



Short communication

Highly active Rb/Cu/YCeO₂ catalyst for the storage of nitric oxide under lean conditions

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ABSTRACT

A novel Pt-free Rb/Cu/YCeO₂ catalyst was applied to the adsorption of NO under oxidizing conditions. The results show a much greater performance of this catalyst relative to a Pt/Ba/Al₂O₃ catalyst. The results suggest that the presence of copper promotes the oxidation of NO to NO₂, with the latter molecules being readily adsorbed. Infrared experiments show a variety of nitrate/nitrites on the catalyst surface under reaction conditions. The addition of Rb resulted in copper being more resistant to reduction. The copper phase remained highly dispersed even after the addition of Rb.

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1. Introduction

Lean-burn engines are commonly used throughout industry due to the efficient combustion of hydrocarbons. However, the excess of air favors the consumption of the fuel but it also increases the generation of different oxides of nitrogen (NO_x). The oxidizing environment containing these contaminants does not allow an efficient reduction by traditional three-way catalysts and therefore a different approach is needed. In this sense, the NO_x storage and reduction (NSR) technology has attracted a lot of attention. It consists of a catalyst that adsorbs and reduces the generated NO_x compounds in alternating cycles. We have previously shown that copper based catalysts (noble metal free), promoted by an alkali and supported on TiO₂, have a high activity as adsorbents of NO [1,2]. In a similar approach, Li et al. [3] showed that a CuO/TiO₂ catalyst is an active NO adsorbent when doped with cerium. Lin et al. [4], using a CuO_x-CeO₂ oxide mix doped with barium and Peralta et al. [5] using Ba,K,Co/CeO₂ catalysts, showed that these materials were active not only storing NO but also oxidizing soot. In the same way, we demonstrated that sodium-copper catalysts supported on CeO₂ were highly active for adsorbing NO [6]. In this work we selected a more reactive alkali metal from Group I, such as rubidium. Ceria is known to be a very weak basic oxide and we demonstrated before the synergic effect of coupling ceria with sodium. Being rubidium a more

reactive metal, we expect that any synergic effect between both metals will be increased when adding rubidium. Here we explore the use of rubidium as a promoter of a copper supported Y-stabilized CeO₂ catalyst. The results are contrasted with different characterization techniques.

2. Experimental

The catalysts were prepared by a reverse micelle method. Briefly, a stock solution of 62 wt.% polyethoxylated hexanol and 38 wt.% 1-pentanol (Merck) is prepared. Then 45 ml of stock solution is added under stirring to 45 ml isooctane. Separately 9.3 g of cerium (III) nitrate hexahydrate and 0.91 g of yttrium (III) nitrate hexahydrate (both from Aldrich) are dissolved in distilled water and added to the previous mixture (*solution 1*). A second mixture, *solution 2*, is prepared containing 45 ml of stock solution, 45 ml of isooctane, 6.6 ml of ammonia (25%, Merck), and 93.4 ml of distilled water. Then, *solution 2* is added dropwise to *solution 1* under strong stirring at room temperature and left overnight. The measured pH of the final solution was 11.4. The recovered solid, denoted as YCeO₂, is oven-dried and calcined at 500 °C for 3 h. The nominal loading of yttrium was 10% molar. The same procedure was used to obtain yttrium-free CeO₂ support. The support was wet-impregnated with 2.5 w/w% of copper using Cu(NO₃)₂·3H₂O (Merck) and then dried and calcined at 500 °C for 3 h. Part of the copper-impregnated catalyst was further impregnated with 5 w/w% Rb using rubidium nitrate (Aldrich). Hereafter, the calcined catalysts supported on either CeO₂ and yttrium-doped CeO₂ will be denoted as

