

Structural Feature and Catalytic Performance of Cu Species Distributed over TiO₂ Nanotubes

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TiO₂, which is chemically stable but active in promoting catalytic effects, has been used as a support for metal oxide catalysts in many reactions including oxidation of CO and hydrocarbons and selective catalytic reduction (SCR) of NO because of the high activity of the supported species at relatively low temperatures. For a support, a large surface area is the essential feature to disperse the active species. In addition, the microstructure or morphology of the support framework or the method that the active species are introduced affect not only the dispersion but also the structure and chemical environment of the active species. In the present work, we intended to explore the possibility using titanate-derived TiO₂ nanotubes to improve the metal-oxide dispersion over TiO₂ and thus the activity of the resulting catalysts.

Titanate-based nanotube aggregates prepared from hydrothermal treatment on TiO₂ in alkali solutions have been shown to possess a large surface area. Upon mild calcination (< 400°C), the nanotubes exhibit a well-defined phase of the anatase TiO₂ while still retain the tubular structure. The titanate nanotubes are believed to form through scrolling the sheets peeled off from the titanate matter. This leads to a multilayer feature for the tube wall. By using this titanate-nanotube aggregate as a support, it is expected that the layered structure would provide sites for the intercalation of metal ions, thus to assist accommodation of the active species as well as to prevent agglomeration of the species in the subsequent calcination for phase transformation into anatase TiO₂. The highly dispersed metal oxide over a support is believed to be the active phase for heterogeneous catalysis. A high capacity and even distribution for ruthenium ions over this tubular titanate have been reported.

In our research, Copper oxide was deposited on tubular TiO₂ via Cu²⁺ introduction into a titanate nanotube aggregate followed by calcination. The titanate has a layered structure allowing Cu intercalation and can readily transform into anatase TiO₂ via calcination for condensation of the constituting layers. The activity of the tubular catalysts, with a Cu content of 2 wt.%, in selective NO reduction with NH₃ was compared with those of other 2 wt.% Cu/TiO₂ catalysts using TiO₂ nanoparticles (ST01 and UV100) as the support. The Cu species supported on the nanotubes showed a higher activity than those supported on the nanoparticles. The catalysts were designated as Cu/NT for Cu supported on the nanotubes and Cu/UV and Cu/ST for Cu supported on the UV100, and ST01 nanoparticles, respectively. After vacuum drying at 110°C for 12 h, the Cu-loaded nanotube specimen was also calcined at 400°C for 1 h to give the final catalyst (Cu/NT1; 2 wt.% in Cu).

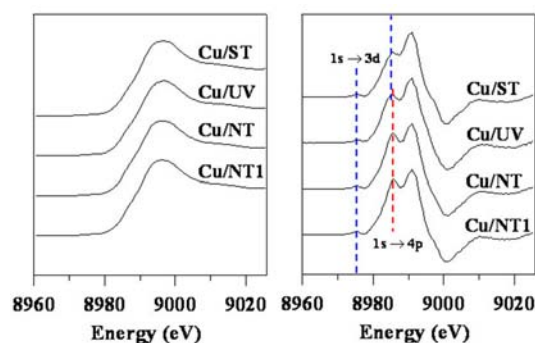


Figure 1. XANES spectra and their first derivatives of the Cu-loaded (2 wt.%) TiO₂ catalysts.

XANES analysis showed that the Cu species on all the TiO₂ supports are in the +2 state (Figure 1). EXAFS investigations of these catalysts reflected higher degrees of CuO dispersion and Cu²⁺ dissolution into the TiO₂ lattice for the tubular Cu/TiO₂ catalysts (Figure 2). Absence of CuO bulk detection by a temperature-programmed reduction analysis for the tubular catalysts confirmed the high CuO-dispersion feature of the tubular catalysts. The dissolution of Cu²⁺ to form a Cu_xTi_{1-x}O₂ type of solid solution was improved by using an in-situ ion-intercalation method for Cu deposition on the nanotubes. A fraction as high as 40% for Cu²⁺ dissolution was obtained for the tubular catalysts while only 20% for the particulate catalysts. The Cu_xTi_{1-x}O₂ species were considered one form of the active sites on the Cu/TiO₂ catalysts. This specific feature of the tubular titanate is its structural similarity with the TiO₂ anatase. Taking advantages of this feature and the layered structure, metal ion-loaded TiO₂ catalysts with high degrees of metal ion dispersion and solid solution formation, and thus a high activity, can be obtained.

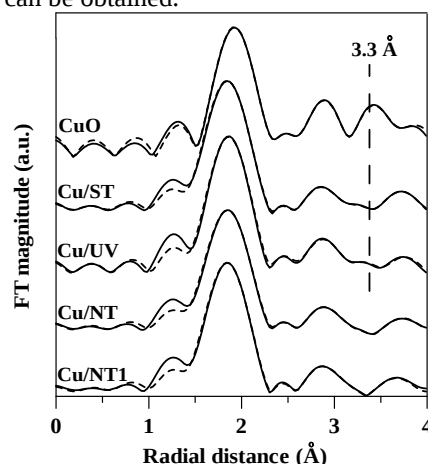


Figure 2. The Fourier transformed $k^3\chi(k)$ EXAFS of the reference CuO and Cu-loaded (2 wt.%) TiO₂ catalysts. The dash-line curves denote the best fitting of the EXAFS spectra.