Short communication

Highly active copper-based Ce@TiO$_2$ core-shell catalysts for the selective reduction of nitric oxide with carbon monoxide in the presence of oxygen

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ABSTRACT

A novel core-shell K/Cu/SmCe@TiO$_2$ catalyst is here reported being highly active on the selective reduction of nitric oxide with carbon monoxide under oxidizing conditions. It was found that the reaction proceeds with the generation of nitrates and nitrites adsorbed on the support and ionic nitrates adsorbed on alkaline sites. Full conversion of CO was achieved from 255 °C and 97% NO conversion was reached at 330 °C.

1. Introduction

The increasing regulations on the emission of pollutants and the high prices of noble metals impose new challenges in terms of finding low cost formulations of catalysts capable of reducing gaseous contaminants. From a practical point of view, the selective reduction of NO with CO is an interesting alternative of transforming both pollutants into inert compounds. Both components are usually present in the combustion gases, CO acts as the reducing agent to react with NO, and the whole reaction occurs under an oxidizing atmosphere.

The literature reports several noble metals studied in the selective reduction of NO with CO [1], with the most active catalyst being based on iridium [2]. On the other hand, given the increasing prices of noble metals and the uncertainties on their future availability, great efforts are currently been put in finding alternative catalytic systems active in this reaction and containing no noble metals. However, most transition metals poorly behave in this reaction and generally the reducing agent, CO, is fully converted into CO$_2$. The latter occurs due to the oxidizing conditions in which this reaction takes place. Thus, the challenge is to be able to selectively occupy the reductant, CO, to reduce the nitric oxide instead of being directly oxidized into CO$_2$. In previous works, we have shown that copper based catalysts are able to either store-and-reduce NO or oxidize CO [3,4]. The present study applies a novel

potassium-copper-based Ce@TiO$_2$ core-shell catalyst to the reduction of NO with CO under a highly oxidizing atmosphere.

2. Experimental

A reverse micelle method was used to prepare the Ce@TiO$_2$ core-shell support, with the core being TiO$_2$ nanoparticles and the shell corresponding to CeO$_2$ (nominal thickness: 2 nm). A mixture of a commercial surfactant (Tomadol 91-6, Air Products) and n-amyl alcohol (Merck), 62 wt% and 38 wt%, respectively was added to 56 ml isooctane and 80 ml distilled water under stirring and at room temperature, obtaining a clear and stable solution. The added water contained dissolved cerium (III) nitrate hexahydrate and Samarium (III) nitrate hexahydrate (Sigma Aldrich). The latter compound was added to increase the thermal stability of the final support. The as-received TiO$_2$ nanoparticles (Sigma Aldrich) were added to the previous microemulsion. A second microemulsion was prepared containing only the surfactant, n-amyl alcohol, isooctane and water, with the latter diluting 6.5 ml of NH$_3$ (25%, Merck). This latter solution was dropwise added to the first microemulsion under strong stirring. The resulting precipitate was subjected to solvent extraction using hexane in a Gregar extractor for 6 h. The obtained SmCe@TiO$_2$ support was then dried and calcined at 500 °C for 3 h. Then the active phases were added by wet

impregnation of solutions containing the respective copper and sodium precursors (metal loading: 2.5 wt% Cu and 5 wt% K). The final catalyst is hereafter referred as K/Cu/SmCe@TiO$_2$. A reference sample prepared by simple wet impregnation is denoted as K/Cu/SmCe/TiO$_2$ (same loadings as before). The final catalysts were calcined at 500 °C for 3 h in a muffle furnace. The activity of the catalysts (0.42 g) was determined in a 1 cm I.D. plug-flow quartz reactor prior reduction at 500 °C for 1 h in a flow of 10 cm^3/min of a mixture of 5% H$_2$ balanced in Ar. The gaseous mixture consisted of 1% CO, 500 ppm NO, 10% O$_2$, balanced in He, flowing at 50 cm^3/min (GHSV = 10,000 h^{-1}). The outlet gases from the reactor were analyzed by an infrared spectrometer (Shimadzu, IRPrestige21) equipped with a 2.4 m Pike gas cell. A chromatograph (Series 580, Gow-Mac) equipped with a 60/80 molecular sieve 5A (Supelco) was also used.

