



## ZrO<sub>2</sub> and Cu/ZrO<sub>2</sub> Sol-Gel Synthesis in Presence of Microwave Irradiation

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**Abstract.** The sol-gel technique with a microwave irradiation was used to synthesize ZrO<sub>2</sub> and Cu/ZrO<sub>2</sub> solids at various pH values and hydrolysis catalysts. Microwave irradiation induces ZrO<sub>2</sub> tetragonal phase formation at almost any pH. The copper was bonded through oxygen bonds to the zirconia lattice. The introduction of copper favored the support acidity.

**Keywords:** zirconium oxide, copper, sol-gel, microwave irradiation, NO<sub>x</sub> reduction

### Introduction

Performance of catalysts depends on chemical composition, microstructure, texture and morphology among other factors. In the case of Cu supported on ZrO<sub>2</sub>, such effects are crucial for the NO<sub>x</sub> reduction reaction. ZrO<sub>2</sub> behaves, indeed, as a superacid support in presence of dopants, i.e., copper is incorporated to the ZrO<sub>2</sub> network and it reaches non conventional oxidation states.

ZrO<sub>2</sub> may crystallize at temperatures close to 400°C in a monoclinic or tetragonal lattice, but in previous works [1, 2] it has been shown that the most important crystalline phase, for catalytic applications, is the tetragonal. Conventionally, these catalysts are prepared coprecipitating soluble salts as zirconium oxychloride and copper chloride. However, this synthesis method provides a poor copper dispersion and a low surface area (70–90 m<sup>2</sup>/g). Furthermore, the particle size distribution turns out to be very broad [3, 4].

The sol-gel method is often recommended as it provides chemically homogeneous solids and well defined microstructures. With this method, copper may be introduced in the xerogels and aerogels of ZrO<sub>2</sub>, but to reach an adequate acidity, sulfuric acid has to be added to the initial sol as hydrolysis catalyst. Still, if copper chloride is added instead of copper sulfate, the activity of the catalyst in the NO<sub>x</sub> reduction is increased [5–7].

Microwave irradiation has been used in the synthesis of many kinds of solids as ceramics [8–10], micro and mesoporous molecular sieves [11–15], nanocomposites [16], among others. This microwave irradiation method reduces the synthesis time and provides solids with different properties from those obtained through more traditional synthesis methods.

In this work we combined both synthesis methods, i.e., sol-gel and microwave irradiation to prepare ZrO<sub>2</sub> and Cu/ZrO<sub>2</sub> catalysts. The gelling conditions and the hydrolysis catalyst were systematically varied. Microwave irradiation was used during the hydrolysis and condensation steps.

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## Experimental

A first group of  $ZrO_2$  samples was prepared from zirconium n-butoxide (80% in n-butanol, Strem Chem.), terbutanol (99%, Merck) and water, using as hydrolysis catalysts HCl (pH = 3, sample Zr-HCl-3),  $H_2SO_4$  (pH = 3, sample Zr-HS-3),  $CH_3COOH$  (pH = 5, sample Zr-HAc-5) and  $NH_4OH$  (pH = 9, sample Zr-NH-9). The mixture was introduced in glass test tubes and the tubes were hermetically closed and placed in a commercial Philco oven operating at 2.45 GHz and 86 W. The irradiation time was 10 minutes. The obtained white gels were dried in air atmosphere at 70°C.

The second group of samples was synthesized similarly, the only difference was that a solution of copper acetylacetonate (98%, Research Chem.) in water/acetone was added. The amount of copper acetylacetonate solution was enough to obtain 1 wt% of copper in the catalysts (samples CuZr-HCl-3, CuZr-HS-3, CuZr-HAc-5 and CuZr-NH-9).

All samples were calcined at 250, 400 or 600°C for 4 hours at a heating rate of 5°C/minute.

A Siemens D500 diffractometer coupled to a copper anode tube was used for X-ray diffraction studies. Radial distribution functions were obtained from X-ray diffraction patterns measured with a molybdenum anode tube; only in this way it was possible to reach the required high values of the angular parameter. These diffractograms were the input data for the Radiale program [17].

