Catalytic combustion of acrylonitrile over 3d-transition metals (Cu, Co, Fe) or Pt/SBA-15, Cu/SBA-16 and Cu/KIT-6 mesoporous catalysts

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Introduction
Nitrile gases such as acrylonitrile (C₃H₃CN), acetonitrile (CH₃CN), and hydrocyanic acid (HCN) are hazardous properties, which are commonly classified as volatile organic compounds (VOCs). If the nitrile waste gases are not strongly demanded to prevent emission into the atmosphere, they can lead to seriously environmental problems and affect human beings. The efficiency of removal of them by either incineration or catalytic combustion becomes essential. The relatively lower operating temperature for catalytic combustion associated with a less NO formation makes this technology especially suitable for gaseous nitrile elimination. SBA-15 supported transition or noble metals catalysts were applied to the catalytic combustion of acetonitrile (CH₃CN) and four relevant kinds of mechanism were proposed [1]. Cu/SBA-15 exhibited a nearly complete CH₃CN conversion associated with a N₂ selectivity of around 80 % T > 350 °C. Although hydrocyanic acid (HCN), acetonitrile (CH₃CN) and acrylonitrile (C₃H₃CN) can be assigned to nitrile material, they have different structures and chemical properties. Hence, to detailly investigate the system of nitrile gases catalytic combustion, expand research should be conducted to other nitrile gases over metals/SBA-15. The different types of ordered mesoporous materials, such as MCM-41, SBA-15, SBA-16, and KIT-6, have different space structures, surface areas, pore volumes and pore size distributions. Scare data related to the character of mesoporous support on the copper particles dispersion, reducibility and catalytic behaviour of C₂H₃CN have been reported. Whether the mechanisms for the C₂H₃CN over the metal/SBA-15 conform to the four kinds of reaction mechanisms for CH₃CN catalytic combustion we have proposed needs to be further proved.

Materials and Methods
A series of SBA-15 with different metals (Cu, Co, Fe, and Pt) and the copper loading different mesoporous zeolites (SBA-15, SBA-16, and KIT-6) were used for the catalytic combustion of C₂H₃CN. Meanwhile, the activity and selectivity for the three kinds of nitrile gases (C₂H₃CN, CH₃CN, HCN) over Cu/SBA-15 were contrasted under the similar condition. The catalysts were prepared and characterized by XRD, N₂ adsorption, TEM, H₂-TPR, XPS. Moreover, an attempt to verify the related combustion mechanism has been done based on the diffuse reflectance infrared Fourier transform spectra (DRIFTS) studies.

Results and Discussion
As presented in Figure 1, C₂H₃CN conversions achieving over the investigated catalysts follow a trend of Pt > Co/ ≈ Cu/ > Fe/SBA-15 at 400 °C, however, the yield of mainly desired product N₂ follow the trend of Cu/ > Fe/ > Pt/ > Co/SBA-15 at 400 °C, being correlated well with the redox abilities, metallic state and the chemical nature of the loaded metal species. The conversion of C₂H₃CN and the yield of N₂ were sequentially followed by the Cu/SBA-15 > Cu/SBA-16 > Cu/KIT-6 at above 350 °C, due to the straight cylindrical pores with 2-D arrangement of SBA-15 are beneficial not only to homogeneous distribution of the loaded copper along the pore surface, but also to the formation of highly dispersed Cu²⁺ ions.

Figure 1. Catalytic performance as a function of temperature during C₃H₃N combustion: (a) (Cu, Co, Fe, Pt)/SBA-15; (b) Cu/ (SBA-15, SBA-15, KIT-6)

As presented in Figure 2, the -NCO (2198 cm⁻¹) being the most intermediate over Cu/SBA-15 can be directly oxidized to N₂ and CO₂ under the oxygen-rich condition. However, the CN band (2237 cm⁻¹) of C₃H₃CN is able to be hydrolyzed into acylamino over Fe/SBA-15, leading to an enhancement in the related bands (1571, 1659 cm⁻¹).

Figure 2. DRIFTS of absorbates produced from the flow of C₃H₃CN (0.3 vol %) + O₂ (8 vol%) + He (91.7 vol%) for 25 min: (a) Cu/SBA-15; (b) Fe/SBA-15

Significance
Acrylonitrile was efficiently removed over Cu/SBA-15 with high conversion and high yield of N₂. Meanwhile, the C₂H₃CN combustion mechanisms separately complied with the “N₂ formation” mechanism over Cu/SBA-15 and the “NH₃ formation” mechanism over Fe/SBA-15.

References