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Activity and stability of a CuO/CeO₂ catalyst for methanol steam reforming

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ABSTRACT

The activity and stability of copper supported on cerium oxide have been investigated in the selective production of hydrogen via methanol steam reforming. The catalytic runs were carried out under two different operating regimes: continuous and discontinuous. The main products were H₂ and CO₂ and a minor amount of CO (selectivity to CO was around 6% at 300 °C). In all the cases, the catalyst was initially very active and the activity was lost with the time on stream. The catalyst under a continuous regime was easily regenerated by air at 400 °C. Under a discontinuous mode, the catalyst was self-activated after stop operation and initial conversion was almost recovered. The deactivation could be mainly attributed to the adsorption of carbonate species which were easily desorbed under an inert flow or by burning with air. The pre-reduction of catalyst should be avoided to reach higher stability.

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Introduction

The environmental concerns and the growing in the energetic demand have created the need to use clean fuels and to improve the sustainability of the energy system worldwide [1]. Hydrogen is one of the best options as it produces the double of energy per gram in comparison with other conventional fuels and produces only water as residue of its combustion. It is the ideal fuel for fuel cell applications [2–4]. Supply, storage and handling of hydrogen are problems which should be solved. One of the solutions is the use of hydrocarbons or alcohols as hydrogen carriers. Methanol is considered an attractive raw material due to its high hydrogen/carbon ratio

(4:1) equal to that of methane, no C–C bond, low required temperatures in the steam reforming reaction,



low sulfur content and high availability as a worldwide commodity [5–7]. Besides, it is a liquid at atmospheric pressure and room temperature and it has a low boiling point (65 °C) which allows easy evaporization in the temperature range near to water.

Steam reforming of methanol, SRM, has been studied over different catalytic systems [8–11], particularly over Cu based catalysts, such as Cu/ZnO/Al₂O₃ at temperatures lower than 300 °C [12–18]. Cu–ZnO interactions have been reported to

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have a marked effect in catalytic activity due to the ZnO improved the metal dispersion and reducibility of Cu^{2+} species [15]. However, these catalysts presented some inconveniences: high CO formation, low stability with time due to the tendency of copper sintering and their pyrophoric nature when they are exposed to oxidizing environments. The effects of CeO_2 and ZrO_2 on $\text{CuO-ZnO-Al}_2\text{O}_3$ catalysts have also been examined [14,19].

Recently, new catalytic systems based on CuO and CeO_2 have been considered [20–25]. The high mobility of oxygen and the strong interactions with the supported metal have rendered the CeO_2 a very attractive catalytic support. CeO_2 could decrease the CO concentration in the reformer effluent [25,26] and favor the coke gasification [21]. Marban and Fuertes [27] have reported that the formation of $\text{Ce}_{1-x}\text{Cu}_x\text{O}_{2-x}$ solid solution could lead to a high Cu dispersion after reduction. Patel and Pant [28] have also suggested the use of CeO_2 increases the copper dispersion and the thermal stability. The activity in SRM over CuO-CeO_2 catalysts was significantly affected by the copper amount. Liu et al. [25] have reported an optimal composition of 26.9 wt.% Cu substantially lower than the optimum (80 wt.%) proposed by Oguchia et al. [29]. We have studied supported catalysts with a lower loading (around 5 wt.%Cu) which have turned out to be very active in the methanol steam reforming [30].

In this work the catalytic activity in the methanol steam reforming reaction over a CuO/CeO_2 catalyst is presented under two operating regimes: continuous and discontinuous. Reaction and regeneration cycles are studied. Besides, the oxidation state of active sites and the oxide support role are discussed.

Experimental

Catalyst preparation

CeO_2 used as support was prepared by precipitation method from an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. NH_4OH (0.9 M) was added dropwise until $\text{pH} = 9$ at room temperature under a vigorous stirring. The precipitate was filtered, washed with bi-distilled water and dried under vacuum at 80°C overnight. The dried solid was calcined at 500°C for 4 h in air. The support calcination temperature was chosen with the aim to avoid possible changes in specific surface area induced by operation conditions in reaction. Then, it was impregnated with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ by incipient wetness method. The copper nominal loading was 5 wt.%. This solid dried in vacuum at 80°C overnight, calcined in static air at 400°C for 4 h and it was named CuO/CeO_2 .

Catalyst characterization

The samples were characterized using different physical chemical methods.

BET surface area

BET surface areas were measured by nitrogen adsorption using a Micromeritics Gemini V instrument.

Thermal gravimetry analyses (TGA)

The analyses were recorded using TGA 51 Shimadzu equipment. The samples were heated from room temperature to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ with an air flow of 50 mL min^{-1} .

Temperature programmed reduction (TPR)

Studies were performed in a conventional TPR equipment [30]. In a typical experiment, the samples were treated in He at 300°C for 30 min before the reduction. After that, the system was cooled down to 25°C . The samples were subsequently contacted with a 30 mL min^{-1} flow of 5 vol.% H_2 in N_2 , heated at a rate of $10^\circ\text{C min}^{-1}$ from 25°C to a final temperature of 350°C and held at 350°C for 1 h.