Infrared studies were obtained with a Transform Fourier Perkin-Elmer spectrometer model Paragon 1000. Self-supported samples were prepared and the study was performed in the region 4000 to 400  $cm^{-1}$ .

## Results and Discussion

X-ray diffractograms, Fig. 1, show that  $ZrO_2$  supports treated at 250°C as well as Cu- $ZrO_2$  catalysts are microcrystalline solids, no sharp peaks are observed; only the pH = 9 samples present some diffraction peaks which may be interpreted as crystalline  $ZrO_2$  (JCPDS card 14-0534, tetragonal phase). pH = 9 favors, indeed, the condensation reaction. In this way, larger crystalline particles are formed. No copper crystalline compounds are observed.

As calcining temperature is increased (400 and 600°C) sharp diffraction peaks are obtained showing that zirconia crystallizes with temperature. At 400°C the zirconia peaks were broad showing that the cor-

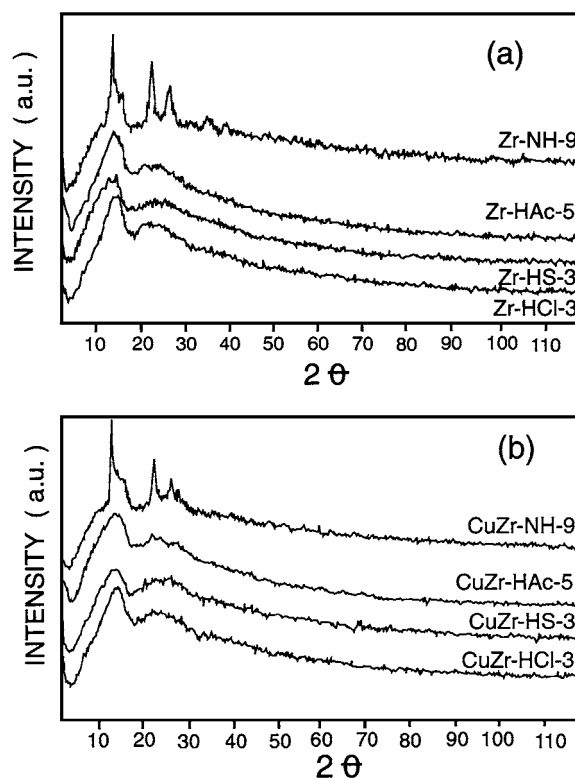


Figure 1. X-ray diffraction patterns of the a)  $ZrO_2$  samples prepared varying the hydrolysis catalyst and b) the Cu/ $ZrO_2$  corresponding samples. All samples were calcined at 250°C.

responding crystallite size was small. When the calcining temperature was 600°C, Fig. 2, the diffraction peaks turned out to be sharp, i.e., the crystalline order was well defined and the corresponding crystals were large, but as the background line was intense even at 600°C, a fraction of the sample was still microcrystalline. Diffractograms of the samples prepared at pH = 3 with HCl present two crystalline phases of  $ZrO_2$  (JCPDS card 14-0534, tetragonal phase and JCPDS card 37-1484, monoclinic phase) whereas all the other preparations only show the tetragonal phase. Samples with or without copper are similar, no crystalline compounds of Cu are found in samples treated either at 400 or 600°C.

