

Cu-zeolites in the Catalytic N₂O Decomposition and Selective Oxidation of Methane: a Combined Spectroscopic-Catalytic Study.

Pieter J. Smeets¹, Julia S. Woertink², Marijke H. Groothaert¹, Emiel J.M. Hensen³, Edward I. Solomon², Bert F. Sels¹ and Robert A. Schoonheydt^{1,*}

¹Center for Surface Chemistry and Catalysis, K.U.Leuven, Heverlee 3001 (Belgium)

²Department of Chemistry, Stanford University, Stanford, CA 94305-5080 (USA)

³Schuit Institute of Catalysis, Eindhoven University of Technology, MB Eindhoven 5600 (The Netherlands)

*Robert.Schoonheydt@biw.kuleuven.be

Introduction

The activation of O₂ and N₂O is a key issue in the decomposition of NO_x and the selective oxidation of alkanes. Transition metal ion (TMI) containing zeolites are often investigated in these reactions [1-3]. Here, the capacity of Cu-zeolites to activate these molecules is investigated with regard to their activity in the catalytic decomposition of N₂O and the selective oxidation of CH₄ into CH₃OH. The results of a combined spectroscopic-catalytic study provide novel insights in the mechanisms and the nature of the active site in these important reactions.

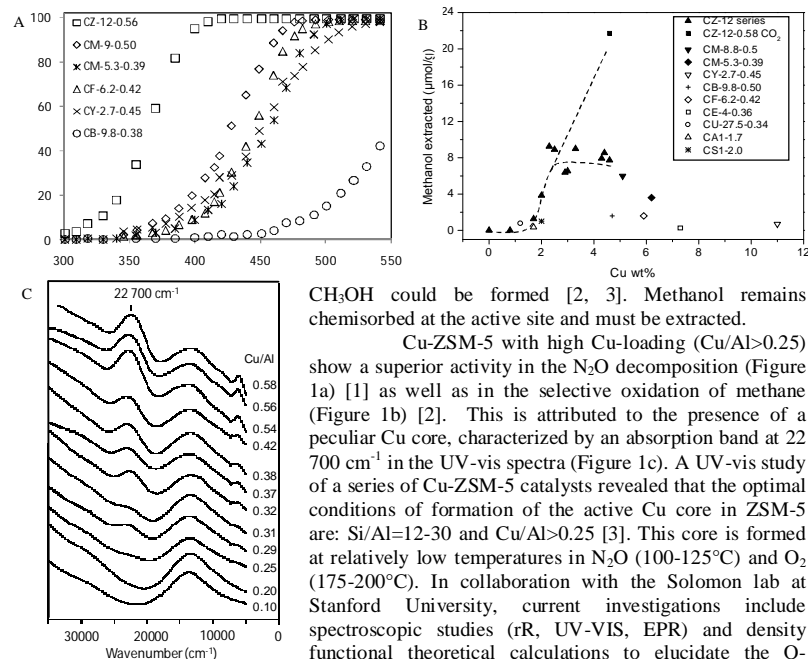
Materials and Methods

Cu-zeolites are prepared via liquid ion exchange of the Na-zeolites with Cu-acetate. The Cu content after exchange is determined by inductively coupled plasma (ICP) after dissolution of the zeolite in HF. The catalysts are denoted as CX-Y-Z, where X represents the zeolite used (Z=ZSM-5, M=MOR, Y=FAU, B=*BEA and F=FER), Y the Si/Al ratio of the zeolite and Z the Cu/Al ratio. In-situ UV-vis measurements were performed on a Varian Cary 5 UV-vis-NIR spectrophotometer. Additional experimental information is given in [1-3].

Results and Discussion

The activation of N₂O and O₂ over Cu-zeolites is studied in two important reactions, namely, the decomposition of N₂O into N₂ and O₂ and the selective oxidation of CH₄ into CH₃OH. In the N₂O decomposition, the activity of Cu-zeolites highly depends on the Cu loading. It is observed that the recombinative O₂ desorption is the rate limiting step. This step requires the migration of deposited O atoms. The encounter probability of O atoms increases with decreasing Cu-Cu distances, i.e. with increasing Cu-loading. The influence on the catalytic activity of O₂, NO and H₂O, which are often present in real exhaust gases of N₂O emitting sources, is also investigated. As O₂ showed no effect on catalytic activity, the dissociative adsorption is slower than the recombinative desorption of O₂, while NO is found to accelerate the migration of the O atoms. Quite unexpectedly, a beneficial effect of H₂O is observed in some Cu catalysts, which is envisioned to be caused by H₂O induced Cu-migrations. Due to this migration, the Cu-Cu distance decreases, facilitating O-migration. In zeolites with low Cu-loading, this reversible migration prevails on the negative competitive adsorption of H₂O [1].

The second reaction investigated in this work is the selective oxidation of CH₄ into CH₃OH. After calcination in O₂, a stoichiometric reaction with CH₄ already occurs at 100°C for Cu-ZSM-5 catalysts. MOR and FER require reaction temperatures of at least 200°C before



CH₃OH could be formed [2, 3]. Methanol remains chemisorbed at the active site and must be extracted.

Cu-ZSM-5 with high Cu-loading (Cu/Al>0.25) show a superior activity in the N₂O decomposition (Figure 1a) [1] as well as in the selective oxidation of methane (Figure 1b) [2]. This is attributed to the presence of a peculiar Cu core, characterized by an absorption band at 22 700 cm⁻¹ in the UV-vis spectra (Figure 1c). A UV-vis study of a series of Cu-ZSM-5 catalysts revealed that the optimal conditions of formation of the active Cu core in ZSM-5 are: Si/Al=12-30 and Cu/Al>0.25 [3]. This core is formed at relatively low temperatures in N₂O (100-125°C) and O₂ (175-200°C). In collaboration with the Solomon lab at Stanford University, current investigations include spectroscopic studies (rR, UV-VIS, EPR) and density functional theoretical calculations to elucidate the O-activated site structure in Cu-ZSM-5.

Figure 1: A) Conversion vs temperature in the N₂O decomposition (1 vol.% in He); B) Amount of methanol extracted after reaction with CH₄ at 150°C; C) UV-vis spectra of a calcined Cu-ZSM-5 series with increasing Cu/Al ratio.

Significance

Cu-zeolites activate O₂ and N₂O already at low temperatures and show promising results in the decomposition of N₂O and the selective oxidation of CH₄ into CH₃OH. These reactions are of key importance in today's sustainable industry. A detailed study of the nature of the active core, responsible for the superior activity of Cu-ZSM-5 catalysts will elucidate the mechanisms of these reactions and lead to further improvement of the activity of these catalysts.

References

1. Smeets, P.J., Sels, B.F., van Teeffelen, R.M., Leeman, H., Hensen, E.J.M. and Schoonheydt, R.A. *J. Catal.* 256, 183 (2008).
2. Groothaert, M.H., Smeets, P.J., Sels, B.F., Jacobs, P.A. and Schoonheydt, R.A. *J. Am. Chem. Soc.* 127, 1394 (2005).
3. Smeets, P.J., Groothaert, M.H. and Schoonheydt, R.A. *Catal. Today* 110, 303 (2005).