X-ray photoelectron spectroscopy (XPS)

The XPS measurements were carried out using a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with pass energy of 30 eV and a Mg $K\alpha$ X-ray source operated at 200 W and 12 kV. The residual pressure inside the analyses chamber was kept at values below $5 \cdot 10^{-9}$ mbar. All binding energies (BE) were referred to the C 1s line at 284.6 eV. Cu 2p, Ce 3d, O 1s and C1s spectra were recorded for each sample. The Auger kinetic energy for the Cu_{LMM} transition was also determined. The data treatment was performed with the Casa XPS program (Casa Software Ltd., UK). The peak areas were determined by integration employing a Shirley-type background. The samples were transferred to the instrument after being exposed to air. Before XPS measurements the samples were treated inside the pre-treatment chamber of the spectrometer as follows:

- The fresh catalyst was heated in a reductive flow (H_2 5%/Ar) at 260°C for 30 min and atmospheric pressure and then was heated in an inert flow (Ar) at 300°C for 30 min.
- The used catalyst was heated in an inert flow (Ar) at 300°C for 30 min and atmospheric pressure.

Catalytic test

The methanol steam reforming reaction was carried out in a glass tubular reactor operated at atmospheric pressure between 260 and 300°C [30]. The feed to the reactor was a gaseous mixture of methanol, water and nitrogen. Methanol and water were fed through independent saturators before mixing. The flow rates of N_2 gas stream were controlled by mass flowmeters. The total flow rate was 82 mL min^{-1} at room temperature with a methanol molar composition of 5%. The $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ molar ratio was 1.2 in all the experiments. The catalyst weight was 300 mg (0.3–0.5 mm particle size range selected after preliminary mass transport experiments to minimize diffusional resistances). The catalyst without pre-reduction was heated to reaction temperature under N_2 flow, then the mixture with $\text{CH}_3\text{OH} + \text{H}_2\text{O}$ was allowed to enter into the reactor to carry out the catalytic test. The reactants and reaction products were analyzed *on-line* by gas chromatography. H_2 , CO_2 , H_2O and CH_3OH were separated by

a 1.2 m Porapak T column and analyzed by TC detector using N_2 as carrier. CO , CO_2 , CH_2O , CH_3OH and other carbon compounds were analyzed by a flame ionization detector after passing through a 1.2 m Porapak T column and a methanizer. The activity was measured under continuous (steady state operation) and discontinuous (shutdown – start up operation) regimes. The continuous runs were carried out during a long time on stream (around 60 h) in an uninterrupted way. In the discontinuous regime the experimental run was interrupted overnight and followed the day after under the same operating conditions. The cooling at room temperature and the heating at the reaction temperature were carried out under N_2 flow, whereas the catalytic bed remained in a static inert atmosphere during the stop. The total reaction time was also around 60 h. The performance of the catalysts was analyzed in terms of methanol conversion and selectivity to products. The methanol conversion was defined as the ratio of reacted methanol mol to fed methanol mol. The homogeneous contribution was tested with empty reactor. This run showed very low activity at 300 °C being the methanol conversion around 5%.

Results and discussion

Some characteristics of CuO/CeO_2 fresh catalyst are shown in Table 1 and they were reported in a previous work [30]. Briefly, the copper chemical composition determined by XRF was 5.48 wt.% near to the nominal value and the specific surface area ($S_{BET} = 39 \text{ m}^2 \text{ g}^{-1}$) was slightly lower than the bare support. After the SRM experimental tests in a continuous mode during 60 h, changes in specific surface areas were observed probably because of sintering of support, Table 1. The TPR profile was characterized by two peaks: a first peak at 154 °C assigned to small particles of CuO and the second one at 190 °C attributed to the reduction of CuO particles in a higher size. The surface oxygen reduction of CeO_2 also contributed to the observed hydrogen consumption [30].

In Fig. 1, methanol conversion as a function of reaction time in the continuous regime is shown at 260, 280 and 300 °C reaction temperatures. CuO/CeO_2 catalyst, without a previous reduction, was very active with initial conversions higher than 80%. H_2 and CO_2 were the main products. In all the cases the hydrogen selectivity, S_{H_2} , was 100%. CO was also detected and its amount depended on reaction temperature, Table 2. The CO selectivities varied from 3.8% to 6.4% at 260 and 300 °C, respectively, after ~370 min in reaction. In all the cases the conversion decreased with time on stream while the product selectivities were nearly constant. The conversion losses were 76% at 300 °C, 78% at 280 °C and 67% at 260 °C, after 3000 min in

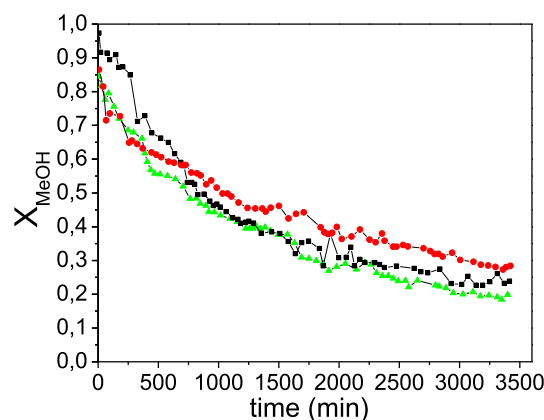


Fig. 1 – Methanol conversion in methanol steam reforming over CuO/CeO_2 under continuous mode: ■ 300 °C; ▲ 280 °C; ● 260 °C.

