Figures

Photo-assisted SCR over highly dispersed silver sub-nanoparticles in zeolite under visible light: an *Operando* FTIR study

Houeida Issa Hamoud,^a Mama Lafjah,^b Fatima Douma,^{a,b} Oleg I. Lebedev,^c Fatiha Djafri,^b Valentin Valchev,^a Marco Daturi,^a Mohamad El-Roz^{a*}

^a Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France.

^b Université d'Oran 1, Laboratoires de Chimie des Matériaux, Algeria.

^c Normandie Université, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 Caen, France.



Figure 1. (A) Powder X-ray diffractograms (PXRD) and (B) Nitrogen adsorption (closed symbols) and desorption (open symbols) isotherms of ZX-V and Ag@ZX-V samples.



Figure 2. (a) HAADF–STEM images of Ag@ZX-V nanoparticle close to [001] zone axis. Triangle shape and Ag filled with an evident hexagonal arrangement of the channels. (b) HAADF-STEM image of Ag@ZX-V in the presence of non-loaded FAU nanoparticle marked by a white rectangle. The contrast is very low due to the presence only relatively light elements in zeolite (Si, O). (c) Enlargement image of selected in (b) non-loaded FAU nanoparticle with resolved lattice plains.



Figure 3. DR-UV-Vis spectra of (a) ZX-V,(b) as prepared Ag@ZX-V and (c) Ag@ZX-V activated at 150°C under Ar samples. Insert: the images of the pellets of the corresponding samples.



Figure 4. (A) IR spectra of ZX-V and Ag@ZX-V under 10 torr of CO. The spectra are subtracted from the spectra of the activated samples under vacuum (before CO adsorption). Inset: zoom on the IR spectra in the vibration region of 4000-2500 cm⁻¹. (B) Evolution of the band intensities of adsorbed CO on Ag@ZX-V.



Figure 5. NO_x conversions over ZX-V and Ag@ZX-V under visible light for a room temperature photo-assisted SCR-NH₃ reaction. The negative values correspond to an increase in the corresponding gas. The NO_x values at the steady state before irradiation are used as references. Uncertainty estimated at 5 %. Reaction conditions: m_{cat} = 20 mg; Lamp Xe; $\lambda >$ 390nm; T=25°C; gas mixture: 150 ppm of NO_x, 150 ppm of NH₃, 667 ppm of CO, 5 % CO₂, 10 % O₂, 50 ppm of HC and 2 % of water; Total flow= 31 cc.min⁻¹.



Figure 6. NO_x conversions over (A) ZX-V and (B) Ag@ZX-V samples during the photo-assisted SCR-NH₃ reaction in the dark and under visible light at T = 150 °C. The NO_x values at the steady state before irradiation at 25 °C are used as references. Uncertainty estimated at 5 %. Reaction conditions: m_{cat} =20 mg; Lamp Xe; λ >390 nm; irradiance =110 mW/cm²; T=25°C; gas mixture: 150 ppm of NO_x, 150 ppm of NH₃, 667 ppm of CO, 5 % CO₂, 10 % O₂, 50 ppm of HC and 2 % of water; Total flow = 31 cc.min⁻¹.



Figure 7. IR spectra of (A) ZX-V and (B) Ag@ZX-V recorded at the steady-state of photo-assisted SCR-NH₃ reaction at RT in dark (a), RT under visible irradiation (b) and at 150 °C in dark (c) and under visible irradiation (d). Reaction conditions: m_{cat} = 20 mg; Lamp Xe; λ >390nm; irradiance =110 mW/cm²; gas mixture: 150 ppm of NO_x, 150 ppm of NH₃, 667 ppm of CO, 5 % CO₂, 10 % O₂, 50 ppm of HC and 2 % of water; Total flow = 31 cc.min⁻¹.



Figure 8. IR spectra of Ag@ZX-V sample recorded during the SCR-NH₃ reaction at (A) RT and (B) $T = 150^{\circ}C$ under visible irradiation (photo-assisted SCR-NH₃). Reaction conditions: 7 spectres/min; $m_{cat}=20$ mg; Lamp Xe; $\lambda > 390$ nm; irradiance = 110 mW/cm²; T=25°C; gas mixture: 150 ppm of NO_x, 150 ppm of NH₃, 667 ppm of CO, 5 % CO₂, 10 % O₂, 50 ppm of HC and 2 % of water; Total flow= 31 cc.min⁻¹.



Figure 9. Time-evolution of NO_x in the gas phase over Ag@ZX-V during photo-assisted SCR-NH₃ reaction in the dark and under visible light at (A) RT and (B) $T = 150^{\circ}C$.



Figure 10. Time-Evolution of NH_4^+ ions (indicated by the black line, reporting band area integral intensity at approximately 1400 cm⁻¹) and NH_3 coordinated to Lewis acid sites overlapped with water (indicated by the red line, reporting band area integral intensity at approximately 1643 cm⁻¹) at (A) RT and (B) 150°C during photo-assisted SCR-NH₃ reaction over Ag@ZX-V catalyst. Integral values are expressed in cm⁻¹.



Scheme 1. The proposed photo-SCR reaction mechanisms at RT and $T = 150^{\circ}C$, over Ag@ZX-V catalyst.