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Nitric oxide reduction catalyzed by amorphous copper–zirconium and copper–titanium alloys

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Abstract

Amorphous alloys have been regarded as interesting from the catalytic point of view because they lack of long range ordering. Moreover, the surface of amorphous alloys is rich in low-coordination sites and defects which play an important role in catalysis. Amorphous Cu–Zr and Cu–Ti ribbons were produced by melt spinning methods. The surface of amorphous materials was prepared, before catalytic tests, by immersion in HF solutions or by H_2 flow reduction. A selective dissolution of first transition metals was exhibited by HF surface pre-treatment. A porous and Cu-rich surface was obtained. In the reduction of NO_x with propylene in presence of O_2, amorphous ribbons exhibited an initial high activity that decreased until the steady-state was reached. This behaviour can be explained with the oxidation of copper active sites by the oxygen contained in the reaction stream. Cu–Zr alloys showed higher catalytic activity than Cu–Ti alloys. Moreover, the HF treatment increased the activity of the materials, and the HF treated alloys were more active than the H_2 treated alloys.

Keywords: Amorphous alloys; Activation surface treatments; Nitric oxide reduction; Propylene; Catalyst

1. Introduction

The development of melt quenching methods allowed metallic glasses to become available from the beginning of the of 1970s, and these metastable materials have attracted the attention of researchers because of their exceptional physical and chemical properties. Since polycrystalline bimetallic catalysts are widely used, and there is a strong structure dependence of the reaction rate in many reactions, the use of amorphous alloys in catalytic syntheses has received considerable attention [1]. In fact, these materials are thought to consist ideally of metal clusters similar to the ones employed in conventional catalysts. However, they are of uniform size, self-supported and placed in a homogeneous chemical environment. The metal ribbon exhibits no porosity and the active surface is very similar to the geometrical surface. Then, the reagent's diffusion towards the active sites is not hindered by porous framework as in supported catalysts [2]. Since amorphous materials can be prepared in a broad range of compositions relatively free from thermodynamic constraints, the possibility of developing special catalysts of high selectivity is large [3]. Unfortunately, the amorphous alloys prepared by liquid quenching do not show high catalytic activity, because the surface of these materials is covered by an oxyhydroxide layer [4]. For this reason glassy alloys are not directly used, but some surface treatments are applied for the enhancement of the catalytic activity.

In the past years amorphous alloys were the subject of many studies [5–13]. Most of these investigations were carried out on zirconium and titanium materials, especially alloyed with copper. In these catalysts the active metal is copper and the activation treatments are made to obtain a surface copper enrichment. In oxidant environment of reaction, the most effective activation treatments to enhance the catalytic activity of Cu–Ti and Cu–Zr alloys are carried out both by immersion in HF solutions and by H_2 attack at reaction temperature [14].

In this work the effect of activation treatments in HF or in H_2 on Cu–Zr and Cu–Ti amorphous alloys structures

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and their catalytic performance in the NO_x reduction with propylene in presence of O_2 is reported and discussed.

2. Experimental details

One mm wide, 30 μm thick $Cu_{60}Zr_{40}$, $Cu_{60}Ti_{40}$ and $Cu_{40}Zr_{60}$ ribbons were produced by melt spinning method in vacuum at a cooling wheel rate of 3000 cm s^{-1}. The catalytic tests were carried out in a flow-type microreactor (Fig. 1) with about 0.6 g alloy and GHSV 26 550 h^{-1}. The reaction products (N_2 and NO) were subjected to GC analysis by a HP 6890 Plus gas chromatograph with thermal conductivity detector, a 6 ft length molecular sieve 5A column, and He as carrier gas. The gas reactant moisture was composed of 630 ppmv of NO_x, 1370 ppmv of C_3H_6 and 7.7% vol. of O_2. The temperature of reaction was 260°C.

The amorphous alloys underwent two different activation treatments: one with immersion in 1 M HF solution for 1 min, washed with H_2O and still wet put into reactor; one with H_2 stream at 230°C for 4 h into the reactor. The structure of the alloys was studied by X-ray diffraction (XRD). X-ray diffraction patterns were collected with a Bragg–Brentano powder diffractometer using Cu Kα radiation ($\lambda = 1.54178$ Å) and a graphite monochromator in the diffracted beam. The surface of the alloys was investigated by scanning electron microscopy (SEM) with a Cambridge Stereoscan 440 microscope equipped with EDX microbeam.

3. Results and discussion

The amorphous condition of the as-quenched materials was checked by X-ray diffractograms. Only broad peaks characteristic of an amorphous structure are observed (Fig. 2).