Table 2 – Catalytic results in the methanol steam reforming reaction over a CuO/CeO_2 catalyst under a continuous regime.

| Reaction temperature, °C | Reaction time, min | X_{MeOH} % | S_{CO_2} % | S_{CO} % |
|--------------------------|--------------------|--------------|--------------|------------|
| 260 | 370 | 63.5 | 96.2 | 3.8 |
| 280 | 371 | 63.2 | 95.0 | 5.0 |
| 300 | 389 | 73.1 | 93.6 | 6.4 |

$W/F_{MeOH} = 1940 \text{ g min mol}^{-1}$.

reaction. After this period the conversion reached an almost stable value between 20 and 30%. The deactivation rate was slightly lower at 260 °C.

To understand better the deactivation phenomena, the catalyst was submitted to an *in situ* regeneration process after the experimental runs. After the stop of reactive feed, the regeneration was carried out at 400 °C under an air flow for 1 h. The regeneration products (CO_2 and CO) were recorded by a gas chromatograph with a flame ionization detector after passing through a methanizer. The CO_x presence in the reactor effluent was associated to the burning of adsorbed carbonaceous species. Additionally, the oxidation of Cu^0 species occurred during the regeneration process. Once the system was regenerated the reactor was cooled down until the reaction temperature and a new experimental run was carried out. After 600 min under reforming conditions, a new regeneration–reaction cycle was repeated. The results illustrated in Fig. 2 show that the initial conversion was almost recovered. A

Table 1 – Some characteristics of CuO/CeO_2 catalyst.

| Sample | Fresh | $S_{BET} (\text{m}^2 \text{ g}^{-1})$ | | | wt.% Cu | XRD phases |
|-------------|-------|---------------------------------------|-----------|-----------|---------|-------------|
| | | After used in SRM | | | | |
| | | At 260 °C | At 280 °C | At 300 °C | | |
| CuO/CeO_2 | 39 | 35 | 36 | 30 | 5.48 | CeO_2-CuO |

S_{BET} of CeO_2 support = $44 \text{ m}^2 \text{ g}^{-1}$.

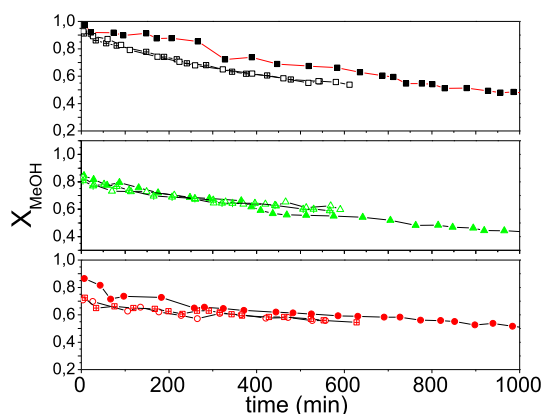


Fig. 2 – Catalytic tests at ■ 300 °C; ▲ 280 °C; ● 260 °C; Full symbols, experimental runs over fresh catalyst and open symbols, after air regeneration at 400 °C.

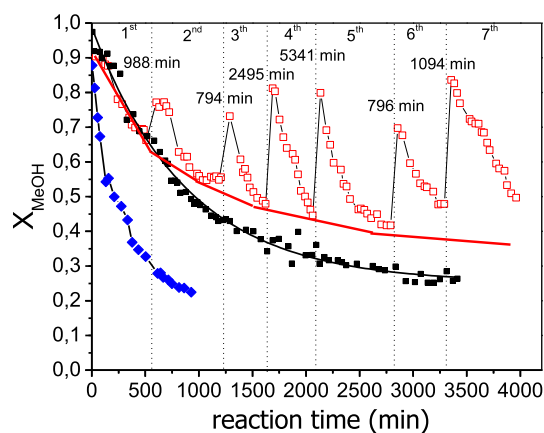


Fig. 3 – Methanol conversion over CuO/CeO₂ at 300 °C: ■ Discontinuous test ■ Continuous test. ♦ Pre-reduced catalyst at 260 °C.

loss of 15% was only observed at 300 °C after 600 min. The deactivation was a reversible process at low reaction temperatures. The activity recovery of catalyst after being treated in air at 400 °C suggested that the deactivation process could be attributed to the carbonaceous species formation on the catalyst surface which were eliminated by combustion. The carbon amounts were low. TGA experiments (not shown) of used catalysts did not reveal a significant weight loss, probably due to the simultaneous carbonaceous deposit combustion and the copper oxidation. These carbonaceous deposits could be carbonate or formates [31] and they were very reactive since they could be removed by air at 400 °C. The activity loss observed on the catalyst operated at 300 °C suggests that two simultaneous processes occur: the deposition of carbonaceous species (reversible process) and the sintering of active phase (irreversible process) which is more likely at high temperatures. Liu et al. [25] have also reported carbon deposition on 3.9 wt.%Cu/CeO₂ (0.8 wt.% at 220 °C and 1.7 wt.% at 240 °C after 24 h in SRM). They have also claimed that the carbonaceous deposits formed on the catalyst surface caused the catalyst deactivation.