Conventional methods [18] provide 100% of tetragonal phase only if the pH is 3–4 or 13–14 at 600°C. For pH 7–10, note that the tetragonal percentage reaches a value as low as 8% [19]. This comparison shows that the crystallization mechanisms follow different routes in each preparation method. Therefore, microwaves appear to induce crystallization of the tetragonal phase

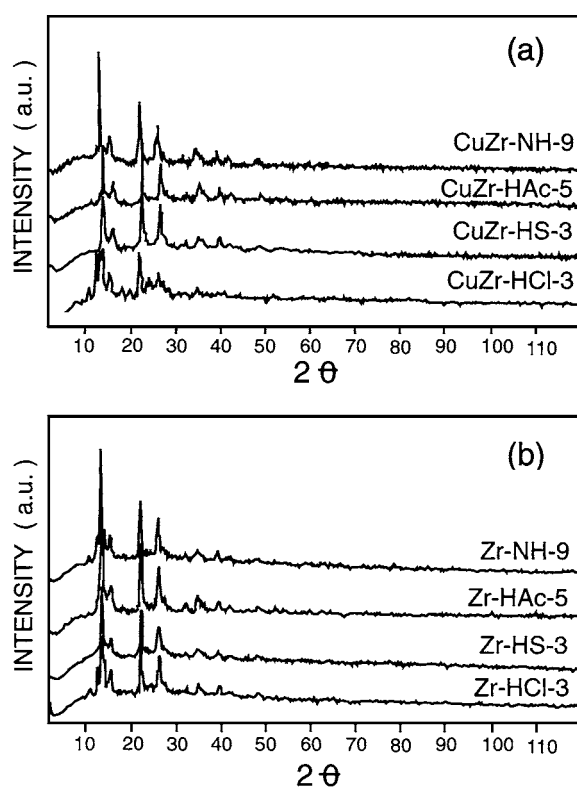


Figure 2. X-ray diffraction patterns of the a) ZrO<sub>2</sub> samples prepared varying the hydrolysis catalyst and b) the Cu/ZrO<sub>2</sub> corresponding samples. All samples were calcined at 600°C.

at almost any pH and monoclinic phase formation is inhibited. It has to be emphasized that the tetragonal phase is the catalytically active structure.

From these X-ray diffraction patterns radial distribution functions were determined to study the short range order in each sample. In all samples treated at 250°C the main peaks are similar showing that the short range order is comparable from sample to sample. In Fig. 3 the first peak at  $r = 1.6$  Å may be attributed to an O—O distance present in the ZrO<sub>2</sub> structure as well as to organic radicals. The variable amount of such radicals explains the difference in the intensity of this peak. The next interatomic distance is at  $r = 2.10$  Å which is the Zr—O distance. At values between 3.4 and 3.6 Å a broad and intense peak due to Zr—Zr and O—O distances appears. A second Zr—Zr distance is present at 4.20 Å; this peak is clearly resolved in samples Zr-HCl-3 and Zr-HAc-5, it seems, therefore, that these samples are better structured than the other two in this domain. The peak at 5.10 Å corresponds to Zr—Zr and O—O distances. It has to be emphasized that only the sample Zr-NH-9 presents intense peaks for distances longer than 6 Å, this sample is, indeed, much more crystalline. The intensity of the peaks of the radial distribution functions of the other samples treated at 250°C for radii larger than 6 Å is very low, hence for radii larger than this value, the materials are not ordered at all. They are, then, constituted

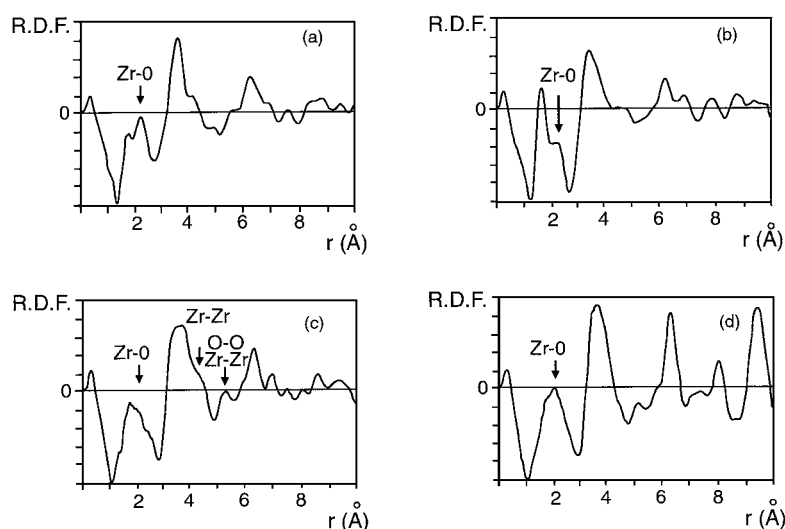


Figure 3. Comparison between the radial distribution functions of the ZrO<sub>2</sub> supports prepared with different hydrolysis catalysts and treated at 250°C: (a) HCl-3; (b) HS-3; (c) HAc-5; (d) NH-9.