Samples of each catalyst were additionally studied by temperature programmed reduction (TPR) experiments in a 5% H$_2$/Ar stream using a 10 °C/min ramp. In these experiments, 0.1 g of catalyst were loaded into the reactor and oxidized in situ in a 20 cm^3/min stream of pure O$_2$ at 500 °C for 1 h. The crystal structure of the different catalysts was determined by X-ray diffraction on a Siemens D-5000 diffractometer using Cu Kα radiation at a scan rate of 0.02 degrees per minute. The surface area (BET) and pore size distribution of the various prepared samples were obtained from N$_2$ adsorption isotherms using a Micromeritics 2010 adsorption apparatus.

3. Results and discussion

3.1. Activity on the selective reduction of NO with CO

One of the difficulties of reducing nitric oxide with CO is the presence of oxygen in the reaction stream, because oxygen tends to preferentially react with CO to produce CO$_2$. Thus, the challenge for the catalyst in an oxidizing environment is to have a high selectivity of using CO in the reduction of NO, instead of being directly oxidized to CO$_2$.

Fig. 1 shows that the K/Cu/SmCe@TiO$_2$ catalyst achieves full CO conversion at 255 °C and it maintains the same activity at higher temperatures. On the other hand, NO conversion reaches 97% around 330 °C. In the low temperature range (below 250 °C), NO conversion seems high but this behavior rather corresponds to physical NO adsorption with the surface of the catalyst forming nitrates and nitrites [5,6]. As the temperature increases, these species desorb and the NO adsorption effect is lower, which is reflected on a lower conversion of NO (or rather storage of NO). Above 270 °C, the NO reduction reaction proceeds. In the case of the reference K/Cu/SmCe/TiO$_2$ catalyst (dashed line), prepared by impregnation, both NO and CO conversion are lower. If potassium is not present in the catalysts, Fig. S1A, the Cu/
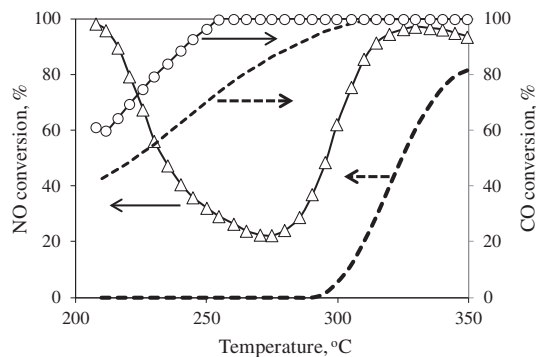

Fig. 1. Activity on the selective reduction of NO with CO for the K/Cu/SmCe@TiO$_2$ catalyst. As a reference, the activity of a K/Cu/SmCe/TiO$_2$ catalyst prepared by wet impregnation is also included in (A) (dashed line). All samples were reduced in-situ at 500 °C before reaction.
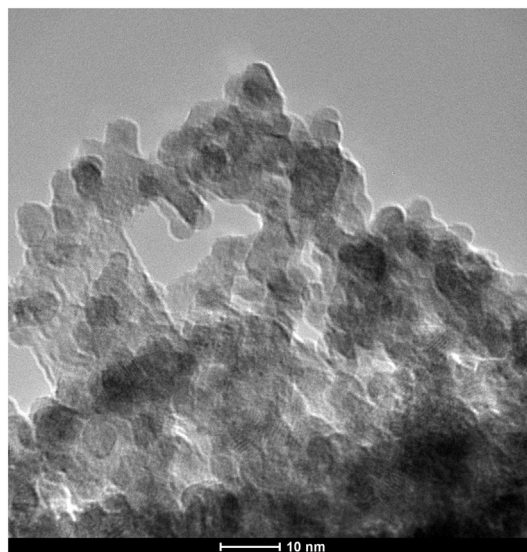

Fig. 2. TEM image of the calcined K/Cu/SmCe@TiO$_2$ catalyst.

SmCe@TiO$_2$ catalyst is very active in the CO oxidation reaction with full conversion within the whole temperature range studied and 65% NO conversion at 316 °C. Copper is known for being active oxidizing CO to CO$_2$[7] and for oxidizing NO to NO$_2$[8], with the latter species being purge out of the reactor. The SmCe@TiO$_2$ support by itself, Fig. 1SB, possess some activity in the reduction of NO but mostly oxidizing CO [9].