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Rb/Cu/CeO₂ and Rb/Cu/YCeO₂, respectively. A reference 1%Pt/10%Ba/Al₂O₃ catalyst was prepared by a sequential wet-impregnation of Al₂O₃ support (Merck) using barium nitrate (Merck) and tetraammineplatinum (II) nitrate (Sigma Aldrich). After each impregnation the catalyst was calcined at 500 °C for 3 h. Adsorption experiments were conducted in a plug flow reactor using a ratio of catalyst weight to volumetric rate, W/F, of 0.5 g · s · cm⁻³ at 250 °C. The gas feed consisted of 500 ppm NO and 10% oxygen, balanced with He. The outlet gases from the reactor were analyzed by an infrared spectrometer (Shimadzu, IRPrestige21) equipped with a 2.4 m Pike gas cell and a gas chromatograph (GowMac, Series 580). The chromatograph was equipped with a 60/80 Carboxen 1000 column (Supelco). The TCD and injector were both at 120 °C. The temperature of the oven was initially at 40 °C for 4 min, then increasing up to 100 °C at 20 °C/min. The carrier gas was helium at 30 ml/min.

Fractions of the catalyst samples were additionally studied by temperature programmed reduction (TPR) experiments in a 5% H₂/Ar stream using a 10 °C/min ramp. The crystal structure of the different catalysts was determined by X-ray diffraction on a Siemens D-5000 diffractometer using Cu K α radiation at a scan rate of 0.02°/min. The surface area (BET) and pore size distribution of the various prepared samples were obtained from N₂ adsorption isotherms using a Micromeritics 2010 adsorption apparatus. HR-TEM was performed in a FEI (Titan 80-300) microscope at 200 kV.

3. Results and discussion

3.1. NO adsorption experiments

One of the most studied NSR catalyst reported in literature is the Pt/Ba/Al₂O₃ catalyst [7–11], which was also prepared in this study and used as a comparison reference. The results of the nitric oxide storage capacity on the Rb/Cu/CeO₂ and Rb/Cu/YCeO₂ catalysts at 0.5 g · s · cm⁻³ are shown in Fig. 1A. It can be observed that the breakthrough points of the Rb/Cu/YCeO₂ and Rb/Cu/CeO₂ catalyst are much higher than

the Pt/Ba/Al₂O₃ catalyst (dashed line). In fact, the NO uptakes up to the breakthrough are Pt/Ba/Al₂O₃, Rb/Cu/CeO₂, and Rb/Cu/YCeO₂ catalysts are 0.04 mmol/g, 0.173 mmol/g, and 0.372 mmol/g, respectively.

In order to compare the contribution of the copper and rubidium phase, separate catalysts were prepared and studied. Fig. 1B shows that the ceria support is able to adsorb NO, but after 35 min it slowly deactivates. No improvement is shown when Rb is added to the ceria support. On the other hand, the copper phase shows higher NO adsorption than the bare CeO₂ and Rb/CeO₂ materials. It is only when rubidium and copper are together on the CeO₂ support that the activity is much higher.

A similar behavior is observed on Fig. 1C for the Rb/Cu/YCeO₂ catalyst. The support by itself is able to show some activity on NO adsorption with a breakthrough point after 60 min. Again, the addition of Rb to the YCeO₂ support leads to a lower activity, whereas the Cu/YCeO₂ catalyst shows a higher NO adsorption with a breakthrough point similar to the YCeO₂ support but with a slower decay on the NO adsorption activity. It is clear that a synergetic effect is observed when both phases are present on the Rb/Cu/YCeO₂ catalyst with a breakthrough point at 150 min. Fig. 1D shows the presence of NO₂ at the outlet of the reactor. Gaseous nitrogen was not observed on the outlet on any of the experiments. It can be observed that both catalysts do not show NO₂ during the full adsorption of NO, which indicates that all the produced NO₂ is being adsorbed up to the respective breakthrough point. No other N_xO_y species were observed during the reactions. These activity results indicate that it is only when both phases of Rb and Cu are simultaneously present on the catalysts that the higher activity on NO adsorption is observed. The latter would be due to the favored oxidation of NO to NO₂ on copper [12]. The alkaline and copper phase must interact closely in order for the NO adsorption to occur at a higher rate. The NO₂ produced on copper sites would be readily adsorbed on contiguous alkaline sites [1,6,13]. Our previous results using a commercial yttrium-doped CeO₂ support impregnated with copper and sodium hydroxide showed even higher activities than the catalyst presented in this work [6]. We have found

