Crystal-plane effects on the catalytic properties of TiO_2-based nanocrystals

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Introduction

TiO_2 is one of the most important metal oxides that have wide applications in the environmental catalysis. The building of various TiO_2 nanostructures has achieved great success due to the development of synthetic methods. The physiochemical properties of TiO_2 nanostructures are proved to be related with its surface structures. In the past few years, TiO_2 nanocrystals (TiO_2 NCs) with specific planes exposed have drawn great attention due to the new physicochemical properties. Through controllable chemical synthesis, some infrequent crystal planes of TiO_2 can be obtained. These infrequent planes may show higher surface energy and active surface reactivity compared to conventional thermodynamically stable planes.

Recently, our group has developed a new strategy to control the crystal planes of TiO_2 nanocrystals. Using these TiO_2 nanocrystals with specific planes exposed, we have investigated the crystal-plane effects on the catalytic properties of TiO_2-based nanocrystals.

Materials and Methods

TiO_2 nanocrystals are prepared through hydrothermal method. Au/TiO_2 catalysts are prepared by the deposition-precipitation method. Photocatalytic organic transformations are performed under UV light. The CO oxidation of Au/TiO_2 catalysts are performed in a flow microreactor.

Results and Discussion

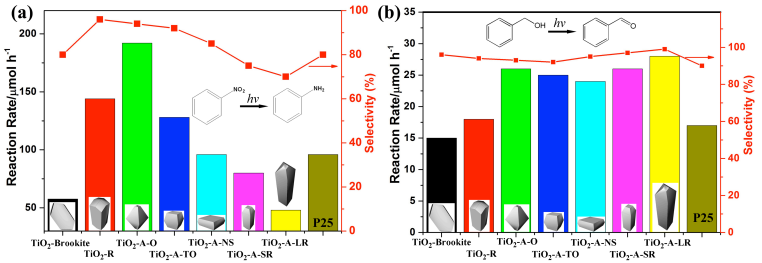

Figure 1. Photocatalytic performances of TiO_2 NCs with different crystal forms and crystal planes in (a) reduction of nitrobenzene to aniline and (b) oxidation of benzyl alcohol to benzaldehyde.

In the controllable synthesis of TiO_2 nanocrystals, $Ti(OH)_4$ was used as the precursor and different anions (including oxalates, lactates, fluorions, sulfates, and acetates) were used as capping agents without any other organic surfactants. These anions can selectively adsorb on the specific crystal planes of anatase, leading to the phase and facet control of TiO_2 nanocrystals. Photocatalytic selective reduction of nitrobenzene and selective oxidation of benzyl alcohol are employed as a probe reaction to test the redox properties of the as-prepared TiO_2 nanocrystals. The reduction ability of different anatase crystal planes can be ranked as {101} > {001} > {100}. While, the oxidation ability of different planes can be ranked as {101} ≈ {001} ≈ {100}. Surface and electronic structures should be the origin that account for their different activity orders in different reactions.

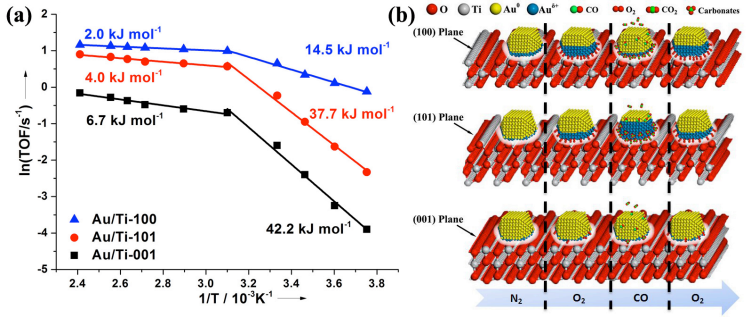

Figure 2. (a) Kinetic studies of CO oxidation reaction on Au/TiO_2 catalysts with different TiO_2 crystal planes. (b) Schematic illustration of dynamic changes of Au NPs in Au/Ti-100 (top), Au/Ti-101 (middle), and Au/Ti-001 (lower) in different atmospheres at 303 K.

Furthermore, we investigate the crystal-plane effects on the metal-oxide interactions. Au nanoparticles are loaded on TiO_2 nanocrystals with different crystal planes exposed ({100}, {101}, and {001} planes). Kinetic studies of CO oxidation (**Figure 2a**) show that the catalytic activities of three as prepared Au/TiO_2 samples follow this order: Au/TiO_2-{100} > Au/TiO_2-{101} > Au/TiO_2-{001}. Furthermore, different mechanisms exist at low temperatures (<320 K) and high temperatures (>320 K). With the help of ex-situ XPS and in situ DRIFTS, the interactions between substrate molecules and different Au/TiO_2 interfaces are investigated. We find that the activation of O_2, as well as the formation and desorption of carbonates are greatly dependent on the crystal planes of the TiO_2 support. A schematic illustration of the dynamic changes of Au NPs in Au/Ti-100, Au/Ti-101, and Au/Ti-001 in different atmospheres at 303 K is presented in **Figure 2b**.

Significance

Surface structures and electronic structures of different anatase TiO_2 nanocrystals should be the origins accounting for their discrepancies in catalytic performance. To some extent, when we try to correlate the photoactivity of TiO_2 nanocrystals with their morphologies, we should only discuss their relationship on specific reactions. For Au/TiO_2 catalysts, different surface structures of different TiO_2 crystal planes will affect the interaction between the Au/TiO_2 interfaces and the substrate molecules (CO and O_2), resulting their different catalytic properties.

References

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2. L. Liu, X. Gu, Z. Ji, W. Zou, C. Tang, F. Gao and L. Dong, *J. Phys. Chem C*, 2013, 117, 18578-18587.