3.2. Morphology of the catalyst

Since the preparation method and the various calcination treatments might affect the structure of the support, electron microscopy was used to observe selected calcined catalysts. As an example, the SEM image of the K/Cu/SmCe@TiO$_2$ catalyst in Fig. S1A shows large agglomerations of heterogeneous small particles. The TEM images, Fig. 2 and Fig. S2B, shows that the agglomerates consist of clusters of small rounded particles of 5–10 nm in size. It is not possible to distinguish the core-shell structure clearly and there is no clear indication on the formation of copper or potassium particles.

3.3. Diffuse reflectance infrared experiments

In order to observe the adsorbed species during reaction, diffuse reflectance infrared experiments were conducted at a fixed temperature of 330 °C, where the approximate maximum conversion of NO occurred. To facilitate the comparison between infrared spectra all Figures use the same scale. Although the adsorption of CO on the surface lead to a variety of carbonates and carboxylate species, it is well known that the simultaneous presence of NO and CO ends up populating the catalyst surface by nitrogen-containing species [10]. In other words, the carbon-based species are displaced by the nitrogen containing species. Fig. S3C shows also no formation of carbonyl complexes above 2000 cm^{-1} under reaction conditions (only gas phase CO and CO$_2$ are observed). Among the nitrogen-based adsorbed species, the majority corresponds to different types of nitrites and nitrates, which frequently overlap forming a variety of infrared peaks in the range of 2000–1000 cm^{-1}[5]. Observing the K/Cu/SmCe@TiO$_2$ catalysts, Fig. 3 (top curves), the formation of bidentate nitrates occurred at 1248 cm^{-1} and 1305 cm^{-1} with the latter band associated with the adsorption occurring on alkaline sites [5,11,12] which evolves in time into ionic nitrates at 1373 cm^{-1}[11,13–16]. The broad band at 1573 cm^{-1} is linked to the formation of chelating bidentate nitrates on the support, whereas the band at 1545 cm^{-1} corresponds to monodentate nitrates
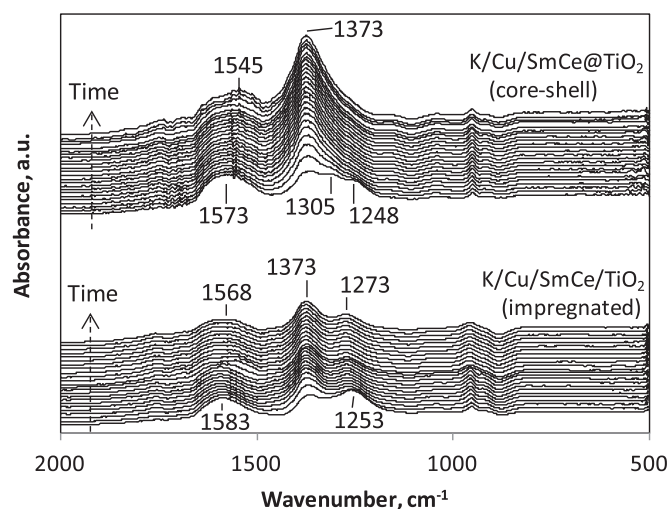
Fig. 3. DRIFT spectra of the selective reduction of NO with CO at 330 °C on K/Cu/SmCe@TiO$_2$. For comparison, the impregnated sample K/Cu/SmCe/TiO$_2$ is also included. All samples were diluted in KBr (catalyst/KBr = 1:9). Reaction conditions: 500 ppm NO, 1%CO, 10% O$_2$, He balance. Total reaction time: 2 h. The samples were reduced in-situ at 500 °C for 30 min before reaction.