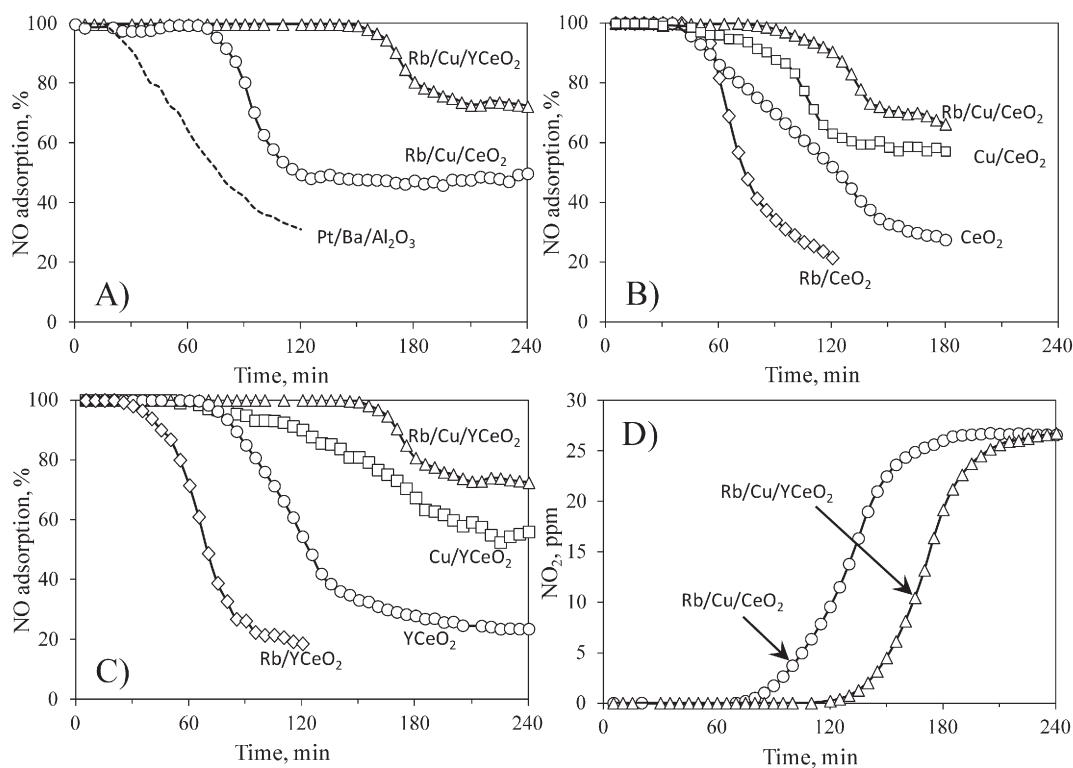


Fig. 1. (A) Activity of the Rb/Cu/CeO₂ and Rb/Cu/YCeO₂ catalysts in the storage of NO. As a reference, the activity of 1%Pt/10%Ba/Al₂O₃ is also included (dashed line). NO adsorption activity of: (B) Rb/CeO₂ and Cu/CeO₂ catalysts, and (C) Rb/YCeO₂ and Cu/YCeO₂ catalysts. For comparison, the bare CeO₂ and YCeO₂ supports and the Rb/Cu/CeO₂ and Rb/Cu/YCeO₂ catalysts are also included in (B) and (C). (D) NO₂ detected at the outlet of the reactor during the NO adsorption on the Rb/Cu/CeO₂ and Rb/Cu/YCeO₂ catalysts.

Table 1
BET surface area and pore volume determined by N₂ adsorption.

