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Short Communication

WGS activity of a novel Cu–ZrO_2 catalyst prepared by a reflux method. Comparison with a conventional impregnation method

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ABSTRACT

The activity in the WGS reaction of Cu/ZrO_2 catalysts prepared by a method of refluxing in an aqueous NH_4OH solution is studied. It is shown that at 3% Cu load the methods of impregnation over monoclinic or tetragonal ZrO_2 do not produce active catalysts for the WGS reaction. However, the method of refluxing generates highly active catalysts with Cu loads of 3% (w/w) or higher. The activity of the catalysts prepared by refluxing is associated with the formation of small Cu clusters, which would allow the regrouping of the H atoms to generate molecular H_2 in the presence of the crystalline tetragonal ZrO_2.

1. Introduction

Considering the high levels of pollution produced by the combustion of organic materials, energy conversion by H_2 fuel cells is a very attractive alternative since the only product is H_2O [1]. Hydrogen can be generated in various ways, such as water electrolysis processes, reforming of natural gas with water vapor, and reforming alcohols. The output stream from a hydrocarbon (e.g., natural gas) reformer contains large amounts of CO, between 8% and 10% [2]. This CO can be conveniently transformed into CO_2 through the WGS reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$, thereby increasing the concentration of H_2 in the effluent. Industrially, the WGS reaction takes place in two stages: a high temperature stage (HT-WGS between 350 and 450 °C) using a catalyst based on Fe and Cr oxides in which the CO content is reduced to levels close to 3%, and a second lower temperature stage (LT-WGS, between 200 and 300 °C), in which the CO level is reduced to about 1% using a Cu/ZnO or Cu/ZnO/Al_2O_3 catalyst [3].

The commercial catalyst based on Cu–ZnO has some problems such as low stability above 300 °C and that it is pyrophoric when exposed to air [4]. Also, since the reduction of the catalyst is highly exothermic, the reduction must be carried out slowly. These characteristics make it inconvenient for use in vehicles, leading to the study of other catalytic systems. Ruettinger et al. [5] reported a new catalyst that can replace Cu/ZnO, with the advantage of not being pyrophoric, but no details are given of its composition. Ilinich et al. [6] report on the activity of a Cu–Al_2O_3–$CuAl_2O_4$ catalyst. Other supports, like Al_2O_3 [7,8] or MnO [9], have also been reported in the literature.

Some years ago Ko et al. [10] reported that Cu–ZrO_2 catalysts prepared by coprecipitation have good catalytic activity in the WGS reaction, even better than that of a commercial Cu–ZnO–Al_2O_3 catalyst. In a more recent publication [11], we showed that both the Cu load and the crystalline phase of zirconia have a substantial effect on the activity of Cu catalysts supported on ZrO_2. We found that active WGS catalysts are obtained when tetragonal ZrO_2 was used and only when bulk CuO was formed. On the other hand, the catalysts prepared on the monoclinic ZrO_2 are completely inactive in any range of copper loading studied here. Therefore, it was found that the active copper phase on tetragonal zirconia was bulk CuO.

Beside the work mentioned above, and to the best of our knowledge, there are no other reports on the use of the Cu–ZrO_2 system in the WGS reaction. The study of the Cu/ZrO_2 system is interesting not only because of its possible applications as a WGS catalyst, but because it is used in reactions in which the WGS reaction takes part, such as the reforming of alcohols [12].

This paper reports the activity of a new type of Cu–ZrO_2 catalysts prepared by a reflux method developed in our laboratory [13], and compares it with the activity of Cu/ZrO_2 catalysts prepared by the traditional method of ZrO_2 impregnation. The reflux method not only generates tetragonal zirconia but also produces particles of CuO of higher size than those obtained using the impregnation method with tetragonal zirconia as support. Therefore, the catalysts prepared by reflux are good candidates for the WGS reaction, which motivates a more profound study of these materials.

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2. Experimental

2.1. Catalyst preparation

2.1.1. Reflux method

The method has been described in detail elsewhere [13]. Briefly, approximately 6 g of commercial hydrous zirconia (MEL Chemicals) is refluxed for 9 h in an ammonia solution containing the appropriate amount of Cu nitrate. Then, the resulting solid is filtered, dried at 105 °C overnight, and calcined in an oven at 500 °C for 3 h.