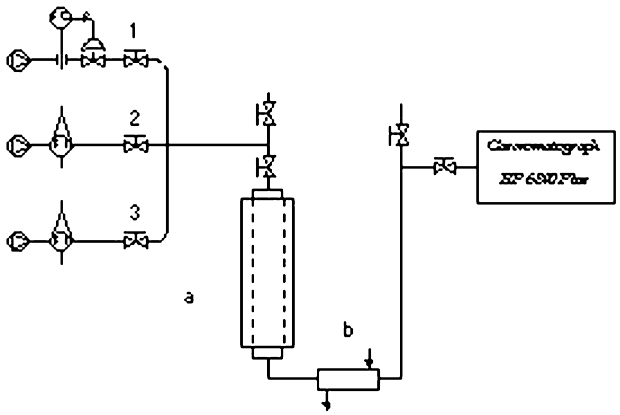

Fig. 1. Catalytic plant for the reduction of NO_x with propylene: (1) is C_3H_6 in He gas cylinder; (2) is O_2 in He gas cylinder; (3) is NO_x in He gas cylinder; (a) is the reactor and (b) is the water cooling of products.

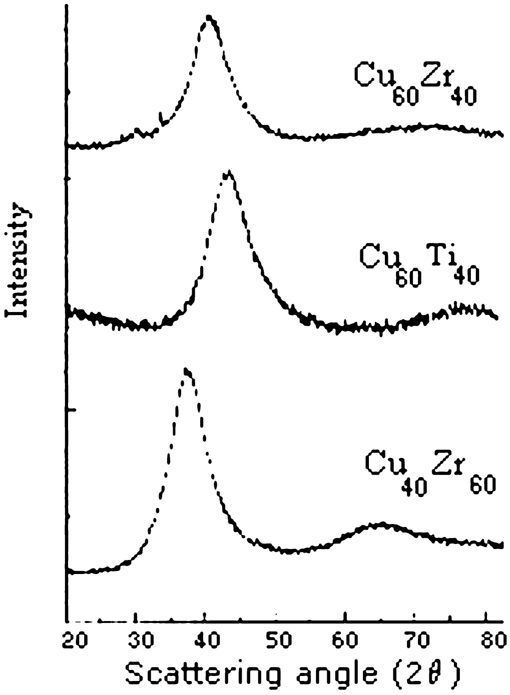

Fig. 2. X-ray patterns of the as-quenched amorphous materials.

The first-neighbour distance a, evaluated by the Bragg relation, is multiplied by a correction factor of 1.23 [15]

$$a = \frac{1.23\gamma}{2 \sin \theta_b}$$

and the results are summarized in Table 1.

The results are in agreement with data obtained with XRD structure factors and/or neutron scattering diffraction factors reported in literature [16].

The surfaces of the two sides of the as-quenched alloys show the characteristics of metallic glasses prepared by melt spinning methods (Fig. 3). The inner sides show small, parallel grooves due to contact with the cooling wheel. The outer sides exhibit large randomly located hillocks.

Fig. 4 summarizes the catalytic behaviour of $Cu_{60}Zr_{40}$ catalyst after different pretreatments. Note that the reactor is continuous and the figure reports the activity variations vs. time.

The HF treated material exhibits a high catalytic activity which decreases in the course of the reaction until it reaches stable and low activity after 150 min. The catalytic performance of H_2 treated material is weaker than the HF

Table 1
X-ray peaks angle and first neighbour distance *a* of as quenched alloys

Alloy	θ_b (degree)	*a* (nm)
$Cu_{60}Ti_{40}$	42.5	0.2615
$Cu_{60}Zr_{40}$	40.6	0.2732
$Cu_{40}Zr_{60}$	37.4	0.2957

