

Development of Diesel Oxidation Catalyst for Low Temperature Aromatic Oxidation

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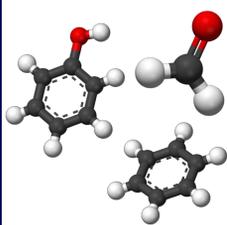
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Abstract

Volatile organic compounds (VOCs) has been known to be one of the major contributors to air pollution. High amount of VOCs would be emitted from automobile engines during cold start. Catalytic oxidation is a promising way to remove due to concerning for energy savings, operating cost. Platinum group metals (PGMs) are widely employed as an active component for the catalytic oxidation of VOCs due to good oxidation capability, while it is very expensive. Since transition metal oxides have also been known to be good oxidation catalysts, they may be rival to PGM based catalysts for VOC removal. In this work, we reports the cerium zirconium mixed oxides (CZ) containing benzene oxidation catalyst. In addition, the evidence of active sites and reaction mechanism will be presented.

Introduction



Secondary fine dust



harm to human

Volatile organic compounds (VOCs) are harmful itself to human body and possible cause of particulate matter. Numerous technology has been developed to remove VOCs. The catalytic oxidation is the promising way but need cost-efficient catalyst development.

VOCs Removal Technology

Technology	Feature	Limitation
Thermal incineration	- Highly removal efficiency (95~99%)	- High temperature operation 800~1200) - High utility cost - Poorly controlled process
Adsorption	- Slow initial adsorption rate	- Periodic Ads.-Des. operation - Only highly diluted VOCs
Biochemical	- Highly selective, eco-friendly	- Concentration sensitive
Catalytic oxidation	- Energy-efficient - Low concentration VOC removal	- Catalyst cost (ex. noble metal) - Deactivation

Catalyst preparation

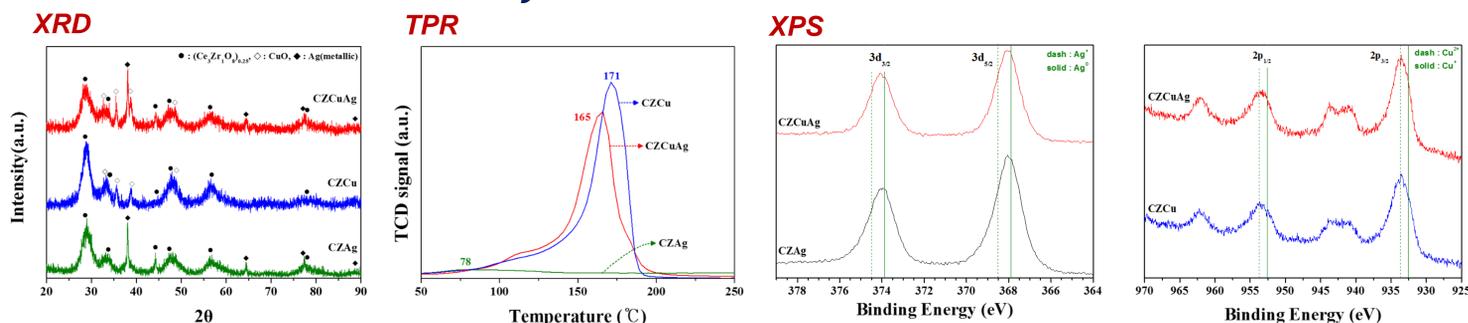
Aqueous precursor solution
(Ce, Zr, Cu, Ag nitrate)

co-precipitation
(pH= 10 by 1 M NaOH)

stirr at RT for 16 h
aging at 80 °C, for 2 h
Calcine ar 400 °C, for 4 h

CZCuAg catalyst

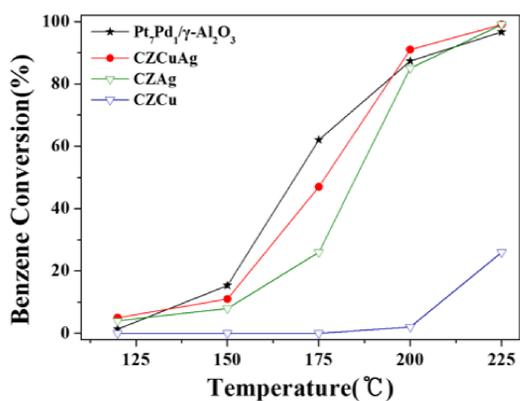
Catalyst characterization: Active structure



The presence of CuO and metallic Ag are confirmed by XRD. Two components exist as separate phases. The reducibility of CuO in CZCuAg is higher than CuO in CZCu. Ag might help the reduction of Cu by promote H₂ splitting.

