TRANSIENT MULTI PULSE METHOD FOR THE DETERMINATION OF N₂O – INTERACTION WITH ZSM-5 TYPE ZEOLITES

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Received November 11, 2004
In revised form February 1, 2005
Accepted February 15, 2005

Abstract

Multipulse experiments reveal qualitative and quantitative, time-resolved information about the interaction of N₂O with ZSM-5 type zeolites under conditions of catalytic applications, like the mechanism of N₂O decomposition, amount and reactivity of an atomic surface oxygen species.

Keywords: Nitrous oxide, zeolite, surface oxygen, transient method

INTRODUCTION

Iron-containing zeolites of ZSM-5 type are very promising catalysts for N₂O abatement in waste gases [1,2] as well as for partial hydrocarbon oxidations with N₂O as oxidant [3,4]. In both applications, extra-framework iron species inside the zeolite channels are assumed to be active sites for the formation of an atomic surface oxygen species according to reaction. For partial oxidations of hydrocarbons this oxygen species and the corresponding sites were designated as "α-oxygen" and "α-sites", respectively, by Panov et al. [3]. A remarkable

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difference between catalysts for N₂O abatement and partial oxidations using N₂O is the iron content in the zeolite: lower contents for partial oxidations (≤ 0.5 wt.% Fe) [3,4], higher contents for decomposition (> 1 wt.% Fe) [6-8]. The formation of atomic surface oxygen species is assumed to be an important initial step in the catalytic cycle for both applications. The following scheme, reactions (1) - (4), concludes the mechanism of formation and consumption of the surface oxygen species up to the application [3,5,9]:

\[
\begin{align*}
Z + N_2O &\rightarrow N_2 + Z-O \\
2Z-O &\rightarrow O_2 + 2Z \\
Z-O + N_2O &\rightarrow N_2 + O_2 + Z \\
Z-O + R &\rightarrow R - O + Z
\end{align*}
\]

Reactions (2) and (3) are rate determining for the formation of molecular oxygen [9] and usually occur at temperatures higher than 573 K, if no other reactant is present [3,5]. In reaction (4) R represents a reductant molecule which is oxidized by the surface oxygen species to an oxygenate R-O, e.g. benzene - phenol, methane – methanol, even at room temperature [3] or which is used in N₂O abatement, e.g. NO [2,6], different hydrocarbons [2,10].

Several research groups investigate the formation and stability of the surface oxygen species and the corresponding active sites in the zeolite. The first and the most prominent method to determine the amount of the surface oxygen species is the N₂O decomposition in a static vacuum set-up, temperature programmed [5] or isothermal at 523 K [1,11,12], and isotope exchange with ¹⁸O₂ [1,11-13]. Later on, other isotopic labeling experiments [8] and transient step experiments [8,14,15] have also been applied. Despite the abundant literature on this topic, the nature of the oxygen species is still not clear. One reason is that the conditions of most studies, like in the static vacuum system, differ from those of catalytic applications. Moreover, investigations focus on zeolites either with low or high iron contents which are differently prepared.

In this work a transient multipulse technique is presented as a sensitive method for investigating the interaction of N₂O with different ZSM-5-type zeolites under conditions of catalytic applications. Using this technique the amount, stability and reactivity of the surface oxygen species can be investigated with high resolution. Compared to other techniques, it is possible to investigate formation and nature of this oxygen species as function of the state and oxygen loading of the zeolite. Therefore, all single steps in the reaction scheme (1)-(4) can be investigated separately and resolved in time. In the following, this technique is applied to differently pretreated ZSM-5 zeolites with high and low iron content.