also on the support ([5] and references there within). Although carbonates usually appear in the range of 1560–1400 cm^{-1}, they easily reacts with NO and nitrates species end up populating the surface [10,17]. On the other hand, the spectra of the Cu/SmCe@TiO$_2$ catalyst, Fig. S3A, only shows the formation of chelating bidentate nitrates on the support at 1571 cm^{-1} and 1300 cm^{-1}[18,19], which were stronger than those observed on the SmCe/TiO$_2$ support (Fig. S3B). The impregnated sample, Fig. 3 (bottom curves), showed similar spectra to that observed on the K/Cu/SmCe@TiO$_2$ catalyst, with the exemption of the band at 1273–1253 cm^{-1}, which has been assigned to monodentate nitrates adsorbed on the TiO$_2$ support [20]. Nevertheless, the existence of monodentate nitrates adsorbed on the K/Cu/SmCe@TiO$_2$ catalyst is not ruled out. In fact, it is very likely that these species are being hindered by the most intense ionic nitrate absorption band at 1373 cm^{-1}. In other words, the long tail at low wavenumbers induced by the latter band might be a convolution of peaks, possibly involving monodentate nitrates as well. The absence of bands at 1273–1253 cm^{-1} on the Cu/SmCe@TiO$_2$ catalyst and the SmCe@TiO$_2$ support, suggests that the formation of monodentate nitrates is favored by the presence of potassium. Also, the contribution of ionic nitrates is much lower at 1373 cm^{-1}, which agrees with the lower activity shown by the impregnated K/Cu/SmCe/TiO$_2$ catalyst. The appearance of the ionic nitrates at 1373 cm^{-1} when potassium is present, indicates that these species are likely being adsorbed on alkaline sites contiguous to copper sites.

3.4. Temperature programmed reduction (TPR)

The reducibility of the catalyst was studied by temperature reduction with hydrogen and the results are presented in Fig. 4. The Cu/SmCe@TiO$_2$ catalyst shows a typical sequential reduction profile corresponding to the reduction of: i) highly dispersed CuO species in close contact with the support (190 °C), ii) small and dispersed oxide clusters not forming crystallite yet (219 °C), and small crystallites of CuO (242 °C) [21,22]. When potassium was added, the reduction of copper for the K/Cu/SmCe@TiO$_2$ catalysts occurred at higher temperatures, which has been ascribed to a higher interaction between the alkali and the copper phase, which makes the copper oxide less reducible [23]. The latter effect was more prominent in the impregnated K/Cu/SmCe/TiO$_2$ catalysts, with the reduction of small copper clusters shifting to even higher temperatures. The broad increase in the base line above
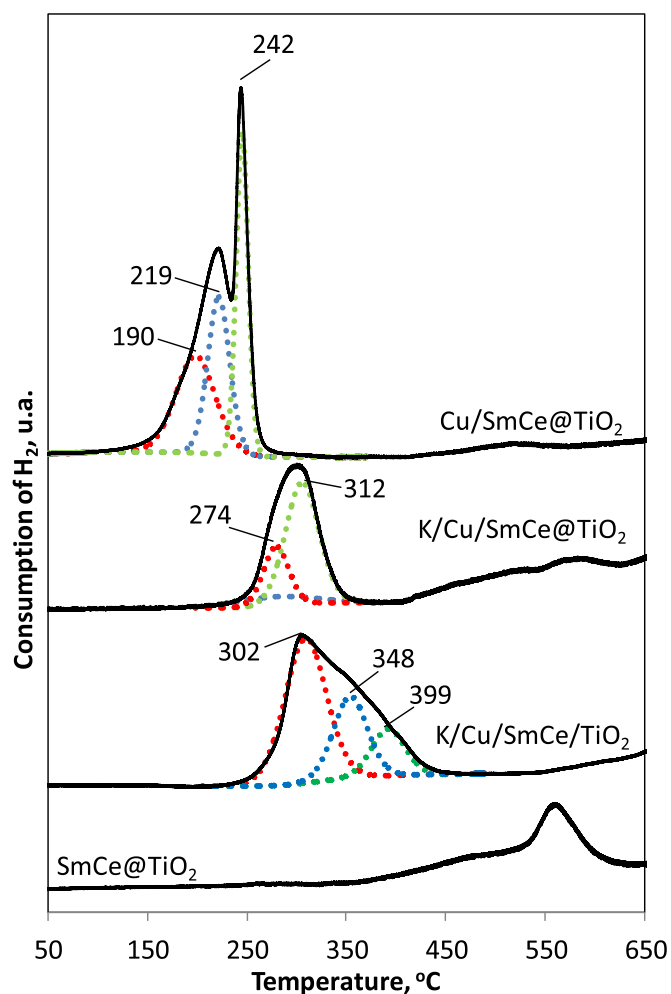

Fig. 4. H$_2$-Temperature programmed reduction (from top to bottom) of: Cu/SmCe@TiO$_2$, K/Cu/SmCe@TiO$_2$, K/Cu/SmCe/TiO$_2$ (impregnated), and the support SmCe@TiO$_2$. Labeled peaks are in centigrade degrees.