In Fig. 3, the methanol conversion is shown under a discontinuous regime at 300 °C. As it was expected the conversion until 500 min was the same as that obtained under a continuous regime. The values under a continuous regime are also illustrated for comparison. After the stop period (which is indicated in minutes into the figure) an activity recovery was observed under the discontinuous mode. The recovery of conversion in an inert atmosphere could be related to the desorption of carbonaceous compounds adsorbed on the catalytic surface and also to the solid characteristics (shown further). Whereas the conversion under continuous mode decreased to 24% after 3300 min in time on stream, the estimated conversion after seven cycles was 36%. In the figure the methanol conversion obtained over a previously reduced catalyst is also presented for comparison. The reduction was carried out at 260 °C for 1 h in a H₂/N₂ flow. The reduction temperature was chosen from the TPR experiment. The initial conversion was 89%, but the activity dropped faster. The

deactivation rate was markedly higher with a conversion loss of 75% after 925 min in time on stream. Although the Cu⁰ species obtained by direct reduction with H₂ could have different properties from those obtained by reduction with methanol, it should be also taken into account that the reduction degree of CeO₂ by H₂ is higher than that obtained under reforming conditions (see further). In literature it has been reported that the oxygen deficiency in CeO₂ favours the formation of carbonate and formate species [32]. This could explain the higher deactivation rate.

This behavior could also indicate that the active sites for this reaction could be a combination of Cu⁰ and copper species in a higher oxidation state, Cu^{δ+}. Different copper species have been claimed to fulfil an important role in the SRM reaction [33–35]. Thus, Cu⁺–O–Cu⁺ sites have been reported as responsible of methanol adsorption and they should be involved in SRM mechanism [15]. Fujitani et al. [34] have agreed that Cu⁺ as well as Cu⁰ are the active species for this reaction, while Idem et al. [35] have reported that the reaction strongly depends on the amount of Cu⁺ species formed on the catalyst. Recently, Turco et al. [36] have shown in a Cu/CeO₂/Al₂O₃ catalyst that the active phase consists of a metallic surface covered by a layer of chemisorbed oxygen. Besides, other authors have also suggested that CeO₂ assists the oxidation of Cu⁰ to Cu⁺ (Cu⁰ + Ce⁴⁺ ⇌ Ce³⁺ + Cu⁺) [37,38]. Then, a possible explanation for the results shown in Fig. 3 could be found assuming that during the cooling in inert, the stop period and/or the previous heating to the reaction, Cu⁰ could be partially oxidized generating Cu^{δ+} by oxygen from CeO₂. Besides, this oxygen could also facilitate the removal of very reactive carbonaceous deposits.

With the aim to study the possibility that CeO₂ assists the oxidation of Cu⁰ to Cu^{δ+}, a sequence of TPR was carried out. For this reason, a fresh catalyst sample was submitted to a typical TPR experiment, R1, from room temperature to 350 °C at a heating rate of 10 °C min⁻¹. After reduction the sample was cooled down until room temperature under the reductive mixture flow and it was kept under reductive atmosphere during c.a. 1000 min. After that, a new reduction

experiment was carried out (R1). This sequence was repeated three times (R2, R3 and R4). TPR profiles are shown in Fig. 4a. In R1, the reduction extent was higher than that corresponding to the total reduction of Cu^{2+} , and as it has been discussed in a previous work, this excess was attributed to a contribution for surface oxygen reduction of CeO_2 [30]. During the first TPR, (R1), Cu^{2+} species were quantitatively reduced to Cu^0 . The following TPR experiments (R2, R3 and R4), without any intermediate oxidation, revealed hydrogen consumptions with similar profiles. This behavior could be attributed to the reduction of species generated from Cu^0 oxidation in the presence of CeO_2 . A similar experiment to that illustrated in Fig. 4a was carried out over Cu supported on ZnO, Fig. 4b. The first TPR, T1, revealed the presence of one peak whereas the second one, T2, was almost flat. The above TPR data suggested that the re-oxidation assisted by CeO_2 could contribute to the formation and stabilization of oxidized copper particles $\text{Cu}^{\delta+}$ under reaction conditions. The performance of the catalyst here described is in line with those results obtained over Cu/ZrO₂ catalyst. Szzybalski et al. [39] have reported, by an *in situ* investigation, a correlation between the amount of oxygen remaining in the copper particles and the catalytic activity in methanol steam reforming. The interaction between Cu and ZrO₂ stabilizes an active copper microstructure that strongly deviates from that of bulk copper metal.

The oxidation states and the composition of the surface elements were obtained by X-ray photoelectron spectroscopy. Figs. 5–8 show the XPS spectra of Cu 2p, Ce 3d, O 1s and C 1s of the fresh and used catalysts. The samples were submitted to different treatments to simulate the catalyst surface under reaction. The Cu 2p spectra show two peaks corresponding to Cu 2p_{3/2} and Cu 2p_{1/2}, Fig. 5. The as-prepared catalyst exhibits the typical XP spectra of Cu^{2+} with Cu 2p_{3/2} and 2p_{1/2} main peaks appearing at 933.5 eV and 952.9 eV, respectively together with strong shake-up peaks at 942.8 eV and 962.0 eV. The intensity ratio of the shake-up satellite to the main peak was 0.56 and 0.53 for the fresh and used sample, respectively, which are in agreement with the value reported for Cu^{2+} [40]. After a reduction treatment (H_2/Ar at 260 °C for 30 min) a lower Cu 2p_{3/2} binding energy (931.7 eV) and the absence of the shake-up peaks clearly indicate the reduction of copper

