

CO oxidation by Ti and Al doped ZnO: the heteroatom activation of adsorbed oxygen

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Introduction

It is desirable to have a selective catalyst that can operate at relatively low temperatures for extended periods of time. An approach that is being explored to improve the catalytic properties of oxide surfaces involves doping the oxide such that one of the cations is partially replaced by a cation dopant. Numerous experimental studies performed on doped oxides suggest that doping is a strategy for improving the catalytic properties.^{1,2} The strategy is demonstrated for Ti and Al dopants into the inert ZnO host to activate two reaction pathways for CO oxidation which are both different from the traditional Mars-van-Krevelen (MVK) mechanism. In the MVK mechanism the metal oxide surface supplies oxygen atoms to the reductant through formation of a surface oxygen vacancy. In contrast, doped ZnO promotes the adsorption and activation of dioxygen on the dopant sites for reaction with CO. Further, surface dopant sites that do not coordinate gas phase dioxygen may themselves give rise to a dopant induced oxygen shuttle by which a surface oxygen vacancy is created from next-nearest neighbor sites through the energetically favorable O transfer to the dopant. The proposed mechanisms are supported by density functional theory calculations and by experiments involving isotopically labeled molecular oxygen.

Materials and Methods

The $M_xZn_{1-x}O_8$ ($M=Al, Ti$) powder catalysts were prepared by sol-gel method, and then calcined to 1000 °C for 4 hours. The powder sample morphology was characterized by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) with energy dispersive X-ray spectroscopy (EDS) attached, BET analysis and X-Ray Diffraction with Rietveld refinement. The activity of the metal oxide catalysts was measured in a packed bed reactor (PBR) with a differentially pumped mass spectrometer connected at the reactor outlet into through a controlled leak, where temperature programmed reaction and partial pressure programmed reaction were conducted. The reactions with isotopically labeled oxygen, $^{18}O_2$, were performed by pre-treating the catalyst to remove all adsorbed $^{16}O_2$, the $^{18}O_2$ was introduced in pulses using a two-position microelectric valve (VICI).

Results and Discussion

On the Al doped ZnO, a uniform phase containing Al was observed without any observable phase separation by HRTEM. The XRD data together with Rietveld refinement indicated that the lattice distortion due to Al substitution was sufficient to quantitatively determine the atomic fraction of Al in the ZnO lattice.

New CO oxidation pathway is proposed and demonstrated, which is different from the traditional MVK mechanism. During temperature programmed reaction, cation

substitutional doping of ZnO with Ti or Al promotes adsorption of O_2 on the dopant. The reaction with isotopically labeled oxygen, $^{18}O_2$, shows the products of $C^{16}O^{16}O$, $C^{18}O^{16}O$ and a small portion of $C^{18}O^{18}O$. We speculate when a dopant replaces a Zn atom at the surface of ZnO, the dopant site enhances O_2 adsorption satisfy its valence. The adsorbed $^{18}O_2$ molecule will react readily with a reductant (CO), producing $C^{18}O^{16}O$. With a roughly equal rate, the MVK pathway is induced around doped site,³ where surface oxygen atom reacts with CO to make a $C^{16}O^{16}O$ molecule.

Significance

The work suggests a new approach to design new catalyst for hydrocarbon conversion by designing specific reactive centers at oxide surfaces.

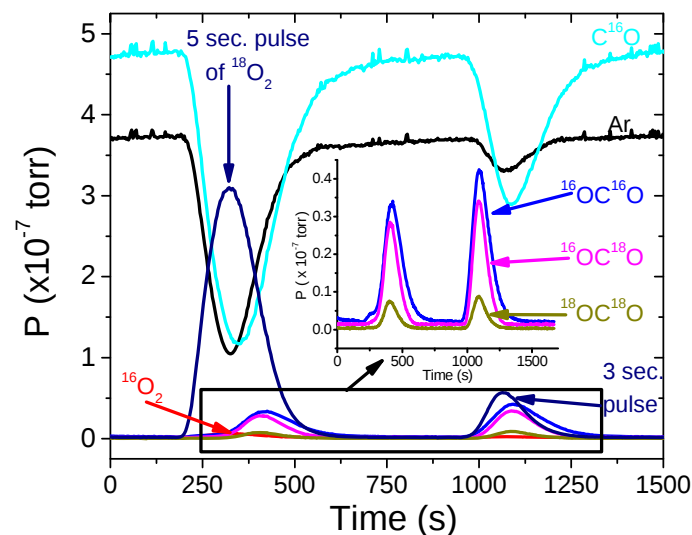


Figure 1. Isotopic labeling of CO oxidation products with $^{18}O_2$ over Ti-doped ZnO at 375°C. The products analyzed following a 3–5 second pulse of $^{18}O_2$ into a reactant stream consisting of CO and Ar. After the pulse of $^{18}O_2$, no $^{16}O_2$ signal was observed, the products $^{16}CO^{16}O$, $^{16}CO^{18}O$ and $^{18}CO^{18}O$ were tracked.

References

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