Selective reduction of NO with CO and naphthalene in the presence of oxygen on a core-shell $CeO_2@TiO_2$ supported copper-potassium-based catalyst

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Abstract: The selective reduction of NO with CO and naphthalene was investigated using a core-shell $CeO_2@TiO_2$ support impregnated with copper and potassium. The selective character of the reaction was due to the presence of oxygen, which induces the unwanted oxidation of CO and/or naphthalene. The latter constitutes a challenge in the reduction of NO because most of combustion processes occur in oxidizing atmospheres. The underway work shows that both $Cu/SmCeO_2@TiO_2$ and $K/Cu/SmCeO_2@TiO_2$ catalysts are able to achieve full conversion of NO at temperatures higher than 225°C and 325°C, respectively.

Keywords: core-shell, copper, NO selective reduction.

1. Introduction

Combustion processes are linked to the generation of a series of harmful pollutants. Among them, nitrogen oxides, NO_x, are partly responsible for the formation of acid rain, fine particles, and ground level ozone, which have a direct impact in human health especially in densely populated cities. Among several approaches to deal with the elimination of these pollutants, the selective reduction of NO points to the use of other molecules present in the gaseous mixture that have the ability to act as reducing agents. In terms of a catalyst usage, the selective abatement of NO with a reducing agent in the presence of oxygen is a challenge because the reducing agent tends to be oxidized instead of reacting with NO. The present study uses a combination of oxides for the elimination of NO in the presence of oxygen and using CO and naphthalene as reducing agents. Naphthalene is added as a representative of usually found volatile organic compounds (VOCs) in combustion effluents. Since copper is known for having oxidizing properties, it was selected for this study. On the other hand alkali metals are naturally present in biomass and it is expected that they will accumulate in time on the surface of the catalysts. Thus, potassium was selected as a component of the final catalyst. Preliminary results are here presented as a part of an underway study involving a variety of characterization techniques.

2. Experimental

A reverse micelle method was used to prepare the $CeO_2@TiO_2$ core-shell support, with the core being TiO_2 nanoparticles (~25nm) and the shell corresponding to Sm-stabilized CeO_2 (nominal thickness: 2.7 nm). Then the active phases, Cu and K, were added by wet impregnation of solutions containing the respective precursors. Both copper and alkali metal supported on CeO_2 and TiO_2 phases have shown before to be active in the oxidation/adsorption of NO [1,2]. The final catalyst was calcined at 500°C for 3 hours in a muffle furnace. The activity of the catalysts was determined in a 1 cm I.D. plug-flow quartz reactor prior reduction at 500°C for 1 hour in a flow of 10 cc/min of $5\%H_2/Ar$. The gaseous mixture consisted of 1%CO, 500 ppm NO, 10% O_2, 1% Naphthalene, balanced in He, flowing at 50 cc/min. The effluent was directed to an infrared spectrometer (IRPrestige-21, Shimadzu) equipped with a gas cell of 2.4 m equivalent path-length (Pike). A chromatograph (Series 580, Gow-Mac) equipped with a 60/80 molecular sieve 5A (Supelco) was also used. A set of characterization techniques such as operando infrared spectroscopy and Raman spectroscopy, BET surface area measurements, temperature programmed reduction with hydrogen, X-ray diffraction, among others, are currently under way to elucidate the different surface phenomena occurring on these catalysts.