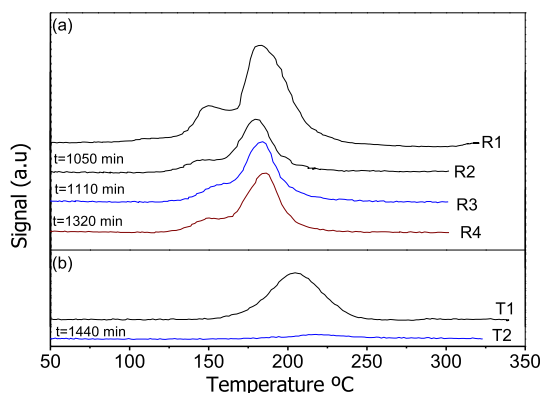


Fig. 4 – Temperature programmed reduction of (a) fresh CuO/CeO₂ and after reduction treatments; (b) fresh CuO/ZnO and after a reduction treatment.

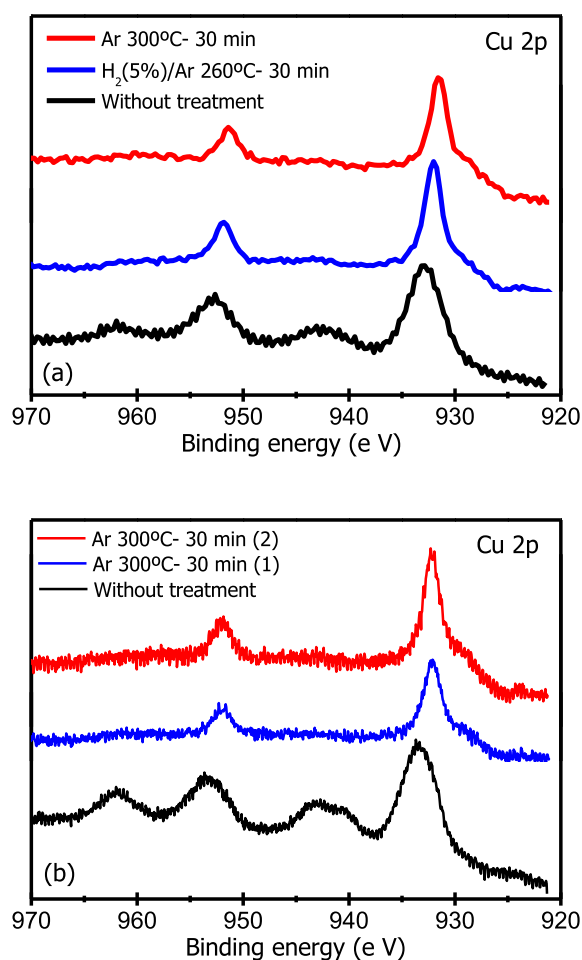


Fig. 5 – X-ray photoelectron spectra of the Cu 2p region for the (a) fresh and (b) used CuO/CeO₂ catalyst.

species (Cu^0). After a subsequent treatment in inert (Ar at 300 °C for 30 min), the Cu 2p_{3/2} binding energy is slightly higher (932.1 eV) suggesting the partial presence of Cu^{1+} . These results indicate that Cu^{2+} is reduced to Cu^0 after a reductive treatment, as expected, and probably it is partially re-oxidized in an inert atmosphere. The Auger parameter (α) could be used as reference for distinguishing the Cu^+ and Cu^0 oxidation states [41,42]. From the Auger electron spectra (not shown), the α parameters were estimated and shown in Table 3. The fresh sample exhibits an Auger parameter of 1849.8 eV, lower than others in literature for the existence of CuO-like species [42] which could be related to the CuO– CeO_2 interactions. Batista et al. [43] have reported a Auger parameter of 1847.2 eV for CuO(1.5 wt.%Cu)/ γ -Al₂O₃ catalyst and they have attributed the difference with bulk compounds to initial state effects (i.e. variation of the core level energies with cluster size) and final state relaxation effects which were correlated with the polarizability of the support. For CuO/ZrO₂ and CuO/SiO₂ catalyst, Espinós et al. [44] have reported values of 1849.6 eV and 1849.8 eV, for ZrO₂ and SiO₂ supported CuO, respectively. They have stated that the α parameter is very sensitive to the dispersion degree of the supported phase and to the type of support on which they are deposited. Auger

