Catalytic behaviour of CuO and Co_3O_4 phases deposited on hollow @SiO_2 and @TiO_2 structures in toluene combustion

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Significance and Relevance

Understanding the real role of interactions between typical components of a supported catalyst of volatile organic compounds (VOCs) combustion was possible by excluding additional parameters that could affect the catalytic behavior of the system (i.e. porosity, morphology and particle size of the support) due to the use of core-shell structures with controlled design. Special attention was paid to the study of the catalytic behavior of CuO and Co_3O_4 phases deposited on @SiO_2 and @TiO_2 spherical supports in 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

VOCs are environmental pollutants recognized as substances causing photochemical smog, as well as carcinogenic and/or mutagenic effects in humans. Therefore, limiting the amount of VOCs released into the atmosphere is crucial for the protection of the environment and human health. A very promising method of controlling VOCs emissions is their catalytic combustion, but it requires the development of appropriately effective catalysts.[1] Particularly important in this context is a deeper understanding of the role of interactions between an active phase and a support, which can lead to improved catalytic properties in this reaction.[2] The dispersion and type of the active phase, as well as physicochemical properties of the support must be selected appropriately when designing catalysts, including novel core-shell materials. The advantage of the latter materials is not only the unique properties related to their nanometric structures, but also the arrangement of the individual components of the system that provides a well-controlled contact between the core and the shell.[1,3] The presented work focuses on the analysis of the catalytic behaviour of CuO and Co_3O_4 phase particles deposited on spherical @SiO_2 and @TiO_2 supports in the catalytic combustion of toluene. The use of supports with comparable particle size, morphology and porosity allowed to minimize the influence of diffusion effects and to expose the real role of the components of the studied systems and their interactions in the catalytic process.

Materials and Methods

The polymer templating method was used for the synthesis of the @SiO_2 and @TiO_2 supports. Oxide phase precursors were deposited on the surface of spherical particles of polystyrene or resorcinol-formaldehyde resin, respectively. Subsequently, the polymer@oxide composites were modified with Cu^{2+} or Co^{2+} cations using wet impregnation. The amounts of the introduced components were chosen to obtain 5, 10 and 15 wt.% of CuO or Co_3O_4 in the final catalyst. The synthesized materials after removal of the polymer core by high temperature calcination were examined using XRD, XRF, UV-Vis-DR, XPS, SEM/EDX, DRIFT and H_2-TPR. Moreover, their catalytic activity in the total oxidation of toluene was tested.

Results and Discussion

The TiO_2 and SiO_2 supports of similar morphology and porosity were synthesized in order to exclude the influence of these parameters on the catalytic activity of CuO and Co_3O_4 phases in the total oxidation of toluene. The supports of uniform spherical shape with comparable BET surface area of 38 m^2/g and 29 m^2/g for @SiO_2 and @TiO_2, respectively, were obtained. Analysis of XRD patterns for these materials confirmed the presence of amorphous SiO_2 phase and TiO_2 in the anatase form. In the next step, the active phase was introduced by wet impregnation by depositing 5, 10 and 15% by mass of the appropriate oxide, respectively. XRD measurements for the catalysts containing Cu showed the formation of the CuO phase. In the case of the Co-containing materials, the Co_3O_4 phase was obtained only for the @SiO_2 support, while for the @TiO_2_Co catalysts, the $CoTiO_3$ phase additionally appeared beside the spinel phase. Similar observations were made based on the results of UV-Vis-DR measurements.

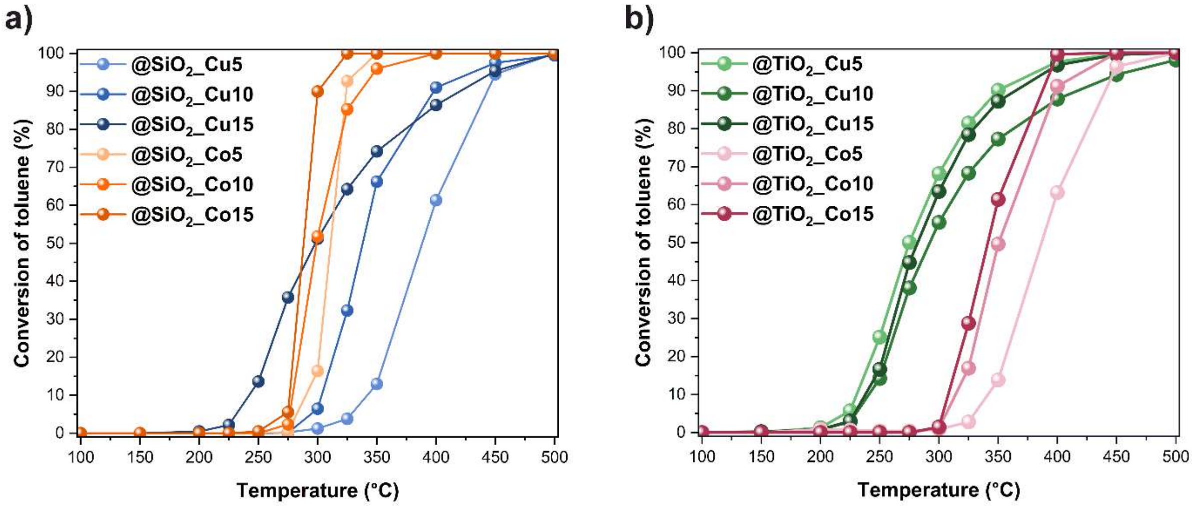

Figure 1. Catalytic activity of (a) @SiO_2- and (b) @TiO_2-based catalysts in total oxidation of toluene.

The synthesized materials were characterized by high catalytic activity in the process of total oxidation of toluene. Depending on the active phase - support system used, the catalytic properties of the studied materials change. The best activity was achieved over the @TiO_2_Cu and @SiO_2_Co catalysts. A stronger interaction of the cobalt oxide precursor with the @TiO_2 support resulted in the formation of the surface $CoTiO_3$ phase, which is more resistant to reduction than Co_3O_4. In turn, separate particles of Co_3O_4 phase were formed on the @SiO_2 support, which more easily participates in the reaction according to the Mars–van Krevelen mechanism. Additionally, it was observed that the presence of copper causes the catalysts to be active already at low reaction temperatures, achieving complete conversion at much higher temperatures than those containing cobalt. In the latter case, there is a small temperature difference from the onset temperature to the achievement of complete toluene conversion. It was found that the formation of the $CoTiO_3$ phase does not have a positive effect on the catalytic activity, causing deactivation of the catalyst in the tested process. On the other hand, the different dispersion of the CuO phase on the SiO_2 support also has an adverse effect on the catalytic performance.

References

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