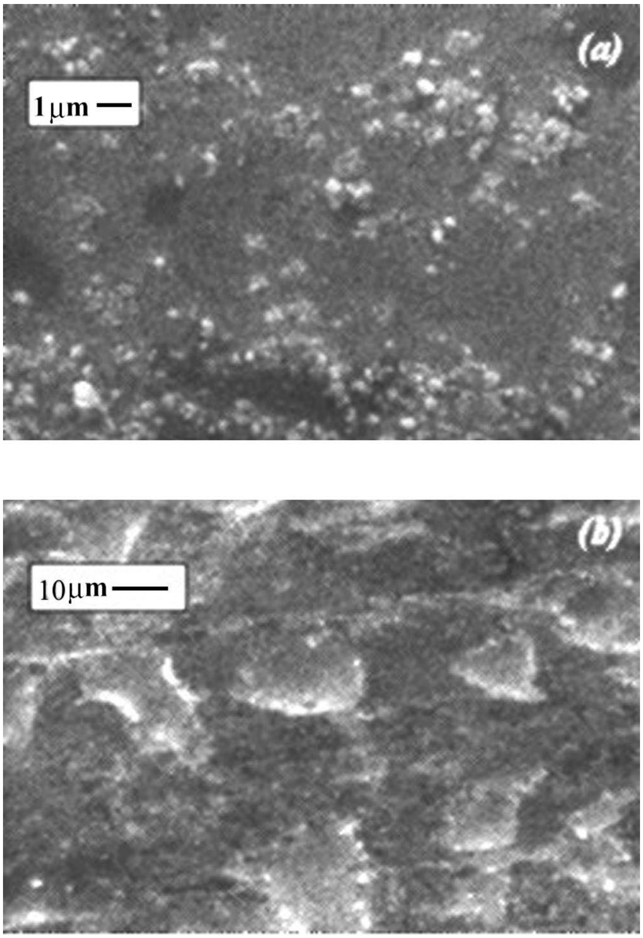

Fig. 3. SEM images of the as-quenched $Cu_{40}Zr_{60}$ amorphous alloy: (a) outer side; (b) inner side.

treated alloy, but the activity vs. time curves show the same value at 150 min. After this period the activity of H_2 treated catalyst decreases to zero. This may be interpreted by the SEM investigation.

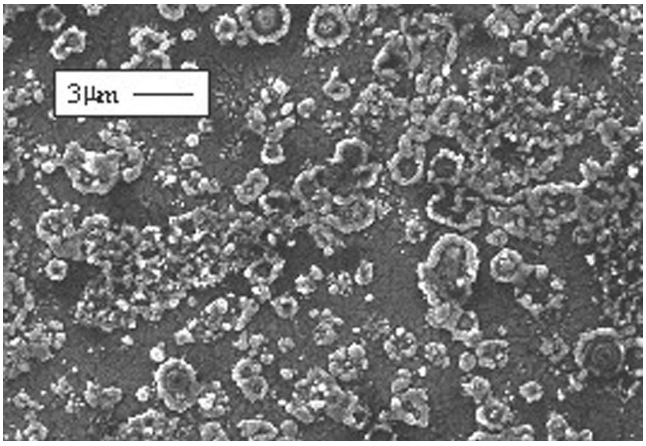

Fig. 5. SEM image of $Cu_{60}Zr_{40}$ catalyst surface treated with H_2.

The H_2 treatment causes a devitrification of the amorphous surface and produces an enrichment of small copper particles (Fig. 5). These clusters are active in NO_x reduction, but the O_2 contained in the reaction stream oxidizes the active sites of the surface and reduces the catalytic activity very quickly.

However, as Fig. 6 shows, the oxidation of copper active sites is partially reversible. In fact, a 2 h hydrogen treatment partially restores the activity of the catalyst. Unfortunately, this restoration process is less and less effective with the reaction process.

Since Zr/Zr oxides dissolve in HF more readily than Cu, HF treatment gives drastic changes in the surface morphology. The HF treatment produces a higher porous surface than the H_2 treatment does, with a high depletion in Zr content, as it can be seen in Fig. 7. These surfaces show higher activity, but the oxidation, due to the reaction stream, produces the same activity depletion observed for the H_2 treated catalyst.

However, the deeper porosity of HF treated surfaces keeps a residual low activity for a long time. The catalytic performance of the $Cu_{60}Ti_{40}$ alloy after different pretreatment is reported in Fig. 8. The H_2 treated sample shows a

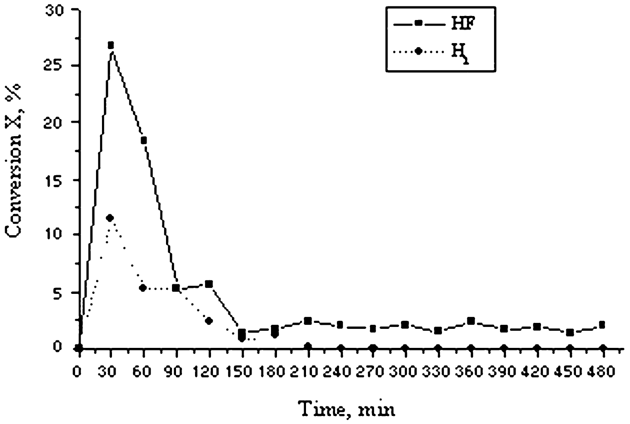

Fig. 4. Time-on-stream curves of $Cu_{60}Zr_{40}$ catalysts pretreated by HF and H_2.