by small nuclei whose diameter is close to 15 Å, these nuclei may be occluded in disordered material.

The samples treated at the same temperature (250°C) and copper impregnated presented radial distribution functions which reproduced the previous results, unfortunately the Cu—O distance is 2.65 Å, very close to the Zr—O distances and the technique, whose error is close to 0.1 Å, do not resolve the complex peaks obtained. However, copper is most probably very disperse and distributed into the ZrO<sub>2</sub> matrix; otherwise we would be able to distinguish some interatomic distances corresponding to CuO for large values of  $r$  where the resolution is better.

The radial distribution functions of the samples treated at 600°C, with or without copper are similar. They present clearly defined and intense peaks up to radii of 10 Å, crystallites of ZrO<sub>2</sub> have sintered. Figure 4 illustrates this result comparing the radial distribution functions of Zr-HS-3 and CuZr-HS-3, both calcined at 600°C.

Infrared spectra, Fig. 5, show that all supports treated at 250°C present a broad band ca. 3420 cm<sup>-1</sup> attributed to the elongation vibration of OH groups present in the solvent as well as in water. In sample Zr-HCl-3 a second band at 1624 cm<sup>-1</sup> can be interpreted as an OH bond flexion, this band is not found in Zr-HAc-5 preparation as the hydrolysis step, in this case, is very fast. In the other syntheses this band is shifted up to 1630 cm<sup>-1</sup>.

The band at 1384 cm<sup>-1</sup> due to the scissor flexion vibration of the CH bond, characteristic of organic residues, was found in all spectra. The bands at 1210

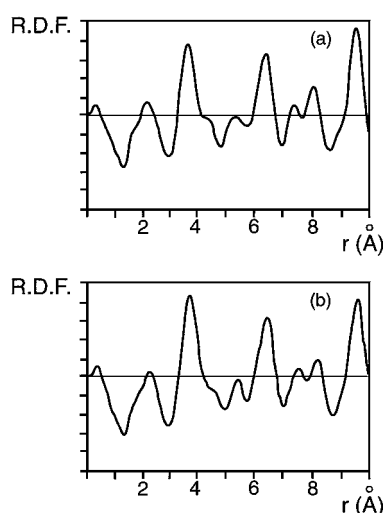


Figure 4. Comparison of the radial distribution functions of the a) Zr-HS-3 and b) CuZr-HS-3 samples treated at 600°C.

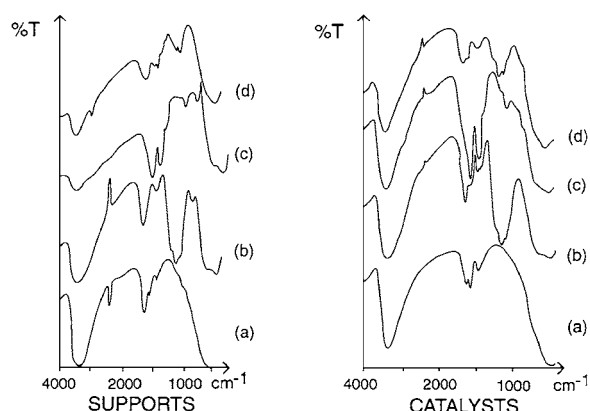


Figure 5. Infrared spectra of the supports and the catalysts treated at 250°C: (a) HCl-3; (b) HS-3; (c) HAc-5; (d) NH-9.

and 1012 cm<sup>-1</sup>, in the sample prepared with sulfuric acid, are due to the strong interaction between sulfate and ZrO<sub>2</sub>. In the same way, the band at 1400 cm<sup>-1</sup> has to be attributed to the S=O bond. The 1130 cm<sup>-1</sup> vibration is an elongation of the O—Zr—O bridged bond which is shifted towards the low energy region as the pH is increased. At pH = 3 zirconia is constituted by small agglomerates whereas at basic pH the condensation is favored and the crystalline particles are larger crystallites, in agreement with the previously discussed X-ray diffraction results.