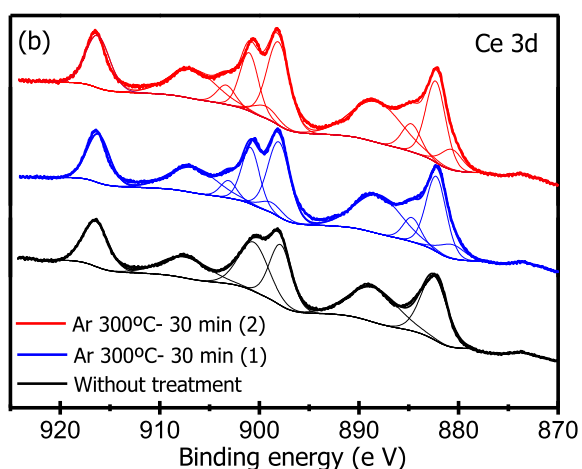
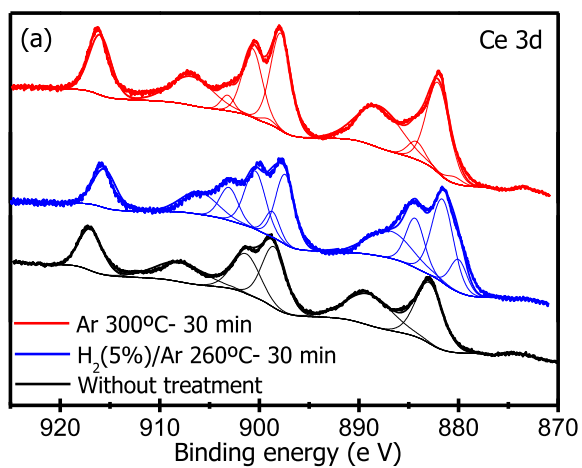


Fig. 6 – X-ray photoelectron spectra of the Ce 3d region for the (a) fresh and (b) used CuO/CeO₂ catalyst.

parameters of 1851.0 and 1850.9 eV for reduced sample and after an inert treatment, respectively, match with that of Cu⁰ rather than Cu¹⁺ [41,42]. Thus, the Auger electron spectra confirm that copper in its metallic state is stable under an inert atmosphere, at least during 30 min under an inert flow.

The Cu 2p spectra for used sample (Fig. 5b) show two peaks corresponding to Cu 2p_{3/2} and Cu 2p_{1/2} and also satellite peaks corresponding to Cu²⁺. The presence of oxidized copper species indicates a reoxidation of surface by air exposure. The BE and α values are the same as those of fresh sample. However, after two consecutive inert treatments the presence of Cu⁰ is confirmed.

The Cu 2p XPS of reduced sample and after inert treatments indicate an important decrease in the surface Cu content. Thus, the surface concentration decreases from 5% to 2–3% on the fresh sample and from 10% to 2% on the used sample suggesting a sintering after the treatments. Therefore, it calls the attention the increase in the surface Cu content after being used in SRM reaction from 0.05 to 0.10. This could be explained due to Cu segregation out of the ceria lattice. The ionic radius of Cu²⁺ (0.76 Å) is smaller than that of Ce⁴⁺ (0.97 Å), hence, there is a possibility of partial Cu²⁺

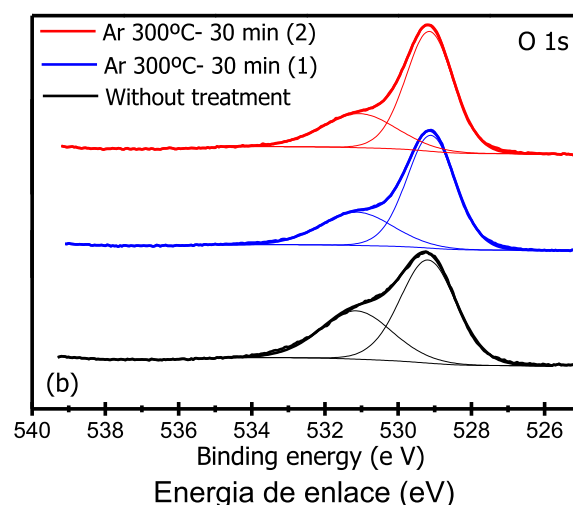
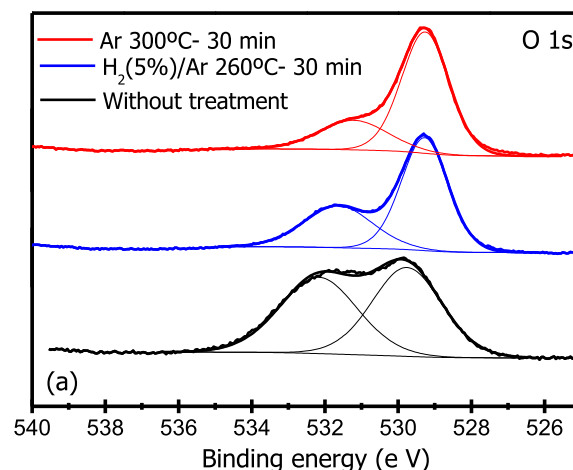


Fig. 7 – X-ray photoelectron spectra of the O 1s region for the (a) fresh and (b) used CuO/CeO₂ catalyst.

incorporation into the ceria lattice during calcination [41]. Other explanation could be a redispersion of the Cu particles due to the changes in the atmosphere during the cooling down of catalytic bed and the heating-up in the inert flow. Similar results were reported on Cu/ZnO water gas shift catalysts for shut-down/start-up operation [45].

Fig. 6 shows the XP spectra of Ce 3d region. For the fresh sample, at least six peaks centered at 882.9, 889.5 and 898.8 eV for Ce 3d_{5/2} and 901.4, 908.5 and 917.2 eV for Ce 3d_{3/2} eV are observed. They refer to three pairs of spin–orbit doublets and correspond to Ce⁴⁺ species in CeO₂. After being reduced in H₂(5%)/Ar, the XP spectrum reveals the presence of Ce³⁺. According to Table 3, the Ce³⁺/Ce⁴⁺ surface ratio increases from 0 in the as-prepared catalyst to 0.33 after reduction, which clearly evidences the support reduction. After an inert treatment in Ar at 300 °C, the Ce³⁺/Ce⁴⁺ surface ratio markedly decreases to 0.07 but it is still higher than the ratio on the as-prepared catalyst. This behavior is an indication of the re-oxidation of cerium although the initial chemical state is not completely restored.

