

Operando-FTIR investigation of bifunctional Pt or Pd,Fe-HMOR catalyst for simultaneous abatement of NO_x and N₂O by CH₄

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Significance and Relevance

The simultaneous removal of NO_x and N₂O is performed by a bifunctional catalyst in which Pt or Pd metal particles located outside MOR channels abate NO_x and Feⁿ⁺ ions located at exchanging sites inside the MOR channels abate N₂O. The reductants/oxidants ratio in the reactant mixture, $CH_4/(NO+N_2O+O_2)$, affects the oxygen transfer processes at the active sites, determining their redox states. The formation of adsorbed NO_y species that can deactivate the catalyst occurs on oxidized sites. The formation of adsorbed NH₄⁺ species probes the Pt or Pd metal nanoparticles formation. The different interaction strength of cations with MOR exchanging sites, weak for Pt and Pd ions and strong for Fe ones, leads to active sites in different locations, aggregated noble-metal nanoparticles on external surface and Fe ions confined inside the channels, guaranteeing simultaneous and nearly independent pathways for the two abatements.

Introduction and Motivations

The primary objective of environmental catalysis is to create innovative processes that reduce atmospheric pollutant emissions from both mobile and stationary sources. Since noble metals are highly effective catalysts for NOx reduction using hydrocarbons¹, and iron-containing zeolites are widely utilized for N₂O decomposition or reduction in nitric acid production², we focused on bimetallic Pt,Fe-HMOR or Pd,Fe-HMOR zeolites. These catalysts showed potential for reducing simultaneously the NO_x and N₂O emissions in a single catalytic bed using CH₄ as the reductant (SCRsim). The synergistic interactions between the active metals was investigated by examining the surface intermediates formed during reactions with varying reactant mixtures.

Materials and Methods

Pt,Fe-HMOR and Pd,Fe-HMOR catalysts were prepared using a commercial HMOR (Si/Al=9.2, Tosoh Corp.) through a two-step procedure. This involved ion-exchange with aqueous solutions of noble metal salts, followed by wet impregnation with Fe(NO₃)₃ solution corresponding to 30% of Fe³⁺-exchange degree. Catalytic activity was evaluated under steady-state conditions using 100 mg of catalyst in a plug flow reactor connected to a flow system at atmospheric pressure, with gas-chromatographic (GC) gas-phase analyses. *Operando*-FTIR studies were carried out on a catalyst wafer (10 mg/cm²) placed in a stainless-steel IR reactor integrated into the flow apparatus. FTIR spectra were recorded during gas flow at temperatures up to 500 °C, concurrently with GC analysis of reactants and products. Characterization of both fresh and used catalysts was performed using AAS, XRD, FESEM-EDX, and *in situ* FTIR techniques to establish a relationship between their structural properties and catalytic performance.

Results and Discussion

The Pd²⁺ ions exchanged into HMOR exhibit an exchange degree of approximately 8%, which is lower than the nominal 23% but significantly higher than that of Pt²⁺, which is only 1.5%. This indicates a weak interaction between noble-metal cations and the zeolite exchange sites, with Pt²⁺ showing an even weaker interaction than Pd²⁺. FESEM analysis reveals that the noble-metal particles, roughly spherical, have a maximum diameter of 60 nm for monometallic Pt catalysts and 300 nm for monometallic Pd catalysts. In contrast, bimetallic catalysts exhibit smaller particles, with maximum sizes of 40 nm for Pt,Fe-HMOR and 200 nm for Pd,Fe-HMOR, suggesting that iron species inhibit sintering during thermal treatment.



Unlike Fe-HMOR, the bimetallic Pd,Fe-HMOR and Pt,Fe-HMOR catalysts are effective for the simultaneous reduction of NO and N₂O using CH₄ as the reducing agent in the presence of low O₂ concentration (2500 ppm), at temperatures \geq 450°C and \geq 400°C respectively, with nearly 100% CO₂ selectivity. N₂O reduction takes place on Fe²⁺ species, which form reactive Fe³⁺-oxo species. NO_x reduction occurs on Pt or Pd particles with a reduced surface that allows the homolytic cleavage of the N-O bond. The temperature at which this step occurs depends on the CH₄ concentration, as CH₄ must be sufficient to reduce the noble-metal oxide surface. The presence of O₂ in the reaction mixture inhibits the reduction of both N₂O and NO_x by maintaining the noble-metal particles in an oxidized state and promoting the formation of poisoning NO_y species, thereby shifting the light-off of SCRsim at higher temperature. Once O₂ is consumed during combustion, CH₄ reduces the noble-metal oxides, triggering the reduction reactions on the metal sites. At temperatures above the light-off, NH₄⁺ species are observed on both bimetallic catalysts, indicating the formation of reactive N, H, C, and O species yielding, besides the main products (N₂, CO₂, CO, and H₂O), NH₃ as by-products (Fig. 1). Ammonia acted as reductant, boosting the reduction of NO_x and N₂O, and in parallel migrates into the zeolite channels, forming NH₄⁺ species on Brønsted acid sites.

A comparison between Pt,Fe-HMOR and Pd,Fe-HMOR reveals distinct catalytic activities in SCRsim: Pt,Fe-HMOR shows higher efficiency for NO reduction, while Pd,Fe-HMOR is more effective for N₂O reduction. The superior NO abatement on Pt,Fe-HMOR is likely due to the easier reducibility of Pt species, reflected in a light-off temperature approximately 50 °C lower than that of Pd,Fe-HMOR. The superior N₂O reduction on Pd,Fe-HMOR may be attributed to the presence of Pd²⁺ and Pd⁺ species located within the MOR channels. These species form nitrosyls stable up to 500 °C, preventing the formation of poisoning nitrates close to Fe²⁺ active sites. This promotes N₂O reduction on iron active sites. In contrast, PtO_x species in Pt,Fe-HMOR are confined to the external surface.

Overall, the structural characteristics of MOR enable the stabilization of Pt (or Pd) and Fe species, creating a bifunctional catalyst. Noble-metal species on the external MOR surface facilitate NO reduction, while Fe^{2+} species within the channels specifically drive N₂O reduction.



Fig. 1 Operando FTIR spectra of surface species during SCRsim at increasing temperature, on catalysts as indicated. In the inset, the reactant conversions vs. T are reported. Reactant concentration: $[N_2O]=[NO]=[CH_4]=0.4\%$, $[O_2]=2\%$ (total flow rate=50 cm³_{STP}/min, He as balance).

References

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