When copper was incorporated, the spectra differed from the corresponding supports, as follows, Fig. 6: the band at ca. 3422 cm<sup>-1</sup> is more intense, therefore, the hydroxylation degree is higher. Copper, indeed, has been incorporated since the gelation step. It is, then, present into the lattice and it retains hydroxyl groups, improving the zirconia acidity. Furthermore it is well known that Cu(OH)<sub>2</sub> is pale blue whereas CuO is black. Our samples were all white which means that hydroxyl

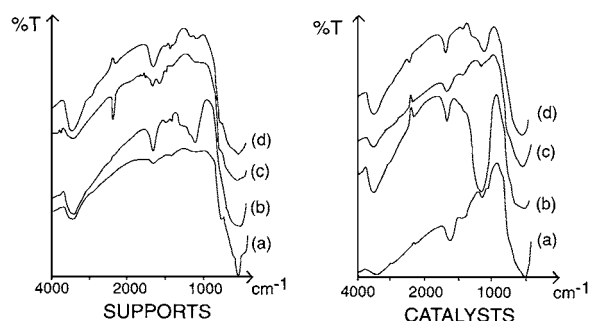


Figure 6. Infrared spectra of the supports and the catalysts treated at 600°C: (a) HCl-3; (b) HS-3; (c) HAc-5; (d) NH-9.

radicals are retained and are not converted to O radicals. In the Zr-HCl-3, the OH flexion water band shifted from 1624 to 1617 cm<sup>-1</sup> with the introduction of copper; this shift only indicates the humidity degree of the sample.

The sample Zr-HCl-3 treated at 600°C spectrum shows that with thermal treatment the band at 3385 cm<sup>-1</sup> is shifted to a higher value (3448 cm<sup>-1</sup>). This support is then partially dehydroxylated. This behavior is reproduced by the other supports, Fig. 6(a). Only the support Zr-HAc-5 does not present a band at 1380 cm<sup>-1</sup> due to the asymmetric flexion vibration of C—H bond, showing that only in this sample all organic residues have been eliminated. In Zr-HS-3 sample treated at 600°C the bands corresponding to sulfate and S=O faded, hence this sample is sulfur free.

The spectra of the copper containing catalysts treated at 600°C, Fig. 6(b), differed from the corresponding supports in the 2289, 1461, 1122 and 1044 cm<sup>-1</sup> bands; these vibrations have to be attributed to copper—oxygen bonds, i.e., to the elongation vibration of Cu—O bonds as copper is in the 2+ valence.

## Conclusion

Samples treated at 250°C were microcrystalline solids, no crystalline copper compounds were observed. However the radial distributions showed that Zr-HCl-3 and Zr-HAc-5 at 250°C were better structured than the Zr-HS-3 and Zr-NH-9 with or without copper.

In all preparations treated at 600°C tetragonal ZrO<sub>2</sub> was obtained; only the HCl, pH = 3, 400–600°C synthesis presented, also, the monoclinic phase. Again diffractograms did not show any copper compound. Microwaves induce tetragonal phase formation at almost any pH, whereas this phase is obtained by conventional sol-gel only for pH 3–4 or 13–14. In this sense, microwave irradiation appears to have an interesting catalytic effect on the physical chemistry of sol-gel reactions. X-ray diffraction and FTIR results

show that copper was bonded through oxygen bonds to the zirconia lattice. Last but not least, copper promoted ZrO<sub>2</sub> acidity.

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