iron sites of Fe-silicalite for methane oxidation at 723 K. Fe-silicalite effectively activates CH<sub>4</sub> when N<sub>2</sub>O and CH<sub>4</sub> are pulsed together in the reactor. However, these oxygen species gradually become inactive for methane oxidation as the time delay between the N<sub>2</sub>O and CH<sub>4</sub> pulses is increased from 0 to 2 s.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** N<sub>2</sub>O reduction; Iron silicalite; Oxygen species; Lifetime; CH<sub>4</sub> oxidation; Mechanism; TAP reactor

## 1. Introduction

N<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O reduction, only few fundamental studies assessing the intrinsic mechanism of N<sub>2</sub>O reduction have been published. Kunimori and co-workers [9–11] reported that methane is effectively oxidized by N<sub>2</sub>O over Fe-beta when both reactants were fed together in the catalytic reactor. Contrarily, the reaction of CH<sub>4</sub> with the N<sub>2</sub>O-pretreated catalyst showed very low activity. Two different oxygen species originated from N<sub>2</sub>O 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<sub>2</sub>O and C<sub>3</sub>H<sub>8</sub> pulses, the importance of the lifetime of oxygen species for N<sub>2</sub>O–C<sub>3</sub>H<sub>8</sub> 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<sub>2</sub>O lost their activity for C<sub>3</sub>H<sub>8</sub> oxidation when N<sub>2</sub>O and C<sub>3</sub>H<sub>8</sub> were fed separately. In contrast, the oxidation of CO by N<sub>2</sub>O 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<sub>3</sub>H<sub>8</sub> and CO to CH<sub>4</sub>. In this paper, we have investigated the mechanism of reduction of N<sub>2</sub>O by <sup>13</sup>CH<sub>4</sub> 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<sub>2</sub>O 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<sub>2</sub>O–CH<sub>4</sub> 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<sup>3+</sup> ions in extraframework positions. A certain fraction of oligonuclear iron-oxo species in the zeolite channels was also

\* Corresponding authors.

E-mail addresses: [evgenii@aca-berlin.de](mailto:evgenii@aca-berlin.de) (E.V. Kondratenko), [jperez@iciq.es](mailto:jperez@iciq.es) (J. Pérez-Ramírez).

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  $\mu\text{m}$ ) was packed between two layers of quartz spheres of the same size fraction in the quartz fixed-bed micro-reactor (6 mm i.d.). Prior to the experiments, Fe-silicalite was pretreated in flowing He (30 ml STP  $\text{min}^{-1}$ ) 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.  $5 \times 10^{14}$  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  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  was investigated at 723 K by means of pump-probe experiments. Mixtures of  $\text{N}_2\text{O}:\text{Xe} = 1:1$  (pump) and  $^{13}\text{CH}_4:\text{Ne} = 1:1$  (probe) were sequentially pulsed in the micro-reactor applying time delays ( $\Delta t$ ) 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),  $\text{N}_2\text{O}$  (2.0), and  $^{13}\text{CH}_4$  (99 at.%  $^{13}\text{C}$ , 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 ( $^{13}\text{CO}_2$ ), 44 ( $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ), 32 ( $\text{O}_2$ ), 30 ( $\text{N}_2\text{O}$ ), 29 ( $^{13}\text{CO}$ ), 28 ( $\text{N}_2$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ), 20 (Ne), 18 ( $\text{H}_2\text{O}$ ), 17 ( $^{13}\text{CH}_4$ ,  $\text{H}_2\text{O}$ ), and 16 ( $^{13}\text{CH}_4$ ,  $\text{O}_2$ ). 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  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  were carried out in the TAP reactor in order to analyze whether the lifetime of oxygen species deposited on the catalyst upon  $\text{N}_2\text{O}$  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 ( $\Delta t$ ) ranging from 0 to 2 s. Isotopically labeled  $^{13}\text{CH}_4$  and non-labeled  $^{14}\text{N}_2\text{O}$  were used to uncouple the analysis of  $\text{N}_2\text{O}-\text{CO}_2$  and  $\text{N}_2-\text{CO}$  in mass spectrometry. The use of the most abundant isotope for methane, i.e.  $^{12}\text{CH}_4$ , makes it impossible due to the identical main AMUs of  $^{14}\text{N}_2\text{O}$  and  $^{12}\text{CO}_2$  (44) as well as  $^{14}\text{N}_2\text{O}$ ,  $^{14}\text{N}_2$  and  $^{12}\text{CO}$  (28).