XPS show higher amounts of metallic Ag in the CZCuAg than CZCuAg and higher amounts of Cu⁺ in the CZCuAg than CZCu. This shows the possible electron transfer from Cu to Ag. The metallic Ag formation may play an important role in benzene oxidation.

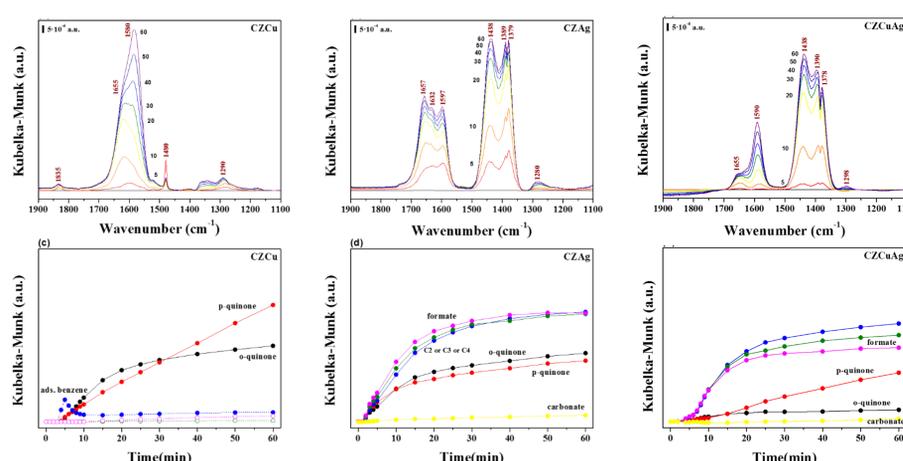
Catalyst Activity



Reaction condition
GHSV (h⁻¹): 100,000
Feed: 150 ppm benzene in air

CZCuAg showed a comparable activity to PtPd based catalyst. Both Ag and Cu play a pivotal role in enhancing benzene oxidation activity.

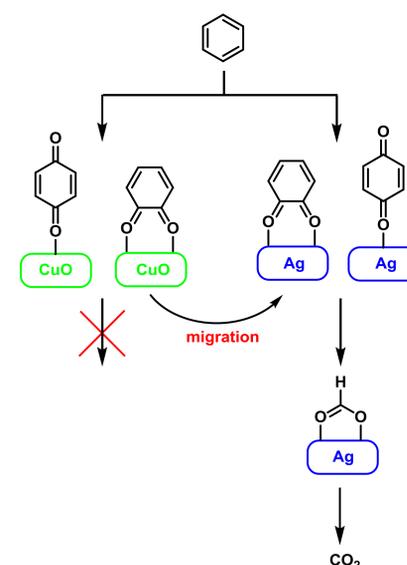
DRIFT study: Reaction pathway



The spectra were collected at 30 °C under the flow of 150 ppm benzene.

The quinone species are mainly observed on the Cu surface and the formate is the major adsorbent on the Ag surface. The formate coverage are higher over CZCuAg than CzAg. The Cu oxidizes benzene to quinones but it cannot further oxidize. Ag can convert quinones to formate and carbonate.

Proposed mechanism



Conclusion

Copper-silver supported on cerium-zirconium mixed oxide (CZCuAg) catalyst for benzene oxidation was developed. The catalyst showed comparable activity to PtPd/Al₂O₃ which is the current state-of-the art catalyst. The XRD analysis revealed that Cu and Ag present separately. The XPS, TPR supported the metallic silver and Cu⁺ are the main species and possible active species in the benzene oxidation. The DRIFT experiments confirmed that the Cu mainly act as benzene adsorption and oxidation to quinonea, and Ag break the C-C bond of quinones to form formate. This dual site mechanism and high surface quinone concentration confirm the migration of quinones from Cu to Ag surface is likely the rate determining step..