Sample	Area m ² /g	Pore volume cm ³ /g
CeO ₂	85	0.22
YCeO ₂	104	0.13
Cu/CeO ₂	76	0.14
Cu/YCeO ₂	89	0.12
Rb/CeO ₂	39	0.17
Rb/YCeO ₂	45	0.09
Rb/Cu/CeO ₂	35	0.17
Rb/Cu/YCeO ₂	51	0.17

that using hydroxide precursors instead of nitrates leads to higher activities, which might explain the slightly lower activity of the Rb-based catalyst presented here where rubidium nitrate was used. Such difference between hydroxide and nitrate precursors of the alkaline metal is currently under study.

3.2. BET area and pore size distribution

Table 1 and Fig. 2 summarize the surface area, pore volume, and pore distribution using the CeO₂ and YCeO₂ supports. It is clear that after adding copper and rubidium, the pore size distribution is similar for the Rb/Cu/YCeO₂ and Rb/Cu/CeO₂ catalysts. Pores larger than 300 Å give most of the contribution to the pore volume, although the asymmetric distribution indicates a contribution of smaller pores as well. In order to rule out the tensile strength effect (the spontaneous evaporation of metastable pore liquid nitrogen) [14], it was checked that the spike at 33 Å appeared on both the adsorption and desorption curves. The latter peak seems to be the remaining contribution of small size pores from the YCeO₂ support as shown in Fig. 2A.

As shown in Table 1, the inclusion of Y is able to achieve a higher surface area of the YCeO₂ support (104 m²/g) compared to the regular CeO₂ support (85 m²/g). It is possible that the thermal stability given by yttrium is due to the occupancy of imperfections of the crystal structure of the support, which prevents the ceria grain growth and the collapse of the area upon calcination [15,16]. On the other hand, the addition of copper results in a decrease of the surface area, which is even more abrupt when adding rubidium. Nevertheless, the simultaneous addition of copper and rubidium ends up with a surface area of 35 m²/g and 51 m²/g for the Rb/Cu/CeO₂ and Rb/Cu/YCeO₂ catalysts, respectively.

3.3. X-ray diffraction

In order to determine the crystalline character of the catalysts after adding copper and rubidium, X-ray diffraction experiments were carried out. As observed in Fig. 3A, the pattern of the Rb/Cu/YCeO₂ catalysts only showed diffraction lines corresponding to the ceria support. As references the YCeO₂ and Cu/YCeO₂ were also included, both showing similar patterns. In all cases, the diffraction profile was that of the CeO₂

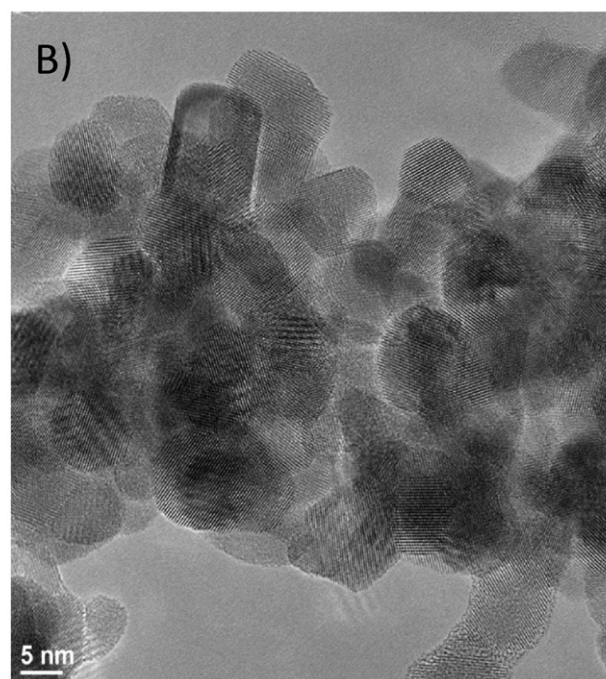
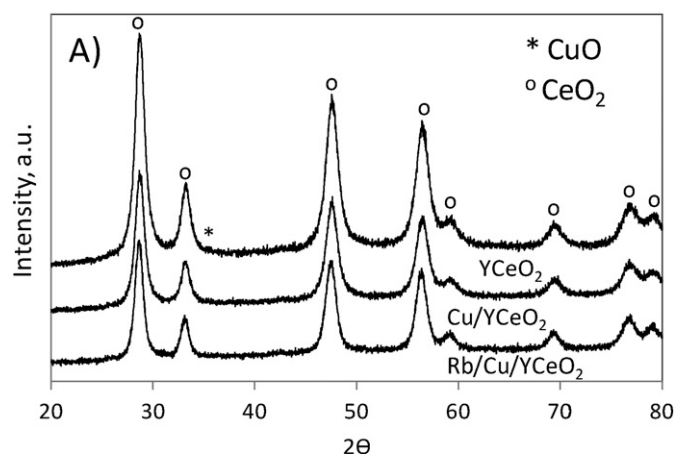