450 °C, which occurred in all samples but more clearly observed in the SmCe@TiO$_2$ support, seems to correspond to a higher interaction of CuO with the support and to the reduction of surface oxygen from the ceria support [21,22,24].

3.5. X-ray diffraction

In order to determine the crystalline character of the studied materials, X-ray diffraction analysis was performed after calcining all samples at 500 °C. The results are shown in Fig. 5. For comparison, the diffraction profiles of CeO$_2$ and TiO$_2$ phases were also included. It can be clearly observed that the predominant phase in all samples was the CeO$_2$ phase (JCPDS 34-0394), which is expected because CeO$_2$ forms the shell of the core-shell structure. It was not possible to observe any diffraction from the Sm$_2$O$_3$ (JCPDS 42-1461) phase for being occluded by the signal from the CeO$_2$ phase. The same was observed with the impregnated K/Cu/SmCe/TiO$_2$ catalysts, meaning that the impregnation was effective at dispersing the CeO$_2$ phase on top of the TiO$_2$ support. Nevertheless, weak signals from the (101) and (004) planes of the anatase TiO$_2$ are observed in all samples at 25.3° and 37.6°, respectively (JCPDS #84-1286). The latter can be explained given the small size of each core-shell CeO$_2$@TiO$_2$ assembly, which allows a small contribution to diffraction from the TiO$_2$ support. In agreement with that observed in the TPR experiments, no diffraction from the copper phase was observed in any of the copper-containing samples, which confirms the high dispersion of this phase throughout the support. Also,
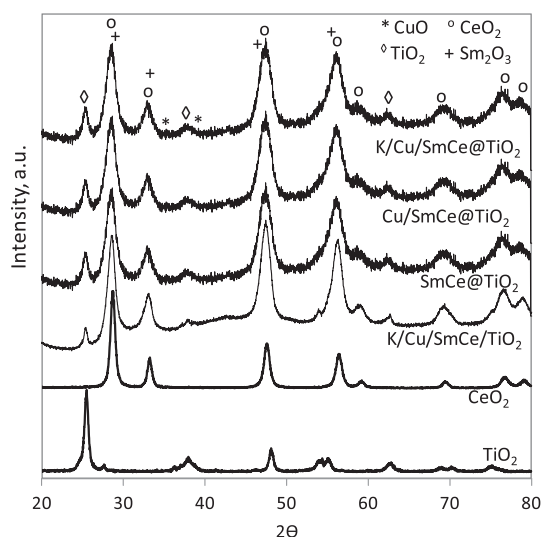
Fig. 5. (A) X-ray diffraction spectra from the $SmCe@TiO_2$, $Cu/SmCe@TiO_2$, and $K/Cu/SmCe@TiO_2$ samples. For comparison, the spectra from the impregnated $K/Cu/SmCe/TiO_2$ catalyst and the bare CeO_2 and TiO_2 supports are also included.

no diffraction was detected from the potassium phase, which might indicate either a high dispersion of the alkali or forming an amorphous phase.

Table 1 shows the BET area and pore volume of the samples used in this study after calcination at 500 °C. The core-shell $SmCe@TiO_2$ support had an area of $101 \, m^2/g$, which decreased down to $78 \, m^2/g$ after adding copper and $46 \, m^2/g$ after adding potassium. In a previous work, we found that potassium remains trapped in the calcined support, which ended up occluding pores and decreasing the surface area [25]. On the other hand, copper is easily dispersed on the support upon calcination and the occlusion of pores by copper is less important. The latter is clearly observed in Fig. S4, which shows that the addition of potassium eliminates smaller pores, whereas adding copper shows only a minor effect.