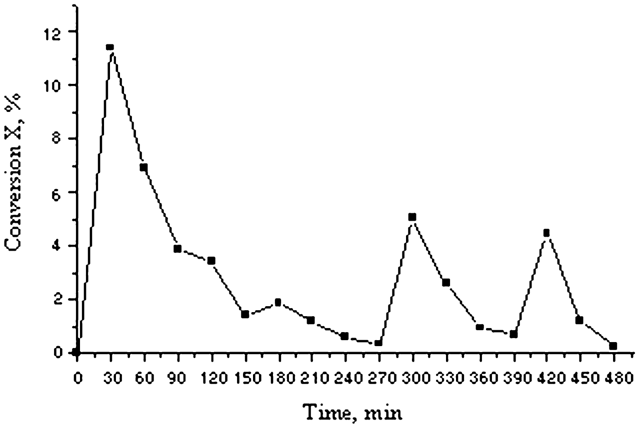

Fig. 6. Conversion of NO_x vs. time of $Cu_{60}Zr_{40}$ catalyst pretreated with H_2: after 270 and 390 min the catalyst underwent an H_2 treatment for 2 h at reaction temperature.

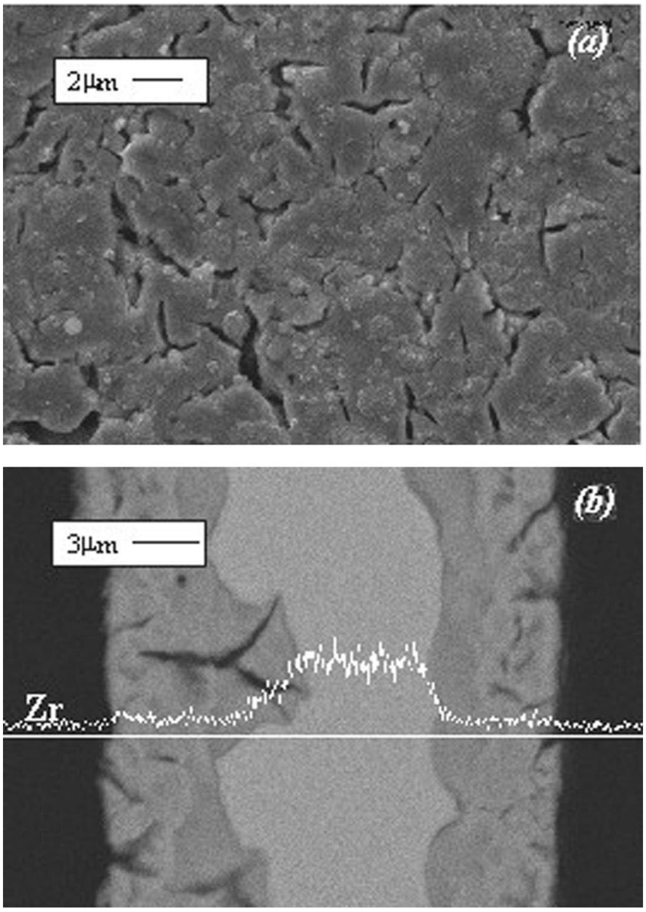

Fig. 7. SEM image of $Cu_{60}Zr_{40}$ catalyst surface treated with HF: (a) top view; (b) lateral view.

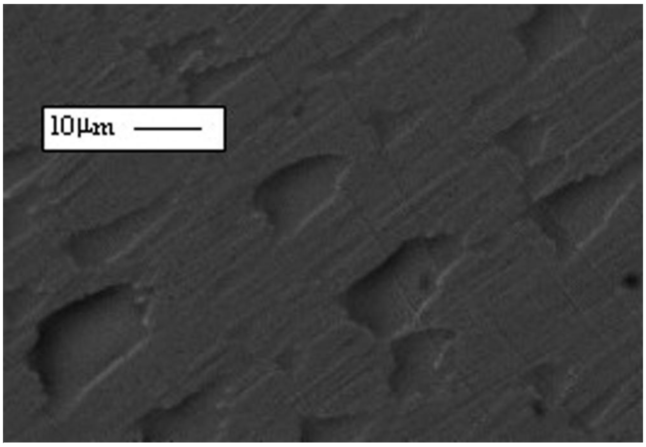

Fig. 9. SEM image of $Cu_{60}Ti_{40}$ catalyst surface treated with H_2.

very low activity for few minutes, while the HF activated material exhibits higher activity for more time. The H_2 activation is not successful in the case of Cu–Ti alloy. In fact, the H_2 treated Cu–Ti surfaces do not exhibit formation of copper clusters as the Cu–Zr surfaces do (Fig. 9).

