Selective catalytic oxidation (SCO) of ammonia to nitrogen over mesoporous zeolite

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Introduction

Ammonia (NH_3) is widely found in industrial processes and the removal of NH_3 from waste gas streams is becoming increasingly important because of environmental concerns. For those many ways to removal NH_3, selective catalytic oxidation (SCO) of NH_3 to N_2 is an ideal technology for removing NH_3 from waste gases, and it has been of increasing interest in recent years[1]. A number of catalysts have previously been applied to oxidize gaseous NH_3, such as noble metal (Pt, Ir and Au), Ni, Fe, and Mn oxides supported on γ - Al_2O_3, CuO/Al_2O_3, Ag/Al_2O_3, Fe-exchanged ZSM-5 and other zeolites. These catalysts exhibited activities for N_2 formation under various conditions. Among these catalysts, metal ion supported on zeolites showed interesting activity and selectivity at low temperatures.

Mesoporous SBA-15 zeolite constitutes one kind of the excellent catalyst support due to its superhigh surface area, ordered pore arrangement, adjustable pore sizes ,and high hydrothermal and thermal stability. For these unique features, in the present study, a wide range of transition metals modified SBA-15 samples (M/SBA-15) [M = (Cu, Co, Fe, Mn, Ni) and Cu supported on SBA-16, KIT-6] were prepared and characterized.

Materials and Methods

The catalysts were prepared using impregnation method. The experiments were run in a quartz fixed-bed reactor (3 cm i.d.). They were conducted at 1000 ppm NH_3, 5% O_2 GHSV = 45,000 h^{-1} and 100 to 500 ºC by steps of 50 ºC. The effluent gases (NH_3, N_2O, NO and NO_2) were monitored an infrared gas analyzer equipped with a 2.4 meter long-path gas cell and TQ analysis software. They were characterized by X-ray diffraction (XRD), surface area (BET), transmission electron microscopy (TEM), temperature-programmed reduction by hydrogen (H_2-TPR), X-ray photoelectron spectroscopy (XPS), temperature-programmed oxygen isotopic exchange (TPOIE) as well as the activity tests for selectively catalytic combustion of NH_3.

Results and Discussion

As presented in **Figure 1A**, it can be found that Co/SBA-15 presenting a strong oxygen mobility than the other two samples and SBA-15 almost have no oxygen mobility. For these three samples, the α_g^t of Cu/SBA-15 decreased most, while for Co/SBA-15 and SBA-15, it only have a little decrease. Nevertheless, we could consider that this reaction remained a good oxide surface characterization due to the limited participation of the bulk oxygen atoms at the temperature studied [2]. At **Figure 1B**, it can be shown that the rate of P_{34} rise follow a decreasing order of Cu/SBA-15 > Cu/SBA-16 > Cu/KIT-6. While the α_g^t of all samples decrease, Cu/SBA-16 shows the highest value 47% at 550 ºC and Cu/SBA-15 shows the lowest one. It can be found that Cu/SBA-15 have the strongest oxygen mobility.

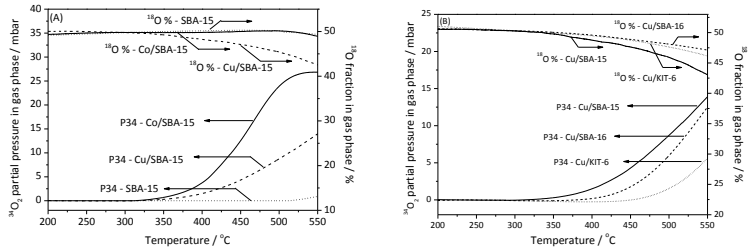

Figure 1. Evolution of the partial pressure of the $^{34}O_2$ and ^{18}O fraction in the gas phase (α_{gt}) versus temperature of reaction for SBA-15, Cu/SBA-15 and Co/SBA-15 (A) and Cu/SBA-16 and Cu/KIT-6 with Cu/SBA-15 (B) in TPOIE.

Figure 2 shows the NH_3 conversion of temperature during NH_3 combustion over catalysts. For M/SBA-15, it can be fund that the NH_3 conversion follow a decreasing order of Cu/ ≈ Co/ > Mn/ > Fe/ ≈ Ni/SBA-15 > SBA-15. And for different zeolites, the sequence is : Cu/SBA-15 > Cu/SBA-16 ≈ Cu/KIT-6. In summary, Cu/SBA-15 is a promising candidate used as a catalyst for NH_3 selective combustion towards unharmful N_2.

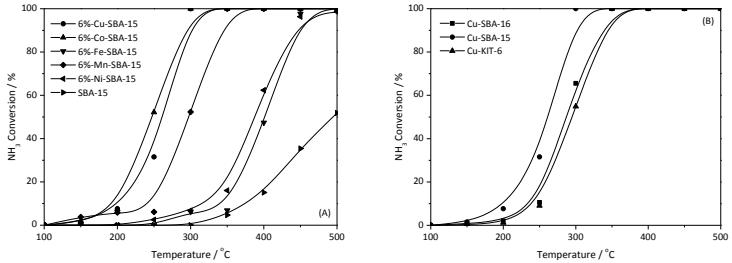

Figure 2. NH_3 conversion of temperature during NH_3 combustion over SBA-15 and (Cu, Co, Fe, Mn, Ni)/SBA-15 (A) and Cu/SBA-16 and Cu/KIT-6 with Cu/SBA-15 (B).

Significance

After impregnating the various metallic components, metal-promoted mesoporous silica exhibits remarkable NH_3 activity, which strongly depends on the essentially chemical nature of metals doped and their dispersity.

Cu/SBA-15 shows the strongest oxygen mobility and best catalyst performance.

References

[1]. Long, R.Q. and R.T. Yang, Selective Catalytic Oxidation (SCO) of Ammonia to Nitrogen over Fe-Exchanged Zeolites[J]. Journal of Catalysis, 2001. **201**(1): p. 145-152.

[2]. Yang, W., et al., Activity of perovskite-type mixed oxides for the low-temperature CO oxidation: Evidence of oxygen species participation from the solid[J]. Journal of Catalysis, 2012. **295**(0): p. 45-58.