The catalysts were prepared with 1%, 3%, and 6% (w/w) Cu content, which are named 1Cu–Zr(R), 3Cu–Zr(R), and 6Cu–Zr(R), respectively. The loading of Cu is adjusted by using refluxing solutions with different concentrations of copper nitrate as follows: a proper amount of commercial hydrous zirconia is mixed with 250 ml of a NH_4OH solution. The concentration of the aqueous ammonia solution used in the refluxed method is 9.4% (w/w). Then depending on the copper loading (1%, 3%, or 6%), an adequate amount of copper nitrate is added to the previous solution to obtain the corresponding metal loading. Then this mixture is refluxed at boiling point for a certain period of time. Finally, the solid is filtrated, dried overnight at 105 °C, and calcined at 500 °C for 3 h. ICP analysis of the filtrated solutions ensures that the added copper was almost fully (more than 99%) incorporated into the support.

2.1.2. Impregnation method

Two series of catalysts were prepared by the dry impregnation method, using tetragonal ZrO_2 and monoclinic ZrO_2 as support. The method has been described in details elsewhere [13]. Tetragonal ZrO_2 was obtained by the previously described procedure, but in the absence of the Cu precursor, as we had described in a previous paper [14]. Monoclinic ZrO_2 was obtained by direct calcination of the MEL commercial hydrous zirconia at 700 °C for 3 h, as described in the same paper [14]. These supports are impregnated with an aqueous solution containing the proper amount of Cu nitrate hexahydrate (Merck, p.a.), to obtain the 1%, 3% and 6% (w/w) Cu loads. In the case of the catalysts prepared over tetragonal ZrO_2, they were also prepared with 4% and 5% Cu loads. The aqueous solution of copper nitrate and the ZrO_2 support are mixed in a beaker under continuous stirring. The amount of aqueous solution is just enough to fill the available pore volume of the support. Water is slowly eliminated by a heated plate under stirring. Once finished, a dried powder is obtained, which is later dried at 105 °C overnight and calcined at 500 °C for 3 h in a muffle furnace.

The nomenclature used for these catalysts is xCu/Zr-y, where "x" indicates the percentage of Cu and "y" indicates the crystalline phase: y = t corresponds to tetragonal ZrO_2, and y = m corresponds to monoclinic ZrO_2.

2.2. Characterization of the catalyst

Determination of the specific BET surface area of the catalysts was made by N_2 adsorption in a Micromeritics Model ASAP 2010 sorptometer. The samples were previously degassed at 200 °C.

The crystal structure of the different catalysts was determined by XRD on a Siemens D-5000 diffractometer using Cu Kα radiation and a scan rate of 0.02° per minute.

The temperature programmed reduction (TPR) analyses were done in a conventional system equipped with a TCD detector, with a flow rate of 20 cm^3/min of a gaseous mixture of 5% H_2 in Ar at a heating rate of 10 °C/min between ambient temperature and 600 °C.

2.3. Catalytic activity measurement

The catalytic activity was measured in a tubular plug-flow reactor loaded with 0.2 g of catalyst. Before reaction the catalysts were reduced in situ at 350 °C for 1 h in a flow of 20 cm^3/min of 5% H_2 in Ar. The gas feed consisted of 2% CO and 6% H_2O, in He. Water was injected by a syringe pump (SAGE Instrument, model 341A) to an evaporator connected in line with the inlet of the reactor and maintained at 150 °C. The CO/He stream flowed through the evaporator at a rate of 70 cm^3/min. The reactor temperature was increased at 3 °C/min up to 300 °C, and kept at that temperature to determine the steady state activity under reaction conditions. The inlet and outlet gases were analyzed in a gas chromatograph (Perkin Elmer Autosystem) equipped with a thermal conductivity detector (TCD) and a CTR-1 column (Alltech), which allowed the determination of the concentrations of H_2, CO, and CO_2.

3. Results and discussion

3.1. Characterization

The BET specific surface area of the various catalysts prepared by the different methods is shown in Table 1. It is seen that the largest specific areas are obtained in the catalysts prepared by the reflux method (around 200 m^2/g), followed by those prepared over tetragonal ZrO_2 (around 100 m^2/g), and finally by those prepared over monoclinic ZrO_2 (30 m^2/g).

The TPRs of the catalysts prepared by the reflux method and by the impregnation method on tetragonal ZrO_2 and monoclinic ZrO_2 are shown in Fig. 1A, B and C, respectively. In the case of catalysts prepared by impregnation, the literature [see 15 and references cited there] reports three reduction peaks: two overlapping peaks at low temperature (<200 °C) assigned to highly dispersed Cu species, and a third peak at a temperature close to 300 °C, associated with bulk CuO.