$^{13}\text{CO}$  and  $^{13}\text{CO}_2$  were the only carbon-containing products detected by MS analysis at the reactor outlet when  $\text{N}_2\text{O}$  and

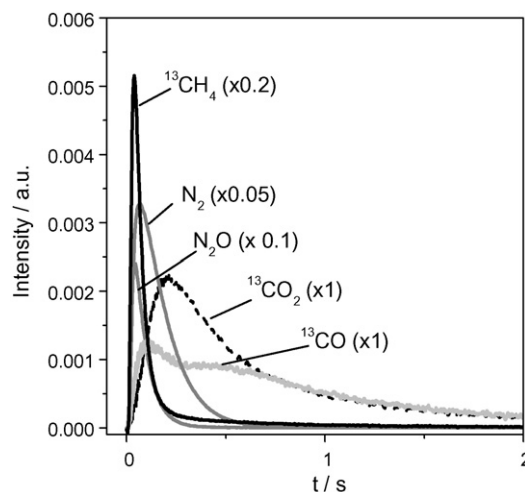


Fig. 1. Transient responses of  $\text{N}_2\text{O}$ ,  $^{13}\text{CH}_4$ ,  $\text{N}_2$ ,  $^{13}\text{CO}$ , and  $^{13}\text{CO}_2$  upon simultaneous pulsing of  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  over Fe-silicalite at 723 K. Pulse size of  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$ : ca.  $5 \times 10^{14}$  molecules.

$^{13}\text{CH}_4$  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  $\text{N}_2\text{O}$ ,  $^{13}\text{CH}_4$ ,  $\text{N}_2$ ,  $^{13}\text{CO}$ , and  $^{13}\text{CO}_2$ , when  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  were simultaneously pulsed ( $\Delta t = 0$  s). The transient responses of  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  have the sharpest shape as a consequence of their consumption. Since  $\text{N}_2$  is formed from  $\text{N}_2\text{O}$ , its transient response is broader and slightly shifted to longer times as compared to that of nitrous oxide. The products of  $^{13}\text{CH}_4$  oxidation, i.e.  $^{13}\text{CO}$  and  $^{13}\text{CO}_2$  appear at similar time as  $\text{N}_2$ . However, their transient responses are considerably broader than that of nitrogen. This indicates a relatively strong interaction of  $^{13}\text{CO}_x$  with Fe-silicalite, as reported in our previous paper for  $\text{N}_2\text{O}-^{13}\text{CO}$  interactions [13].

Fig. 2 compares the degrees of  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  conversion at 723 K for various time delays between the pulsed gases. The

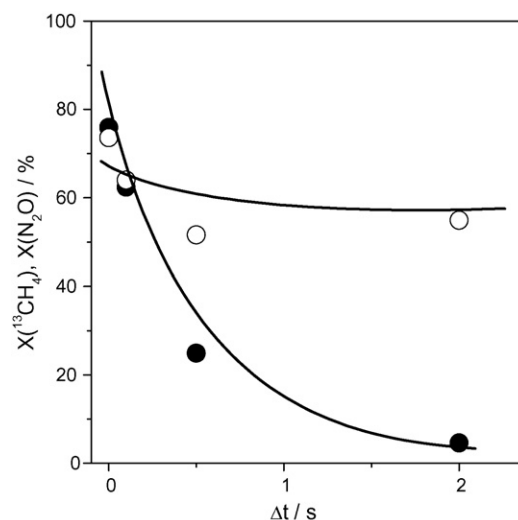


Fig. 2. Conversion of (●)  $^{13}\text{CH}_4$  and (○)  $\text{N}_2\text{O}$  as a function of the time delay ( $\Delta t$ ) between the pulses of  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  at 723 K. Pulse size as in caption of Fig. 1.

Download English Version:

<https://daneshyari.com/en/article/58176>

Download Persian Version:

<https://daneshyari.com/article/58176>

[Daneshyari.com](https://daneshyari.com)