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UHV-TPD STUDY OF NO ADSORPTION/REACTION OVER Cu/ZSM-5

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1. Introduction

The chemisorption state of NO adsorbed on Cu/ZSM-5 was investigated by TPD method in UHV system and was correlated with NO decomposition mechanism. Temperature programmed desorption (TPD) is widely applied to the studies of adsorption/desorption phenomena on single crystal. This technique makes it possible to observe the elementary desorption process occurring on surface. By applying the UHV-TPD technique to the real catlaysts, it is expected that the well-resolved adsorption state of adsorbates on the metal site on support and the interaction between adsorbates could be observed. The effect of partial pressure of NO on the reaction mechanism was discussed.

2. Experimental

TPD study was carried out in typical UHV chamber operating in the pressure range of 10^{-6} - 10^{-9} Torr. The powder sample was deposited on Ta disk by means of slurry technique[1]. Cu/ZSM-5 (420 m^2/g) catalyst having percent ion exchange of 95 was used for this work. The UHV apparatus consisted of a stainless steel vacuum chamber of 2.3 x 10^3 cm^3) connected to an 220 l/s turbo molecular pump (TMP). The TMP may be isolated from the chamber using an ultrahigh vacuum gate valve. The typical base pressure reached in the system is < 1 x 10^{-9} torr. The sample was heated in vacuum to 873 K for about 10 minutes and kept for 5 minutes at the same temperature. After the sample was cooled down to the specified temperature, it was exposed to NO for adequate time at pressure less than 1 x 10^{-6} torr under dynamic pumping conditions.

3. Results and Discussion

UHV-TPD technique working with small amount of powder sample makes it possible to observe the elementary adsorption/desorption process occurring on isolated Cu cation in ZSM-5. The three distinct states of NO adsorbed on Cu/ZSM-5 (T_{ad} = 175K) are indicated by the appearance of the peaks at 210 (α), 330 (β) and 480 K (γ) with the increase of exposure. From TDS of NO adsorbed on CO pre-adsorbed Cu/ZSM-5 at 175K (Fig.1), it is found that β peak is attributable to NO adsorbed on Cu^+ ion, while α peak is due to NO physically adsorbed on support. The β peak obeys the first order kinetics with the desorption activation energy of 12.9 Kcal/mol. At high NO exposure pressure ($\geq 10^{-4}$ Torr), γ peak appears and N_2 and N_2O are produced during TPD, suggesting that dinitrosyl species (γ) active for NO decomposition is developed from NO molecularly adsorbed on Cu^+ ion. TPD peaks at 380 and 640 K due to Cu^{2+}-(NO) and Cu^{2+}-(NO_2) in the atmospheric condition are evolve from γ peak. These results indicate that NO decomposition proceeds via the disproportionation of the dinitrosyl species on Cu^+, leading to the oxidation of Cu^+ to Cu^{2+}.

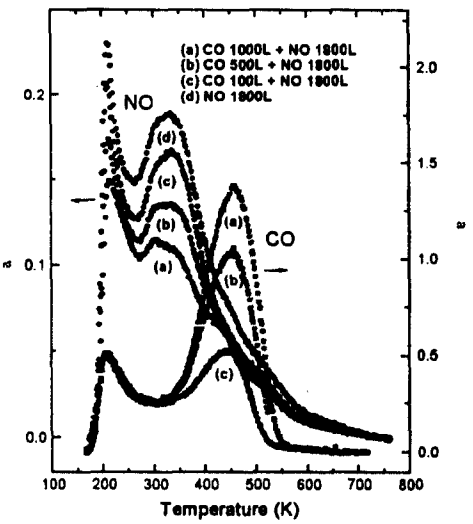

Fig. 1. TPD spectra of NO on Cu/ZSM-5

4. Conclusion

TPD study of NO on Cu/ZSM-5 in UHV condition was very useful to define the binding state of adsorbate and to study the mechanism of NO decomposition.

5. References

[1] P. Basu and J. T. Yates. Jr., Surf. Sci. 177 (1986) 291.