N_2O decomposition on Fe/CHA catalyst using transient response methods

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Significance and Relevance

The decomposition of N_2O, a strong greenhouse gas, has been investigated on Fe/CHA catalysts by Transient Response Methods. A set of transient experiments has been defined to investigate the kinetics of N_2O decomposition. These experiments allowed to gather information on the dynamics and kinetics of the reactions, while the subsequent temperature ramps have given important information on the yet not well understood auto-reduction of Fe. Finally, the oxidation state of Fe after the N_2O decomposition has been assessed by $NO+NH_3$ reduction studies. All the data are then pulled together and considered to model the N_2O decomposition reaction.

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Preferred and 2^{nd} choice for the topic: Automotive and stationary emission control *(or Fundamental advances in understanding catalysis)*
Preferred presentation: Oral only

Introduction and Motivations

Nitrous oxide (N_2O) is a strong pollutant known to have a global-warming impact of almost 300 times higher than carbon dioxide (CO_2)[1]. Among the possible catalysts for the abatement of N_2O, Fe/zeolites represent a valid solution both for their stability, low cost and elevated turnover rates[2,3]. The mechanism for catalytic N_2O decomposition has been extensively studied; however, due to the diverse configuration of the Fe sites involved in the reaction mechanism, the nature and the chemistry of the active species involved remain largely unclear. In this work transient methods are used to investigate iron/chabazite (Fe/CHA) catalysts, promising materials both for NH_3-SCR and N_2O abatement. Eventually, the experimental data are analysed using a PFR transient integral model using a similar approach to that previously used to study redox NH_3-SCR mechanism on Cu/CHA[4].

Materials and Methods

Three different Fe/CHA samples with increasing iron loadings (1% - 2.5% w/w) are investigated in the form of powders (48mg) loaded in a quartz-tube reactor. In all the experiments He is used as a carrier gas and the concentrations of the species are detected through an FT-IR gas analyser and a Mass spectrometer.

N_2O decomposition activity is investigated carrying out Transient Response Methods (TRM) tests: after a pre-reduction with 500 ppm of NO and 500ppm of NH_3, for 1 hour at 550°C, N_2O decomposition is then performed at lower temperatures, either 330, 380 or 430 °C, feeding 500 ppm of N_2O. Then, two different steps are used to investigate the status of the catalyst after the N_2O decomposition: 1) a Temperature Programmed Desorption (TPD) ramp at 15°C/min is run from the decomposition temperature to 550 °C (He carrier, Ar tracer, GHSV= 266250 $Ncc/(h{*}g_{cat})$); 2) a reduction step is performed: 500 ppm NO, 500 ppm NH_3 are fed isothermally (330 °C) for 1 h 20 min (He carrier, Ar tracer, GHSV= 266250 $Ncc/(h{*}g_{cat})$). Lastly, the integral consumption of NO (μmol) and integral of the production of N_2 (μmol) are calculated.

Results and Discussion

On all the samples, a significant consumption of N_2O is observed right after its feed, leading to the simultaneous mirror-like production of N_2 followed, after a few seconds, by the production of O_2 (as shown in Figure 1, panel A). For all the Fe/CHA catalysts, the stoichiometric ratio between N_2O consumed and N_2 and O_2 produced follows the expected of 2:2:1 stoichiometry of the N_2O decomposition ($2N_2O \rightarrow 2N_2 + O_2$) after the initial dynamics. It is worth noticing that N_2O is not adsorbed on the catalyst since there is no release during the final temperature ramp (Figure 1, panel B). However, an evolution of stored oxygen in TPD is present on all the sample, characterized by a distinct peak in the 380-450°C range. It is associated to the auto-reduction of the Fe, previously oxidized during N_2O feed step. When NO+NH_3 reduction protocol is performed after the N_2O decomposition step, consumption of NO and production of N_2 are observed. This is due to the ability of N_2O to re-oxidize the iron sites while decomposing. Calculating the $NO_{consumed}$ /Fe_{sample} ratio for the experiment at the different temperatures it is observed that, as the temperature increases, the ratio decreases evidencing a lower consumption of NO at the higher temperatures (e.g., for the intermediate sample, from 330 to 430 °C the ratio reduces from 67 to 58 %).

This behaviour can also be explained with the ability of Fe sites to "auto reduce" at higher temperatures, thus, less Fe can participate in the following NO + NH_3 reduction. This auto-reduction confirms why when N_2O is fed at these higher temperatures is strongly consumed.

As a preliminary analysis, a Transient Kinetic Analysis (TKA) is performed on the experimental data by means of a PFR transient integral model which incorporates the N_2O decomposition chemistry as a redox mechanism. The redox model for low-T NH_3-SCR over Cu/CHA involved only one active Cu species[4]. Contrarily, for N_2O decomposition on Fe/CHA, this single-site approach fails to model the dynamic profile with accuracy, suggesting the involvement of more than one Fe active site. An example of multi-site model fit is shown in the left panel of Figure 1 as transparent lines.

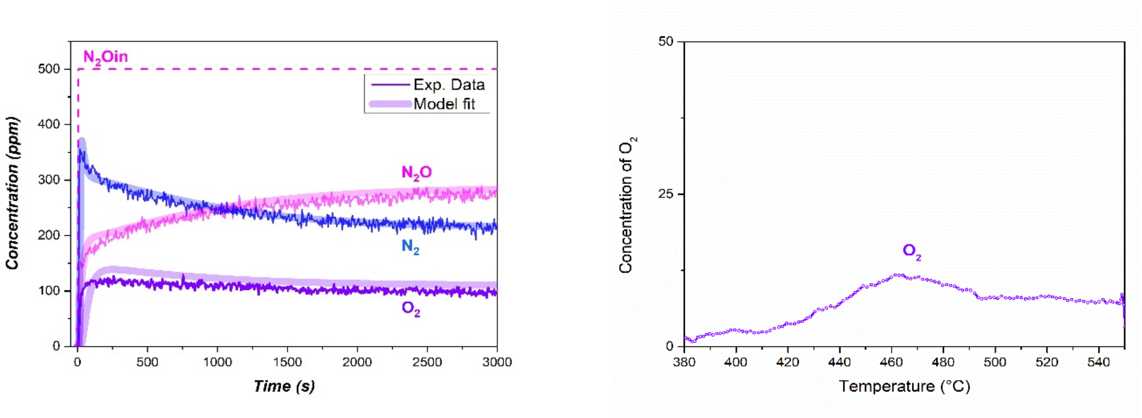

Figure 1 Evolution of N_2, N_2O and O_2 during the feed of 500ppm of N_2O for 1 hour on a Fe/CHA sample pre-reduced (left) and successive evolution of O_2 during Temperature Programmed Desorption (right)

References

1. M. Koebel, M. Elsener, T. Marti, *Combustion Science and Technology*, **1996**, *121*, 85–102.
2. F. Gao, Y. Wang, M. Kollár, N. M. Washton, J. Szanyi, C. H. F. Peden, *Catalysis Today*, **2015,** *258*, 347–358.
3. A. Wang, Y. Wang, E. D. Walter, R. K. Kukkadapu, Y. Guo, G. Lu, R. S. Weber, Y. Wang, C. H. F. Peden, F. Gao, *Journal of Catalysis*, **2018**, *358*, 199–210.
4. N. D. Nasello, U. Iacobone, N. Usberti, A. Gjetja, I. Nova, E. Tronconi, R. Villamaina, M. P. Ruggeri, D. Bounechada, A. P. E. York, J. Collier, *ACS Catalysis* **2024**, *14, 6*, 4265-4276.

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