As seen in Fig. 1A, the catalyst with the lowest Cu load, 1Cu–Zr(R), presents a broad peak centered at 350 °C, which in our previous work was associated with highly dispersed Cu species interacting strongly with the ZrO_2 support [13]. As the Cu load is increased to 3%, the reduction peaks are displaced to lower temperatures. This shift in reduction temperature is not totally clear but one can postulate that at low Cu/(ZrO_2 area) ratios, copper initially occupies sites as isolated Cu^{+2} ions. The latter species strongly interact with the surface atoms of ZrO_2. When increasing the loading of copper, it occupies highly dispersed surface sites but with a weaker interaction with the support. The latter facilitates the reduction of copper. When the Cu load reaches 6%, catalyst 6Cu–Zr(R), two reduction peaks with temperature maxima close to 180 °C and 220 °C are clearly seen. These peaks were associated with the reduction of highly dispersed Cu species, but forming small size CuO clusters [13].

The H_2 consumption curves of the catalysts prepared by the impregnation of the tetragonal ZrO_2 support, Fig. 1B, show that at low Cu loads, on the 1Cu/Zr-t and 3Cu/Zr-t catalysts, only the peaks corresponding to the reduction of highly dispersed species are observed. The catalyst with 4% Cu shows a very small amount of bulk CuO. At higher Cu loads, on the 5Cu/Zr-t and 6Cu/Zr-t catalysts, a third intense peak corresponding to the reduction of bulk CuO appears.

In the case of the catalysts prepared by the impregnation of monoclinic ZrO_2 (Fig. 1C), the reduction peaks of the highly dispersed CuO species are seen with the three catalysts. The peak of bulk CuO

Table 1
BET specific surface area of the various catalysts.

Catalyst	Specific surface (m^2/g)
1Cu–Zr(R)	203
6Cu–Zr(R)	180
1Cu/Zr-t	107
6Cu/Zr-t	102
1Cu/Zr-m	36
6Cu/Zr-m	30

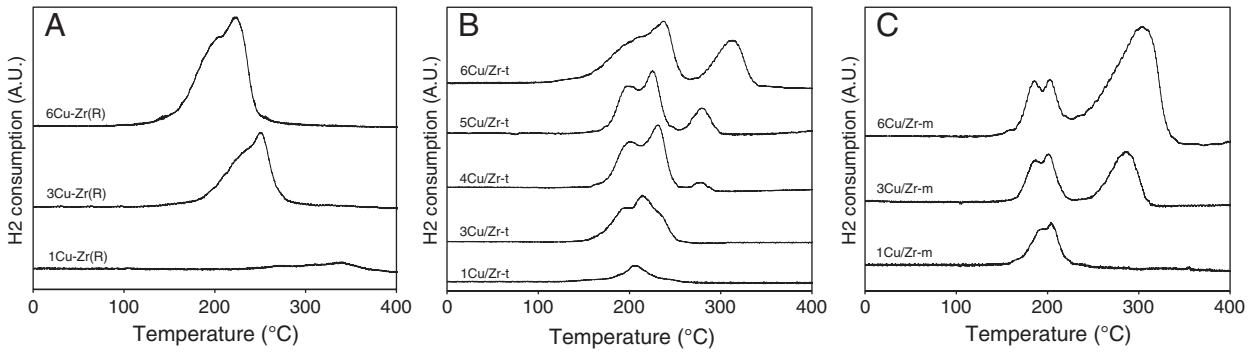

Fig. 1. H_2 consumption profiles during TPR experiments for catalysts prepared by different method: (A) Catalysts prepared by the reflux method; (B) catalysts prepared by the impregnation of tetragonal zirconia; (C) catalysts prepared by the impregnation of monoclinic zirconia.

appears in 3Cu/Zr-m, and the size of the bulk CuO peak of catalyst 6Cu/Zr-m increases. As discussed previously [15], the appearance of bulk CuO depends on the surface area of the ZrO_2, and the results obtained are consistent with a dispersion capacity of 4.5 Cu atoms/nm^2 of ZrO_2. Below that value, highly dispersed Cu species are formed, and at higher values the other CuO species are formed.

Fig. 2 shows the XRD diffractograms of the different catalysts. In Fig. 2A it is observed that the catalysts prepared by refluxing have the characteristic peaks of the tetragonal ZrO_2 structure. No peaks corresponding to bulk CuO are detected in any of these catalysts, in agreement with the TPR experiments.

