

Study of the oscillatory behaviour in N₂O decomposition over Cu-containing ZSM-5 prepared by different techniques

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Highlights

- N₂O decomposition over Cu-ZSM-5 zeolites takes place.
- Spontaneous oscillations in N₂O decomposition occur over Cu-ZSM-5
- Cu-ZSM-5 were prepared by different techniques.

1. Introduction

Nitrous oxide (N₂O) is considered a greenhouse gas since it lasts approximately 150 years in the atmosphere, it has 310 and 21 times greater warming potential than CO₂ or CH₄, respectively, and it contributes to the destruction of stratospheric ozone. The main contributors of the anthropogenic sources include fertilizers, nitric acid, adipic acid, caprolactam and glyoxal production, fossil fuels and biomass combustion, as well as sewage treatment. Nitric acid and adipic acid production plants are thought to be the largest industrial sources of N₂O emissions. As a whole, there is a higher N₂O concentration in tail gas emissions from adipic acid plants (usually 20–40 % v/v) than from nitric acid production (around 300–3500 ppm). It has in fact been reported that around 10% of N₂O released into the atmosphere each year originates from adipic acid production, and hence great efforts have been made to abate high-concentration N₂O. In this scenario, catalytic N₂O decomposition could be a promising alternative solution, as it makes N₂O abatement possible at the emission source at lower temperatures (300–500 °C) than the conventional thermal abatement technology [1]. Then, Cu-containing ZSM-5 zeolite can be a promising candidate for potential applications. On the other hand, spontaneous isothermal oscillations in N₂O decomposition may take place over Cu-ZSM-5, depending on the operating conditions [2,3]. In the present work a set of Cu-ZSM-5 catalysts (nominal content of Cu = 3 and 6 wt.%) prepared by three different synthesis procedures (namely, wet impregnation, ion-exchange, and sublimation) was tested for the N₂O decomposition.

2. Methods

In the typical preparation via wet impregnation and ion-exchange, 20 mM of Cu(NO₃)₂·5H₂O solution is used as the copper precursor. Then, a proper quantity of H-ZSM-5, dependent on the intended copper loading, is added in the copper solution. The synthesis then continues with the stirring of the suspension at 80 °C till the complete water evaporation (wet impregnation) or at 60 °C for 2 h (ion-exchange). In the wet impregnation method, the sample is directly dried overnight at 60 °C, while in the ion-exchange method, the excess liquid is removed via centrifugation and the solid is washed twice with deionized water and ethanol before it is dried overnight at 60 °C. On the other hand, in the preparation via sublimation, CuCl and H-ZSM-5 in a proper proportion (all vacuum-degassed prior to the sublimation) are heated at 300 °C in high vacuum for 20 min. All the dry samples are finally calcined under the flow of He at 550 °C for 2 h and subsequently under the flow of 1%-vol O₂ in He gas at 550 °C for 2 h. Some analytical techniques initially carried out for characterizing the physicochemical properties of the catalysts were ICP-MS, BET, FE-SEM, XRD and XPS.

The catalytic tests were conducted in a fixed-bed U-tube Quartz reactor equipped with a K-type thermocouple, a PID-controlled vertical furnace and a non-dispersive infrared (NDIR) analyzer. 100 mg of catalyst was constantly used in the test. Prior to the test, the catalyst was pre-reduced under 200 ml min⁻¹ of He at 550 °C for 2 h. During the test, a 200 ml min⁻¹ of 1000 ppm of N₂O in He was constantly flowed

through the reactor while the reactor temperature was kept isothermal at various temperatures. For a better observation on the oscillatory behavior, the test was normally carried out between 6 and 12 hours, depending on the catalyst.

3. Results and discussion

The catalytic behaviour towards N_2O decomposition was tested in the 300-500 °C temperature range. As expected, N_2O shows negligible conversion in the absence of the active phase over that temperature range, whereas the Cu-containing catalysts exhibited positive N_2O conversion trends for an increasing reaction temperature. The results shown in Figure 1A confirm that the catalytic performances of Cu-ZSM-5 are strongly affected by the synthesis procedure as well as by the Cu-content (namely, 3 and 6 wt.% of Cu, nominal content). It appears, therefore, that the nature and accessibility of Cu species play a key role on the N_2O decomposition reaction. Under isothermal conditions, different N_2O decomposition trends appear for the prepared catalysts over TOS. Chaotic oscillations during N_2O conversion have been observed for the 3 wt.% Cu-ZSM-5, although with different trends and magnitudes. The N_2O conversion level plays a significant role on the oscillatory rate, whose nature seem so be kinetic, namely attributable to the reaction mechanism. However, at high Cu content (namely, with Cu = 6 wt.%), periodic oscillations in the decomposition of N_2O occur under isothermal conditions, as shown in Figure 1B. In fact, the W/F value play a key role on the oscillation patterns. This finding seems due to local differences of the surface concentrations which cause surface diffusion of the adsorbates. In other words, length scale of the resulting spatio-temporal concentration patterns is no longer governed by atomic dimensions but by the so-called diffusion length. A mathematical description can be obtained in terms of reaction-diffusion equations, that is, a set of coupled nonlinear partial differential equations (Lotka-Volterra model) combining the kinetics with the diffusion of the adsorbed species [4]. In the present study, the preparation method, the nature of Cu cations, the morphological features and the redox properties of copper sites before and after aging treatments were studied by complementary techniques to determine the role of Cu species and diffusive phenomena on the catalytic activity in the decomposition of N_2O .

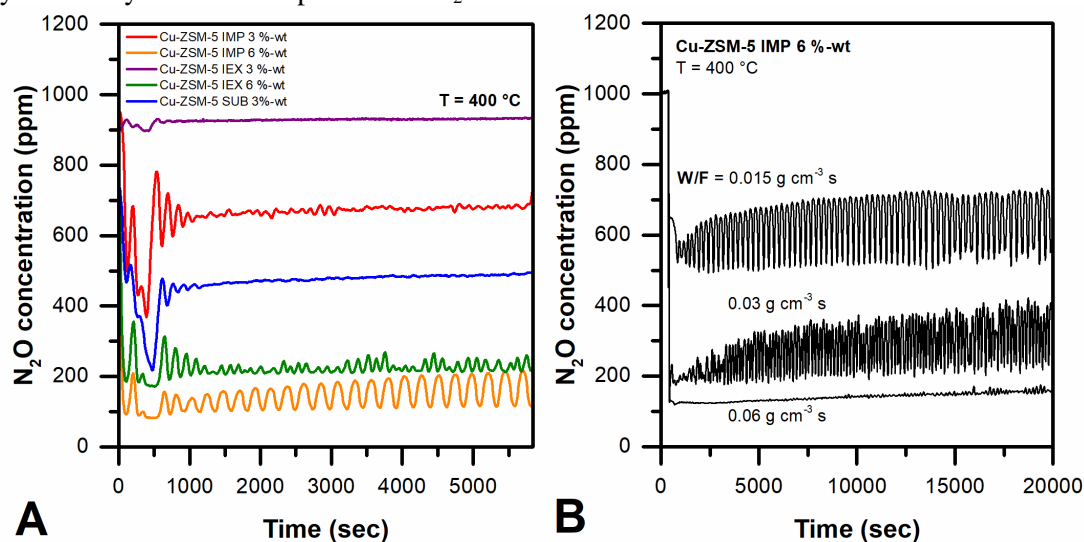


Figure 1. N_2O outlet concentrations as function of time-on-stream in N_2O decomposition at 400 °C on Cu-ZSM-5 systems.

References

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Keywords

Cu-ZSM-5; N_2O decomposition; Oscillations;