Uniform $SiO_2@CeO_2$ core-shell structures doped with CuO and Co_3O_4 as efficient catalysts for toluene combustion

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Significance and Relevance

Finding optimal catalysts for the total oxidation of volatile organic compounds (VOCs) is currently a significant challenge due to an increasing level of air pollution and threats related to the VOCs emission. Oxide systems can be successfully used in this process but they have to be optimally designed in terms of composition and distribution of both active phase and support. The presented work shows the potential of materials based on the synergy between the CuO, Co_3O_4 and CeO_2 phases arranged in one catalytic bed working in the toluene combustion.

Preferred and 2nd choice for the topic: Air cleaning and combustion, Automotive and stationary emission control (2nd choice)
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

One of the most important challenges for environmental sustainability is to reduce the emission of harmful VOCs into the atmosphere. In light of the constantly tightening regulations, many technologies for effective removal of VOCs have been developed, including catalytic total oxidation over materials containing noble metals (e.g. Pt, Pd, Au, Ag) and transition metal oxides (e.g. CuO, MnO_2, Fe_2O_3, Co_3O_4). The transition metal oxide catalysts, despite their lower activity compared to noble metals, are much cheaper and more resistant to poisoning.[1] On the other hand, their lower catalytic activity can be partially compensated by a proper design of active phase support. For example, cerium(IV) oxide can be effectively used in this role. CeO_2 has attractive properties due to a large number of oxygen defects that favor an extraordinary capacity for storing and releasing oxygen. Furthermore, CeO_2 provides enhanced thermal stability and high dispersion of the active phase. Although ceria can act as a single-component catalyst in the VOCs combustion, its activity can be significantly improved by an introduction of transition metal oxides. In such a case, a synergistic effect appears due to the formation of redox pairs Ce^{4+}/Ce^{3+} and $Me^{n+}/Me^{(n-1)+}$ leading to enhanced oxygen mobility. In the presented work, CuO/CeO_2 and Co_3O_4/CeO_2 oxide systems were deposited on nanometric, non-porous SiO_2 spheres to form novel core-shell $SiO_2@CeO_2/MeO_x$ (Me = Cu or Co) catalysts. Such a catalyst grain design allowed for better exposure of the active components of the material to the reaction mixture.[2] The catalytic performance of individual and variously mixed systems in the combustion of toluene, as a representative of aromatic VOCs, was discussed.

Materials and Methods

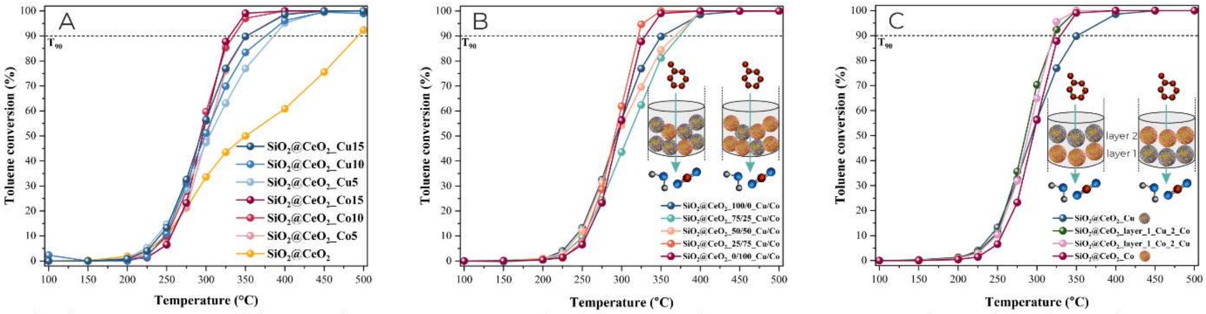
SiO_2 spheres were prepared using the Stöber strategy. To facilitate the deposition of a precursor of another oxide phase on the SiO_2 surface, it was initially modified by anchoring an aminosilane coupling agent, i.e. 3-aminopropyltriethoxysilane (APTES). A core-shell $SiO_2@CeO_2$ support structure was synthesized by precipitation of a CeO_2 precursor on the surface of a spherical silica scaffold at constant pH. Finally, the formed $SiO_2@CeO_2$ support was modified with transition metal oxide precursors using the wet impregnation method to obtain the Co or Cu content of 5, 10, and 15 wt.% in the final catalysts.