Fig. 3. (A) X-ray diffraction of the Rb/Cu/YCeO₂ catalysts along with Cu/YCeO₂ and the YCeO₂ support, and (B) HR-TEM of the Rb/Cu/YCeO₂ catalyst.

support, even in those samples not containing yttrium (not shown). The rubidium, copper, and yttrium phases did not show diffraction on any of the samples, which indicates that these phases are either amorphous or highly dispersed throughout the ceria support. The latter is consistent with Fig. 3B, where no aggregates of rubidium, copper, or yttrium are observed throughout the support.

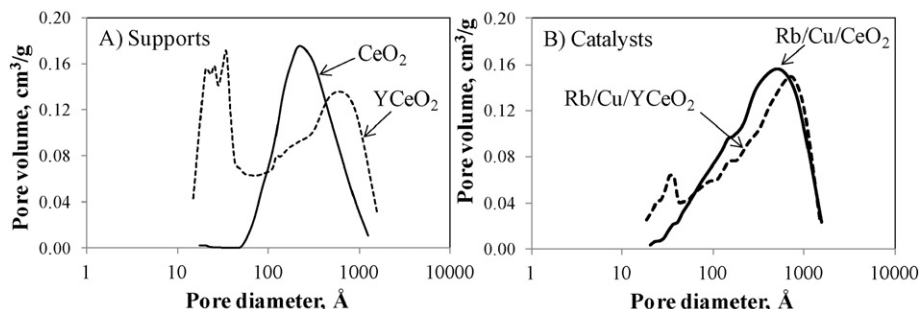


Fig. 2. Pore size distributions of the (A) CeO₂ and YCeO₂ supports, (B) Rb/Cu/CeO₂ and Rb/Cu/YCeO₂ catalysts. All catalysts were calcined at 500 °C prior the analysis.

3.4. Temperature programmed reduction (TPR)

The activity results indicate that it is only when both copper and rubidium are simultaneously present on the catalyst that a synergetic effect is observed. To study this interaction, temperature programmed reduction of the catalyst was utilized. Fig. 4A shows a similar reduction profile on the bare supports between 300 °C and 600 °C, which has been ascribed to the reduction of labile oxygen species [17,18]. On the other hand, when copper was added to the respective CeO₂ and YCeO₂ supports, a reduction profile is observed in the 100–250 °C range, which shows the characteristic three-peak reduction of highly dispersed copper species [1,17,18]. On the other hand, the reduction of the rubidium-impregnated samples gave place to a broad reduction around 520 °C. When both copper and rubidium were present, the reduction of copper observed in Fig. 4B shifted to the 250–360 °C range. The latter shift on the reduction of copper is ascribed to the interaction between the alkaline and copper phases [1,7]. The oxygen removed during reduction is now in the presence of neighboring rubidium, which makes the copper more difficult to reduce, which explains the shift to higher temperatures [19]. In the latter case, the H₂ consumption was much higher than the previous cases (notice the scale on the y-axis), which suggest the mentioned interaction between copper and rubidium.