Fig. 2B shows the diffractograms corresponding to the catalysts prepared by impregnation over tetragonal ZrO_2, in all of which the characteristic peaks of tetragonal ZrO_2 are seen. Furthermore, low intensity peaks corresponding to monoclinic ZrO_2 are seen, indicating the presence of a small amount of this second polymorph. For Cu loads between 1% and 4%, no peaks assigned to bulk CuO are observed. However, when the Cu load is equal to or greater than 5%, in catalysts 5Cu/Zr-t and 6Cu–Zr-t, a peak at $2\theta = 38.7°$ is clearly seen, which is characteristic of the tenorite structure of CuO. It is therefore clear that the formation of crystalline bulk CuO starts with catalyst 5Cu/Zr-t, in agreement with the TPR experiments.

Finally, Fig. 2C shows the diffractograms of the catalysts prepared over monoclinic ZrO_2. In this case the peaks corresponding to ZrO_2 and a small amount of tetragonal ZrO_2 can be seen, in agreement with previous observations [14]. The peaks corresponding to crystalline CuO ($2\theta = 35.5°$ and 38.7°) are not easily observed because they overlap with the peaks of monoclinic ZrO_2 ($2\theta = 35.3°$ y 38.6°). However, in catalysts 3Cu/Zr-m and 6Cu–Zr-m the intensity of the peaks at 35.5° and 38.6° is increased compared to the other peaks of ZrO_2, indicating the formation of bulk CuO, in agreement with the TPR results.

3.2. Catalytic activity

The results of the conversion of CO into CO_2 with the catalysts prepared by the different methods at a constant temperature of 300 °C are shown in Fig. 3. As seen in Fig. 3A, the catalysts prepared by the reflux method show activity at Cu loads equal to or greater than 3%, and the activity increases with the Cu load. Catalyst 3Cu–Zr(R) yields a conversion close to 32%, while catalyst 6Cu–Zr(R) has an activity of around 42%.

Fig. 3B shows the conversion curves over time for the catalysts obtained by impregnation over tetragonal ZrO_2. It is seen that the catalysts with Cu loads between 1% and 4%, 1Cu/Zr-t, 3Cu–Zr-t, and

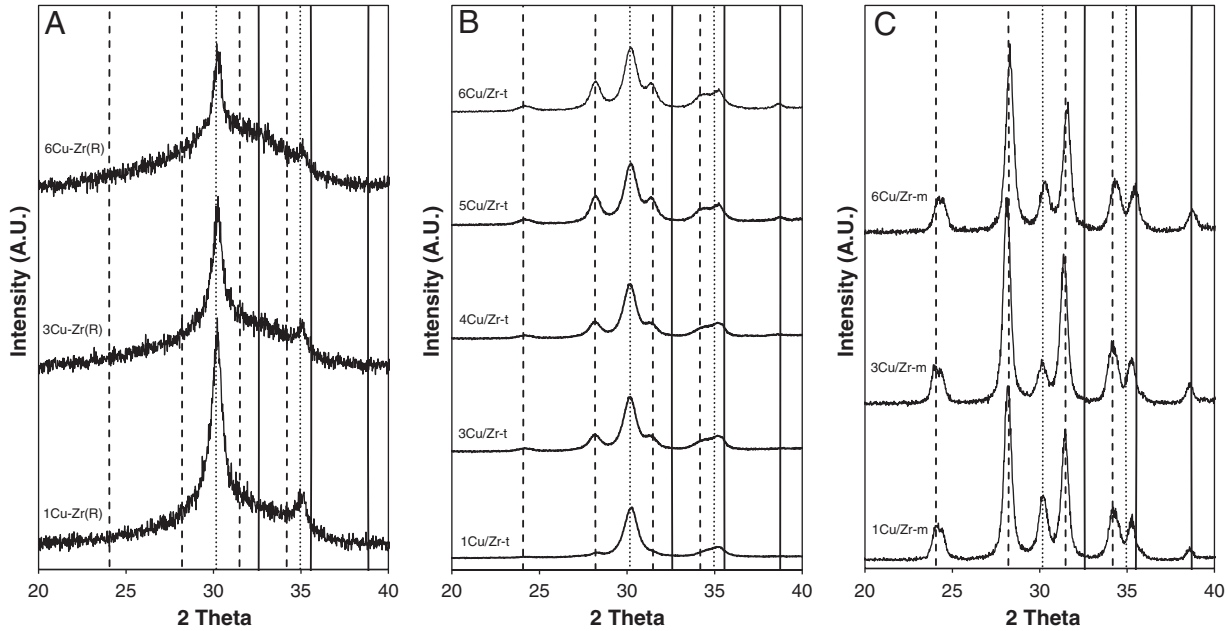

Fig. 2. X-ray diffraction patterns for catalysts prepared by different method: (A) Catalysts prepared by the reflux method; (B) catalysts prepared by the impregnation of tetragonal zirconia; (C) catalysts prepared by the impregnation of monoclinic zirconia. (−) CuO diffraction peaks, (−) ZrO_2 monoclinic, and (…) ZrO_2 tetragonal.