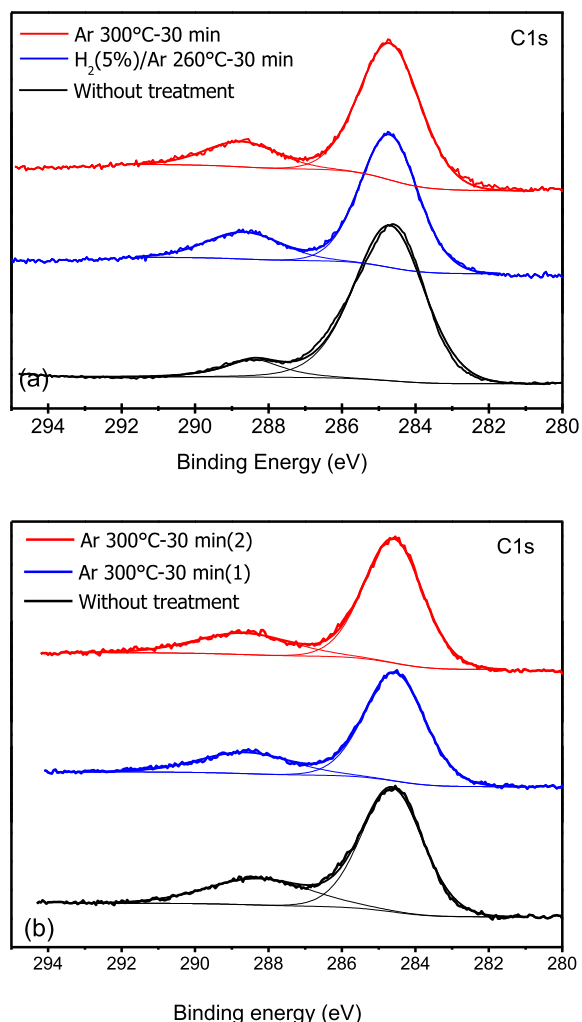


Fig. 8 – X-ray photoelectron spectra of the C 1s region for the (a) fresh and (b) used CuO/CeO₂ catalyst.

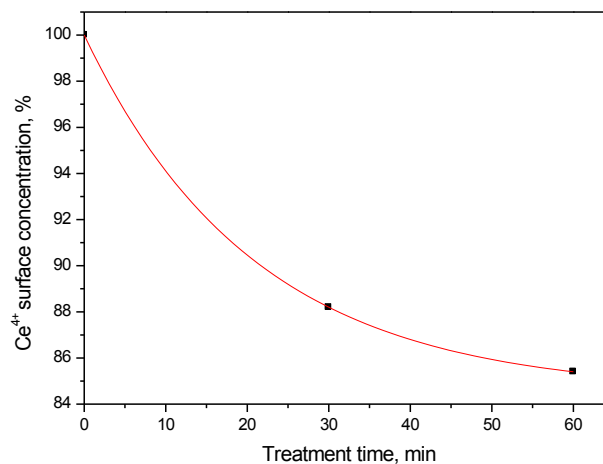


Fig. 9 – Ce⁴⁺ Surface concentration with respect to the total cerium as a function of treatment time for used catalyst.

If there was contamination with oxygen during the stopping time (around 1000 min) in the discontinuous regime, the Cu⁰ can be oxidized to Cu²⁺. According to XPS results, before starting the second reaction cycle, the inert treatment would reduce the copper surface again and this would be the oxidation state before beginning a new reaction cycle. This seems to be in contradiction with the TPR results. However, the time exposed under the inert atmosphere during the shut-down is substantially higher than the time of treatment in the XP spectrometer. Then, an oxidation to Cu^{δ+} assisted by CeO₂ is possible. Besides, an evidence of the Cu^{δ+} presence is the increase of temperature bed at the beginning of each cycle as a consequence of Cu^{δ+} reduction to Cu⁰. Something similar happens with the ceria after reoxidation by contact with air. Ceria is partially reduced by the inert treatment, showing Ce³⁺/Ce⁴⁺ surface ratio of 0.15 after first treatment and 0.17 after the second one. The Ce⁴⁺ surface concentration as regards to the total cerium with cycles, displayed in Fig. 9,

Table 3 – Surface composition, binding energy and α parameter determined by XPS for CuO/CeO₂ catalyst.