In order to have an insight of the reduction profiles shown in Fig. 4D, a set of Gaussian/Lorentzian peaks were added and fitted to each curve using a Marquardt–Levenberg optimization algorithm [20]. Fig. 4E–F shows the contribution of three components which would correspond to the sequential reduction of copper with different degrees of aggregation observed at low temperatures in Fig. 4B. Notice that the Rb/Cu/YCeO₂ catalyst shows a low temperature reduction peak at 312 °C, whereas a similar but weaker peak is observed at 293 °C for the Rb/Cu/CeO₂ catalyst. On the other hand, the mid-temperature reduction peak at 327 °C for the Rb/Cu/YCeO₂ is smaller than the peak at 314 °C for the Rb/Cu/CeO₂ catalyst. A similar high temperature reduction peak is observed at 342 °C for both samples. These results suggest that highly dispersed copper species in high interaction with the support and/or with rubidium are able to favor the catalytic activity [1]. Although the specific mechanism is not clear at the moment, previous results suggest that the NO₂ generated on copper sites area readily adsorbed on contiguous alkaline sites, which is favored on smaller copper species [6,13].

3.5. Infrared absorption experiments

In order to monitor the adsorbed species on the surface of the catalysts, infrared analyses were performed during the NO adsorption

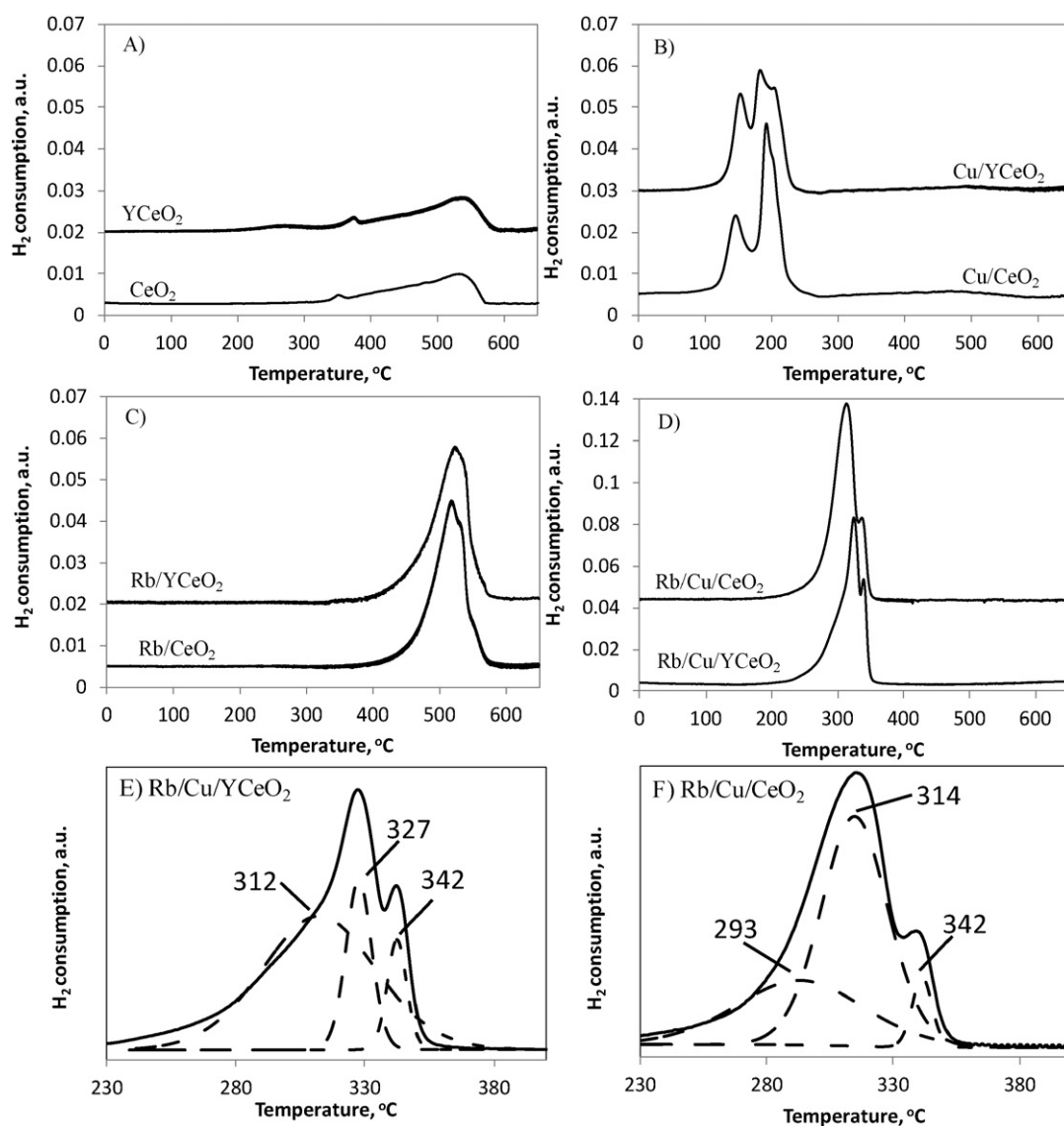


Fig. 4. H₂-temperature programmed reduction of the (A) YCeO₂ and CeO₂ supports, (B) Cu/YCeO₂ and Cu/CeO₂ catalysts, (C) Rb/YCeO₂ and Rb/CeO₂ catalysts, and (D) Rb/Cu/CeO₂ and Rb/Cu/YCeO₂ catalysts.