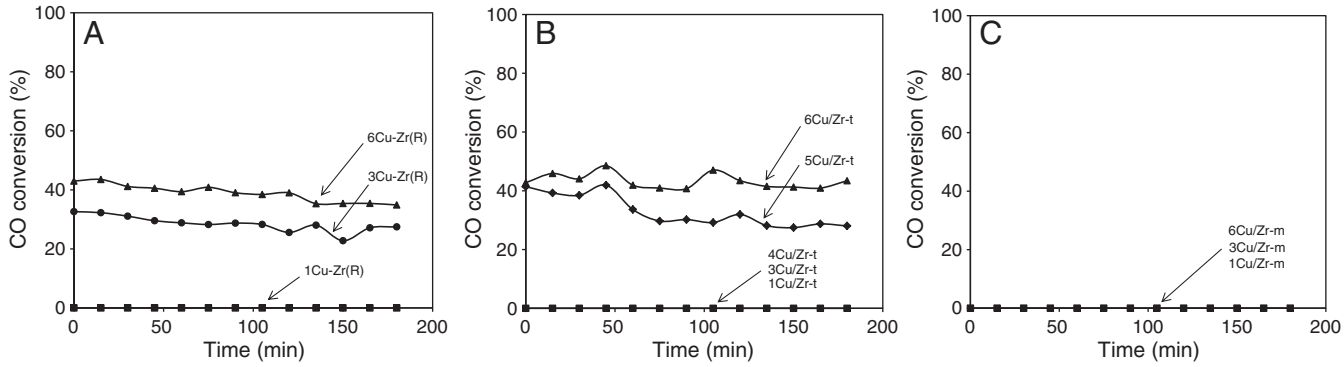

Fig. 3. CO conversion versus reaction time for catalysts prepared by different method at 300 °C. (A) Catalysts prepared by the reflux method; (B) catalysts prepared by the impregnation of tetragonal zirconia; (C) catalysts prepared by the impregnation of monoclinic zirconia.

4Cu–Zr-t, are practically inactive in the WGS reaction. Only when the Cu load is equal to or higher than 5%, i.e. catalysts 5Cu/Zr-t and 6Cu/Zr-t, the catalysts show activity, which coincides with the clear detection of bulk CuO (see Fig. 1B). These kinetics results support the conclusion that the active Cu species in the catalysts supported over tetragonal ZrO_2 is bulk CuO, as stated previously [11]. This result contrasts with that obtained with the refluxed 3Cu–Zr(R), which has a similar activity than the 5Cu/Zr-t but no appearance of bulk CuO (see Fig. 1A).

The activity of the catalysts prepared by the reflux method, in which the bulk CuO species is not formed, may be due to the size of the CuO clusters, which are sufficiently large to fulfill the same function as the bulk CuO in the catalysts supported over tetragonal ZrO_2. According to Fischer and Bell [16], this function would be to allow the association of the H atoms that migrate from the ZrO_2 support to the Cu particles. However, a more detailed study would be needed to confirm this hypothesis. Finally, Fig. 3C shows the results of the conversion of CO in the case of the catalysts obtained by impregnation over monoclinic ZrO_2. It is seen that regardless of the Cu load, and in agreement with our previous work [11], the catalysts supported on monoclinic ZrO_2 have negligible activity in the WGS reaction. The absence of activity on the catalysts prepared on monoclinic ZrO_2 is possibly due to the high stability of formate species on the surface, which decomposition is a necessary step in the formation of H_2 and CO_2 [11].

It is clear, therefore, that at relatively low Cu loads the reflux method generates catalysts that are active in the WGS reaction, something that cannot be achieved using the classical impregnation methods, even when the crystalline tetragonal ZrO_2 phase is used as support. These results not only confirm that the tetragonal phase is a requirement to achieve activity but also they demonstrate that the catalyst's preparation method can help to finely tune the amount of metal needed to achieve an important activity.

4. Conclusions

This paper shows that the method of preparation of CuO–ZrO_2 catalysts by refluxing in an NH_4OH solution generates catalysts that are active in the WGS reaction at Cu loads lower than those found in Cu/ZrO_2 catalysts prepared by impregnation.

This activity at low Cu loads might be explained by the formation of sufficiently large Cu clusters to allow the recombination of H atoms, and by the presence of the crystalline tetragonal ZrO_2 phase.

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