| Sample | Treatment | Cu 2p _{3/2} BE, eV | Cu Auger KE, eV | α eV | Ce 3d BE, eV | Cu/Ce | Cu/O | Ce/O | (C/O) ^a | Relative surface concentration | | | | Ce ³⁺ /Ce ⁴⁺ |
|----------------------------|---|--------------------------------|-----------------------|----------------|-----------------|-------|------|------|--------------------|--------------------------------|------|------|-----------------------|------------------------------------|
| | | | | | | | | | | Ce | Cu | O | C _{288.8 eV} | |
| Fresh | Without treatment | 933.3 | 915.9 | 1849.1 | 916.5 | 0.31 | 0.07 | 0.22 | 0.44 | 0.14 | 0.05 | 0.67 | 0.14 | – |
| | H ₂ (5%)/Ar 260 °C–30 min | 931.7 | 919.3 | 1851.0 | 916.1 | 0.09 | 0.03 | 0.37 | 0.34 | 0.24 | 0.02 | 0.65 | 0.09 | 0.33 |
| | Ar 300°C–30 min | 932.1 | 918.8 | 1850.9 | 916.2 | 0.12 | 0.05 | 0.41 | 0.36 | 0.26 | 0.03 | 0.64 | 0.07 | 0.07 |
| Used in SRM reaction | Without treatment | 933.3 | 916.5 | 1849.8 | 916.5 | 0.59 | 0.17 | 0.29 | 0.50 | 0.18 | 0.10 | 0.61 | 0.11 | – |
| | Ar 300 °C–30 min | 932.2 | 918.8 | 1851.0 | 916.2 | 0.06 | 0.03 | 0.43 | 0.45 | 0.27 | 0.02 | 0.62 | 0.09 | 0.15 |
| | Ar 300°C–30 min | 932.2 | 918.8 | 1851.0 | 916.2 | 0.05 | 0.02 | 0.46 | 0.44 | 0.28 | 0.02 | 0.62 | 0.08 | 0.17 |

BE: Binding energy; KE: Kinetic energy; α : Modified Auger parameter ($\alpha = BE + KE$).

^a Non-adventitious carbon to oxygen (from peak at ca. 531.8 eV) ratio.

decreases tending to a steady-state value. This behavior suggests that during the cycles of “shut down, start up” the ceria remains partially reduced and the active site could be related to $\text{Cu}^0\text{--Ce}^{3+}/\text{Ce}^{4+}$ interactions.

The core-level O1s XP spectra of the fresh and used samples shown in Fig. 7 are broad due to the overlapping of two peaks, indicating the presence of more than one kind of oxygen with different chemical characteristics. The main peak located at 529.7 eV corresponds to the oxygen lattice of cerium oxide and copper oxide and the peak at 532.2 eV could be assigned to oxygen in CO_3^- [32,46]. For the fresh catalyst (Fig. 7a), peaks at 529.3 and 531.5 eV are observed after the treatments in both reductive and inert atmosphere; the first one assigned to oxygen in CeO_2 (the copper is in metallic state). For the used sample the two peaks appear at 529.1 and 531.2 eV regardless of the treatment (Fig. 7b). The peak at 531.5–531.2 eV could be assigned to oxygen species associated to oxidized carbon.

In the C1s spectra for both, fresh and used samples with and without treatments, two peaks are observed, one at 284.6 eV (which corresponds to the adventitious carbon) and other at 288.4–288.8 eV assigned to $-\text{COOR}$: CO_3^- oxidized carbon species [21,32,47], Fig. 8. After treatment in a reductive atmosphere the carbon relative concentration (peak at ca. 288.8 eV) decreases from 0.14 to 0.09. On the other hand, the non-adventitious carbon to oxygen (from peak at ca. 531.8 eV) ratio decreases from 0.44 to 0.34, close to that expected for carbonate. This suggests that a fraction of the non-adventitious carbon which are initially present on the surface of the sample was removed with the reduction treatment at 300 °C during 30 min. For the used sample, a C/O ratio of 0.50 and 0.44 was observed in the sample without treatment and after two treatments in inert at 260 °C, respectively; which could be due to a partial remotion of more labile oxidized carbon species.

In summary, from XPS results it is concluded that the inert atmosphere reduces the surface CuO, the Ce^{3+} is partially oxidized to Ce^{4+} and the $\text{Ce}^{3+}/\text{Ce}^{4+}$ couple is present during reaction. Besides, a substantial amount of carbonates/formates is removed under an inert treatment, allowing the regeneration of the active surface.

According to the results of the present work the best copper species active for SRM on this CuO/CeO₂ catalyst were obtained by reduction of CuO under reaction conditions. These species could have different catalytic properties in comparison with those produced by the pre-reduction with H₂. Besides, the overreduction of CeO₂ is avoided. The deactivation was mainly due to the formation of carbonates and/or formates on the catalyst surface more than sintering. The catalyst activity could be recovered by burning in air at 400 °C or in inert flow at the reaction temperature. The complex structural dynamic of catalyst under reforming conditions should be studied by *in-situ* techniques to get a better understanding of surface state of catalyst under SRM reaction.

Conclusions

Performance in methanol steam reforming over a CuO/CeO₂ catalyst with 5 wt.%Cu was studied by using two operation

regimes: continuous and discontinuous. The continuous tests were carried out at three different temperatures between 260 and 300 °C. In all the cases the catalyst was initially very active but it lost the activity with time on stream. In the discontinuous tests the catalyst was reactivated after the stop period in inert, recovering almost the initial conversion. This behavior was attributed to the desorption of carbonate species. The observed deactivation was mainly assigned to the formation of carbonates and/or formates on the catalyst surface. The catalytic system was easily regenerated by air flow at 400 °C or by inert flow at the reaction temperature reaching almost the same initial conversion. The H₂ pre-reduction of catalyst should be avoided for reaching a higher stability. CuO/CeO₂ is a promising catalyst for SRM able to operate under “shut down-start up” cycles.

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