reaction. Fig. 5 shows the typical formation of a variety of nitrate and nitrite species in all samples [21–24], with trans-hyponitrite species around $1406\text{--}1420\text{ cm}^{-1}$, cis-hyponitrite between $1360\text{--}1320\text{ cm}^{-1}$, chelating nitrite at 1270 cm^{-1} , nitro species at 1500 cm^{-1} , various nitrates between $1610\text{--}1480\text{ cm}^{-1}$ and $1350\text{--}1250\text{ cm}^{-1}$, and ionic nitrates at 1300 cm^{-1} and $1480\text{--}1420\text{ cm}^{-1}$ [25,26]. The formation of these species is weak on the supports containing Rb (Fig. 5C–D), whereas the formation on the copper containing supports is much stronger (Fig. 5A–B). This formation is also ascribed to the in-situ oxidation of NO to NO_2 on copper sites. Since NO_2 is a much more reactive molecule, it is readily adsorbed forming a variety of nitrates and nitrites. Fig. 5E–F shows adsorption spectra for the Rb/Cu/CeO₂ and Rb/Cu/YCeO₂. It should be noticed that the latter catalysts release only very small amounts of NO_2 in the reactor outlet (Fig. 1D), which is much lower than the Cu/CeO₂ and Cu/YCeO₂ samples (not shown).

In summary, the addition of rubidium to ceria-supported copper catalysts results in the in-situ oxidation of NO to NO_2 , with the latter molecules being readily adsorbed in a variety of nitrate/nitrite species. The activity of this novel catalyst is favored by the high dispersion of copper species in close proximity to alkaline sites. More studies are underway to elucidate the actual size of copper particles, the oxidation states of the different metals, and the involved reaction mechanism.

4. Conclusions

It was found that the simultaneous presence of Rb and Cu in a Rb/Cu/YCeO₂ catalyst results in a highly active adsorbent of NO. The addition of Rb resulted in copper being more resistant to reduction. The copper phase remained highly dispersed even after the addition of Rb.

These preliminary results show the great potential of an inexpensive NO sorbent as an alternative to noble metal based catalysts.