This depends on the fact that the Ti oxides are more stable than Zr oxides and the H_2 is ineffective to reduce the oxide layer. The low activity is probably due to a small amount of metallic copper on the inner ribbon's surface [17].

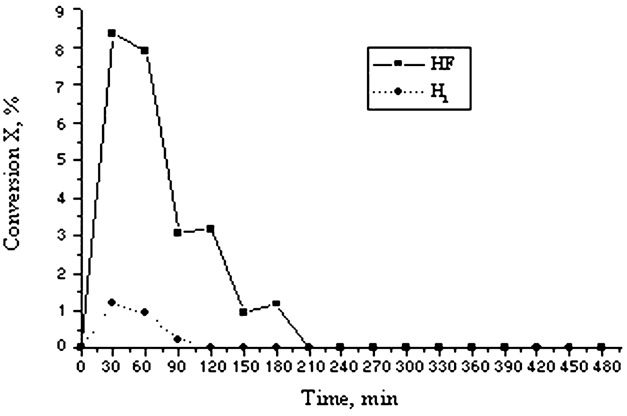

Fig. 8. Time-on-stream curves of $Cu_{60}Ti_{40}$ catalysts pretreated by HF and H_2.

Moreover, because the Ti oxides are less reactive than Zr oxides with HF solutions, the HF treated surfaces show lower porosity than the Zr alloys (Fig. 10). Consequently, a significantly smaller copper exposure occurs and the catalytic activity is lower [11].

In fact, as summarized in Fig. 11, the Cu–Ti catalyst exhibits a lower reactivity than Cu–Zr alloys. However, after 150 min, the catalytic activity of the three materials was found to be about the same. This indicates that the three glassy metals have the same kind of copper active sites, but in different number, in agreement with the SEM observations.

4. Conclusions

Copper containing alloys show catalytic activity in the reduction of NO_x with propylene in presence of O_2 only after activation treatments. However, the O_2 of the reaction

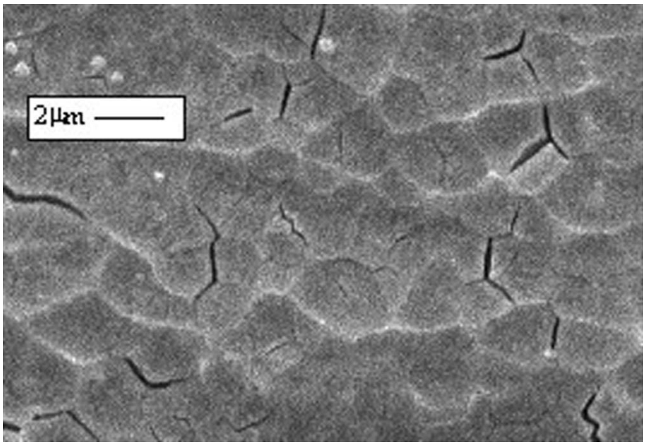

Fig. 10. SEM image of $Cu_{60}Ti_{40}$ catalyst surface HF treated.

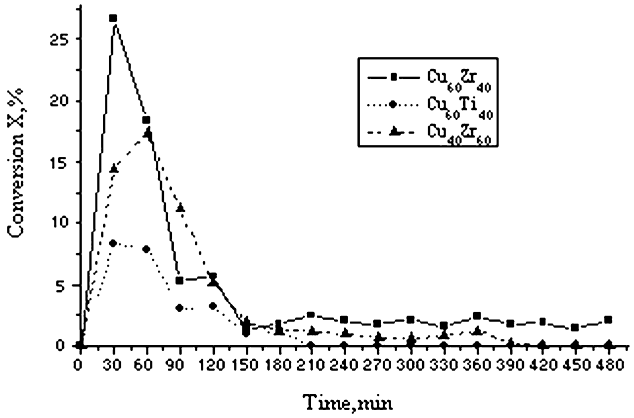

Fig. 11. Comparison of conversion of NO_x vs. time curves of the three materials pretreated with HF.

streams reduces the conversion process to N_2 in a few hours, because it oxidizes the surface copper active sites. Immersion in HF solutions produces a more effective catalyst than the H_2 treatment. This is due to the surface obtained by HF treatments, which is more porous. Moreover, the Zr containing alloys show higher activity than Ti containing materials. In fact, the oxide layers which cover the glassy metals' surfaces are more easily removed in the case of Zr. Besides, the H_2 activation of Cu–Ti amorphous material is ineffective in the reduction of the oxide layers. The similar depletion observed for the catalytic activity on the three catalysts indicates that the active sites are the same in nature but different in number.

Acknowledgements

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