3. Results and discussion

Activity results on the selective reduction of NO with CO and naphthalene are shown in Figure 1 in the 150-350°C range. Both Cu/SmCeO_2@TiO_2 and K/Cu/SmCeO_2@TiO_2 catalysts show full conversion of NO and naphthalene at low temperature, which rather corresponds to physical adsorption on the catalyst surface. Upon increasing the temperature above 200°C, the reaction of all pollutants was observed. Figure 1A shows that the Cu/SmCeO_2@TiO_2 catalysts has a high activity on the conversion of NO, CO, and naphthalene, whereas lower activities are obtained with the K/Cu/SmCeO_2@TiO_2 catalyst (Figure 1B). Regardless the high activity of the Cu/SmCeO_2@TiO_2 catalyst, a fraction of the NO_2 is detected (~20 ppm) in the outlet of the reactor, whereas the K/Cu/SmCeO_2@TiO_2 catalyst did not show any NO_2 on the gaseous outlet. The conversion of NO reached 100% conversion at 225°C and 325°C on the Cu/SmCeO_2@TiO_2 and K/Cu/SmCeO_2@TiO_2 catalysts, respectively. Similarly, the full conversion of CO occurred at 236°C on the Cu/SmCeO_2@TiO_2 catalyst, whereas the same CO conversion was reached at 298°C for the K/Cu/SmCeO_2@TiO_2 catalyst. In the case of the conversion of naphthalene, full conversion was achieved with the Cu/SmCeO_2@TiO_2 catalyst at 250°C, but only a maximum of 66% at 350°C for the K/Cu/SmCeO_2@TiO_2 catalyst. The preliminary results suggest that the inclusion of potassium alters the electronic environment of surface oxygen atoms, which in turn, affects the redox cycles of actives copper species, which is expected with potassium being an electropositive atom. Temperature programmed reduction (H_2-TPR) experiments on the catalysts (not shown) evidence a strong higher-temperatures shift on the reduction profiles for the potassium-containing catalyst, which is consistent with a higher interaction of surface oxygen atoms with the copper phase, and thus, with the latter being more difficult to reduce.

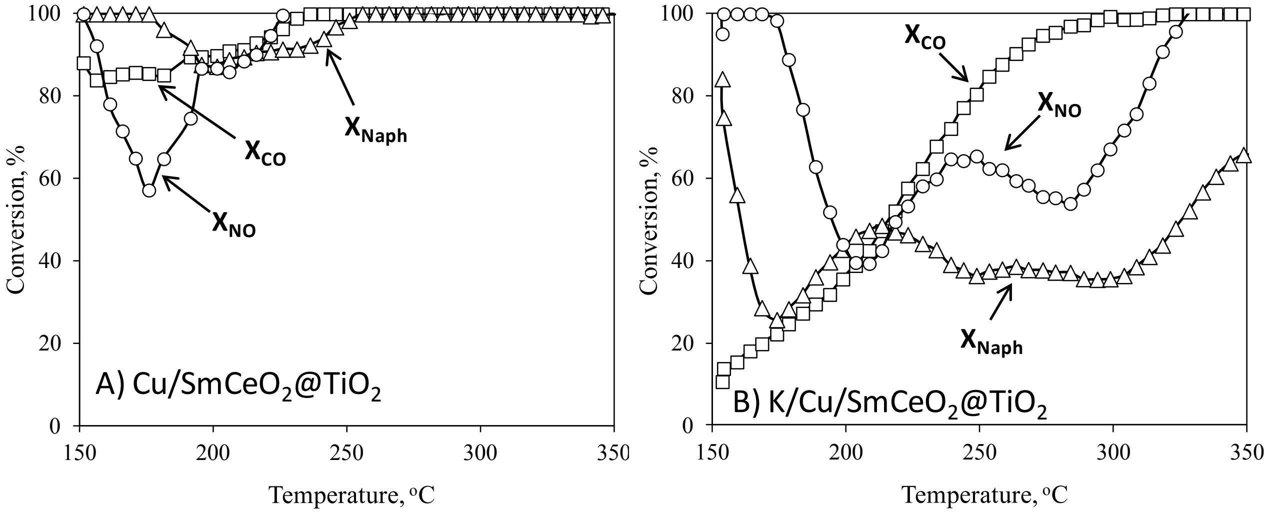

Figure 1. Selective reduction of NO with CO on (A) Cu/SmCeO_2@TiO_2 and (B) K/Cu/SmCeO_2@TiO_2 catalysts. Gas mixture: 1%CO, 500 ppm NO, 10%O_2, 1% Naphtalene, balanced He. Flow: 50 cc/min.

4. Conclusions

The selective reduction of nitric oxide with CO and naphthalene, in the presence of oxygen, was studied. Both Cu/SmCeO_2@TiO_2 and K/Cu/SmCeO_2@TiO_2 catalysts are active in the reduction of NO. The inclusion of potassium leads to a decrease in the conversion of all pollutants, but no generation of NO_2 in the outlet of the reactor. Full conversion of NO at 225°C and 325°C was achieved for the Cu/SmCeO_2@TiO_2 and K/Cu/SmCeO_2@TiO_2 catalysts, respectively. These preliminary results are promising for an active catalyst being able to reduce common contaminant produced during the combustion of biomass.

References

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