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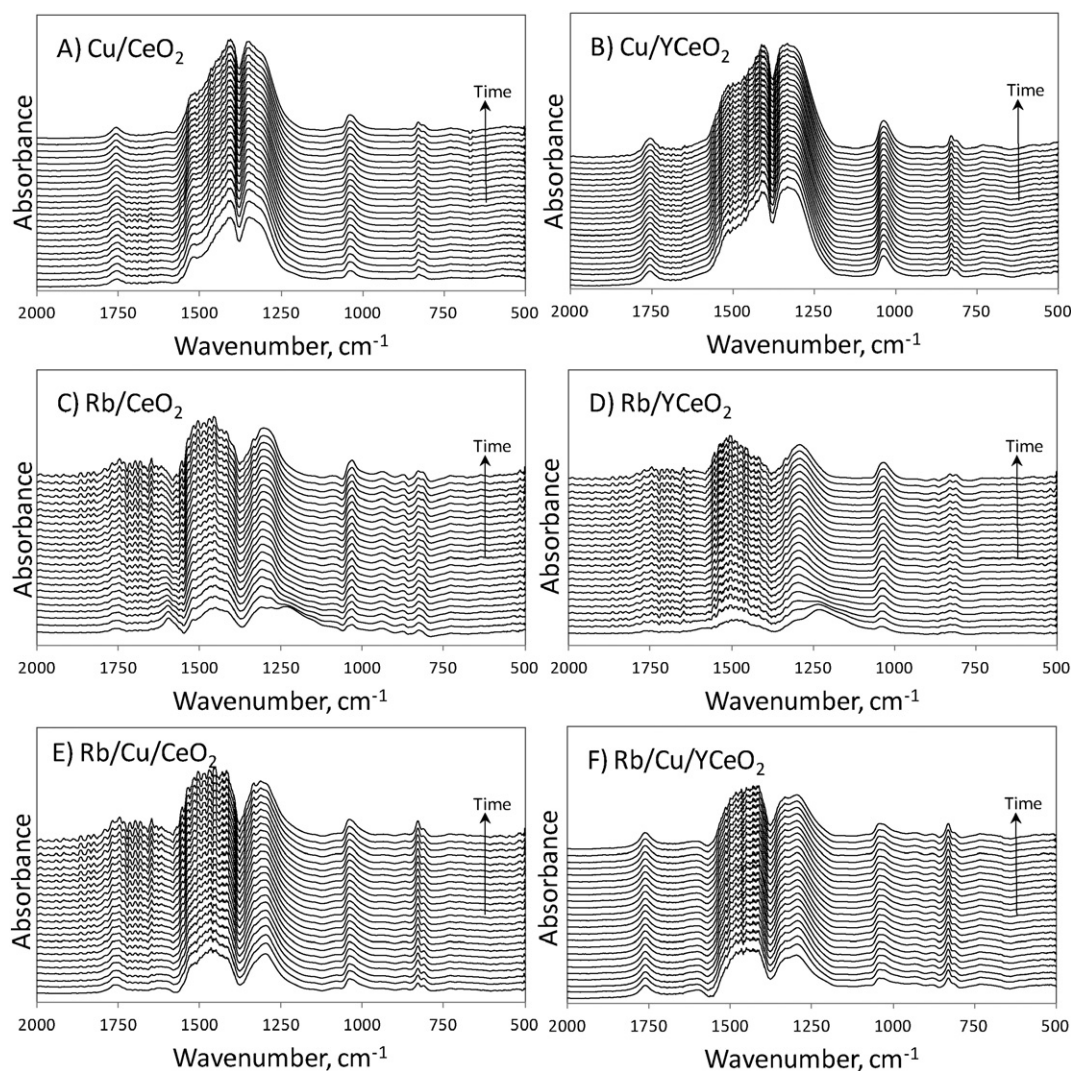


Fig. 5. FTIR spectra of NO adsorption with time on (A) Cu/CeO₂, (B) Cu/YCeO₂, (C) Rb/CeO₂, (D) Rb/YCeO₂, (E) Rb/Cu/CeO₂, and (F) Rb/Cu/YCeO₂. All samples were diluted in KBr (catalyst/KBr = 1:9). Reaction conditions: 500 ppm NO, 10% O₂, He balance; T = 250 °C. The samples were calcined in-situ at 500 °C for 1 hour before the adsorption experiments.

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