Extensive physicochemical characterization was performed for the synthesized catalysts in terms of their morphology (SEM-EDS), surface and bulk composition (XPS and XRF), textural parameters (N_2 adsorption), structure (XRD), chemical environment (UV-Vis-DR), and reducibility (H_2-TPR). Most importantly, the catalytic performance of the developed materials in the combustion of toluene was studied.

Results and Discussion

The SEM images of the $SiO_2@CeO_2$ support revealed the homogeneous distribution of the CeO_2 phase, allowing the formation of the uniform shell while minimizing the presence of small bulk CeO_2 aggregates in interparticle voids. Conversely, the materials after Co and Cu oxide deposition showed slight particle aggregation due to the formation of clusters of active phase species on the support surfaces. However, a consistent spherical shape with a smooth surface was maintained. The deposition of CeO_2 significantly altered mesoporosity of the material. Nevertheless, the subsequent introduction of the active phase affected porosity due to its penetration into the pores formed by the CeO_2 washcoat. The formation of CeO_2, CuO, and Co_3O_4 phases for both the support and the catalysts was confirmed by XRD measurements. The UV-Vis-DR spectrum of the support revealed an absorption band associated with electron transitions in CeO_2. The Co-containing catalysts exhibited two additional wide bands, indicating the presence of Co_3O_4 phase. Furthermore, all copper catalysts displayed a low intense band below 300 nm attributed to the charge transfer $O^{2-} \longrightarrow Cu^{2+}$, validating the existence of small crystalline CuO particles.

The critical aspect of the study was evaluating the activity of the obtained $SiO_2@CeO_2/MeO_x$ core-shell materials in total oxidation of toluene (Figure 1). It was proven that the introduction of CuO significantly lowers the initial temperature of the toluene conversion, while Co_3O_4 promotes superior catalytic performance at higher temperatures. Various arrangements of the bicomponent catalytic bed (containing both $SiO_2@CeO_2/CuO$ and $SiO_2@CeO_2/Co_3O_4$ materials) were tested to ensure operation over a wide range of temperatures. The catalyst composition was mixed in two ways: (i) the Cu and Co-containing catalysts were homogenously mixed at various ratios, or (ii) the catalysts were arranged in layers.



single Cu or Co-containing catalysts

mixed Cu-Co catalysts

layered Cu-Co catalysts

Figure 1. Catalytic activity in the toluene combustion of (A) single Co and Cu-containing, as well as (B) mixed Co-Cu and (C) layered Co-Cu catalysts.

The catalytic results confirm that the catalyst composition, including metal molar ratios, significantly influence the activity in the toluene combustion. The co-performance of the catalysts containing CuO and Co_3O_4 phases exhibits interesting correlations at their direct contact and separation. Furthermore, the stability tests of the developed catalysts in the toluene combustion were carried out at a specific temperature. The catalytic performance was tested alternatively in dry (1000 ppm of toluene in 100 ml/min of air) or wet atmosphere (1000 ppm of toluene in 100 ml/min of air saturated with 10 % vol. of H_2O). The developed systems demonstrated high stability, maintaining a high level of toluene conversion during 24 h measurements.

References

1. Y. Guo, M. Wen, G. Li, T. An, *Applied Catalysis B: Environmental* **2021**, *281*, 119447.
2. A. Rokicińska, P. Łątka, B. Olszański, M. Żurowska, M. Dębosz, M. Michalik, P. Kuśtrowski, *Chemical Engineering Journal* **2024**, *480*, 148173.

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