4. Discussion

The operando infrared experiments on the $K/Cu/SmCe@TiO_2$ catalyst show the formation of bidentate nitrates, which evolved into ionic nitrates as the reaction proceeded. In contrast, the impregnated $K/Cu/SmCe/TiO_2$ catalyst shows that the band associated with bidentate nitrates continues increasing in time and it shifts towards bidentate nitrates adsorbed on alkaline sites. These results suggest that on the impregnated catalyst, the NO_2 generated on copper sites [8] accumulates up to a saturation point in the impregnated catalysts, and then it is eluted with the outlet stream. In the case of the $K/Cu/SmCe@TiO_2$ catalyst, the produced bidentate nitrate species readily react with CO and the surface is never saturated with ionic nitrates (NO_2 not present on the reactor gas outlet). The latter would explain the higher activity observed on the $K/Cu/SmCe@TiO_2$ catalyst. Also, the reaction profiles suggest that the copper sites are never occluded by reaction products

Table 1
BET area and pore volumes determined by N_2 adsorption.

Sample	Area	Pore volume
	m^2/g	cm^3/g
$SmCe@TiO_2$	101	0.24
$Cu/SmCe@TiO_2$	78	0.20
$K/Cu/SmCe@TiO_2$	46	0.19
$K/Cu/SmCe/TiO_2$	24	0.13

since the oxidation of CO is complete in a large range of temperatures. Though, there is likely a competition for active sites between CO and NO. Nevertheless, it is clear is that potassium is needed to favor the reduction of NO. When the reaction proceeds on the $Cu/SmCe@TiO_2$ catalyst (not containing potassium), bidentate nitrates are formed on the support but ionic nitrates are absent, which suggests that ionic nitrates are being adsorbed on alkaline sites on the potassium-containing catalysts. Since copper is highly dispersed, it is likely that the NO_2 produced on copper sites are readily adsorbed on contiguous alkaline sites as ionic nitrates, which further reacts with CO, although the exact mechanism is not clear. On this regard, a specific study is underway including operando DRIFTS and operando Raman to elucidate the mechanism of this reaction.

We have previously observed the high temperature shifting of the reduction of copper when an alkali is added to the catalysts [5,6,23]. Courcot et al. [26,27] proposed that the addition of potassium can facilitate the formation of active surface O^{2-}, which is based on a higher interaction between the potassium and the oxide carriers. Others have also found that alkaline species are able to strongly interact with the copper phase [28], making it more difficult to reduce [29]. In fact, the TPR of the $Cu/SmCe@TiO_2$ (not containing potassium, Fig. 4) shows two effects: i) a higher reduction intensity of the copper species than that of $K/Cu/SmCe@TiO_2$, and ii) the copper reduction occurs at low temperatures. Both effects are the opposite when potassium is present, which can be ascribed to a higher interaction of the potassium phase with copper, which might be facilitated with copper species being highly dispersed. The nature of this interaction is not clear, but it can be speculated that the oxygen involved in this interaction is more difficult to remove during the reduction procedure, and even further, the presence of potassium might able to tune the way the active O^{2-} is involved in different surface reactions. In this regard, Arai et al. [30] found that the addition of sodium to a Cu/SiO_2 catalyst led to a decrease of the electronegativity of copper, increasing the affinity of copper for oxygen, and resulting in a copper phase being more difficult to reduce. Although more studies are needed to elucidate the nature of the interaction between alkaline metals and copper, it is very likely that the involved redox cycles of copper are being affected by the addition of an electropositive atom such as potassium.

5. Conclusions

This study reports a highly active core-shell $K/Cu/SmCe@TiO_2$ catalyst, which is able to reduce NO with CO in a highly oxidizing environment. Highly dispersed copper species in interaction with potassium are able to reduce NO by forming a mixture of adsorbed nitrate and nitrites. The adsorption of these species mostly proceeds on the support, with ionic nitrites adsorbed on alkaline sites. Full conversion of CO was achieved from 255 °C and 97% NO conversion was reached at 330 °C.

This noble-metal-free catalyst contributes to the development of low-cost catalyst having high activity in the elimination of CO and NO under oxidizing conditions.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2017.10.011.

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