

XRD and Raman Identification of the Zirconia Modifications in Copper/Zirconia and Palladium/Zirconia Catalysts Prepared from Amorphous Precursors

Recently, highly active CO_2 hydrogenation catalysts have been obtained from glassy metal alloy precursors, i.e., $\text{Cu}_{70}\text{Zr}_{30}$ (1) and $\text{Pd}_{33}\text{Zr}_{67}$ (2). During *in situ* activation under CO_2 hydrogenation conditions, the zirconium component of the alloy is oxidized. The as-quenched amorphous alloys, which are thermally unstable, are thereby transformed into metal/zirconia systems, in which the oxide matrix is stable with respect to air exposure (3, 4). The resulting active copper/zirconia and palladium/zirconia catalysts contain zirconia in partially crystallized form. To characterize the structure of the crystalline fraction of the zirconia, the catalyst samples have been investigated by X-ray diffractometry (1, 2). For Pd/zirconia, the support matrix is identified as stable, monoclinic ZrO_2 .

In copper/zirconia, on the other hand, a metastable zirconia modification is prevalent, corresponding to either tetragonal or cubic ZrO_2 . As the XRD patterns of these metastable phases are quite similar, additional information is required to distinguish between the two modifications. Both infrared and Raman spectroscopy have been established as suitable techniques to differentiate between tetragonal and cubic zirconia, as the information from the vibrational spectra is complementary to the X-ray diffraction data (5-8). In particular, the Raman spectrum of cubic zirconia is characterized by a single band at 490 cm^{-1} , whereas six Raman bands, with frequencies of 148, 263, 325, 472, 608, and 640 cm^{-1} , have been assigned to the tetragonal modification (8).

In addition to the identification of the zir-

conia modification, particular attention is drawn in the present report to the influence of copper in amorphous Cu/Zr-alloys on the crystallisation behavior of the zirconia. For comparison, two copper/zirconia catalysts were prepared by co-precipitation, drying, and subsequent reduction in a hydrogen atmosphere. These catalysts, denoted as Cu 70 and Cu 50, contain 70 at.% copper and 50 at.% copper on zirconia, respectively. In addition, the catalyst Cu 50 was calcined at 970 K for 2 h and then rapidly quenched to room temperature. Details of the preparation method are reported elsewhere (9). The zirconia reference samples were precipitated, dried, and calcined, or else investigated without calcination. A well-crystalline reference sample of monoclinic zirconia was obtained from Aldrich.

For the Raman spectroscopic experiments, about 100 mg of catalyst powder were pressed into self-supporting disks of 10 mm diameter and 1 mm thickness. Typically, 100 mW of power at 647 nm from a krypton ion laser (Spectra Physics, model 165) were used for excitation. The scattered radiation was analyzed in a double spectrograph (SPEX, model 14018), and detected with an RCA C31034A-02 GaAs photomultiplier. Control experiments have been performed to verify that the zirconium component of an as-quenched amorphous $\text{Cu}_{70}\text{Zr}_{30}$ sample was not modified by the laser illumination at the power levels used in the Raman spectroscopic studies.

XRD measurements were performed on a Philips PW 1700 diffractometer with $\text{CuK}\alpha$ radiation. Step scans were taken over the

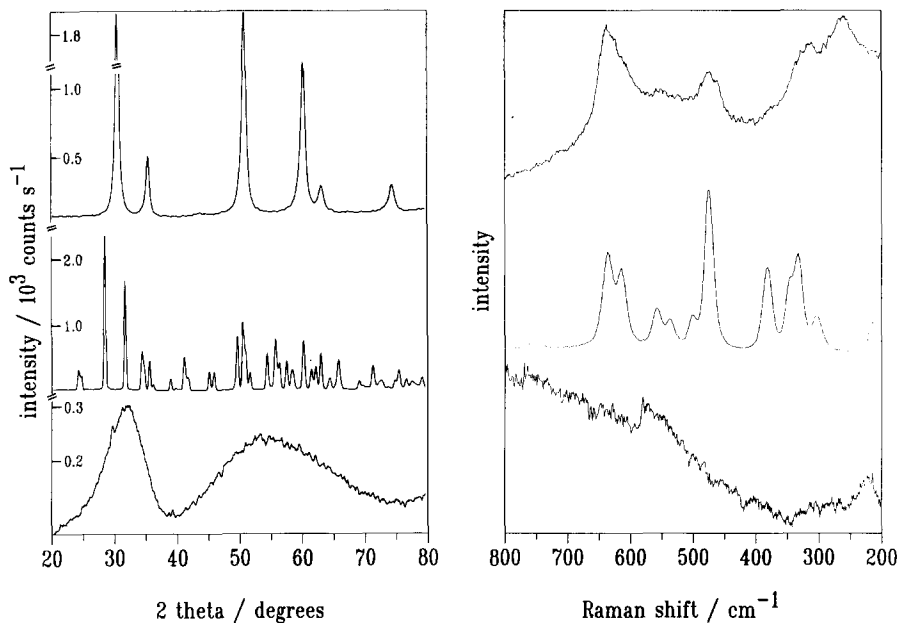


FIG. 1. XRD and Raman spectra of zirconia samples prepared by different techniques. The bottom traces correspond to amorphous zirconia prepared by precipitation and drying at 393 K (7). In the middle traces, the spectra of a commercial, well-crystalline monoclinic zirconia sample are presented. The top traces were recorded on a predominantly tetragonal zirconia sample obtained from the precipitated amorphous zirconia precursor by calcination at 770 K. For experimental details, see text.

range of 2θ from 20° to 80° in steps of 0.025° (2θ) with an integration time of 2 s. A slurry of the catalyst powder in an Apiezon N/toluene solution was spread on a quartz plate. After toluene evaporation, the sample was placed in a rotating sample holder.

In Fig. 1, the XRD patterns (left side) and Raman spectra (right side) of three zirconia reference samples are presented. The spectra of amorphous zirconia (bottom traces) contain only weak, very broad bands. These signals appear at $2\theta \approx 30^\circ$ and 55° in XRD, and around 550 cm^{-1} in the Raman spectrum, in agreement with the literature (7). The commercial ZrO_2 sample (middle traces) shows an XRD pattern which is characteristic for the monoclinic zirconia modification (10). The extremely narrow lines indicate a very well-ordered crystalline structure. The Raman spectrum is exactly identical with the one obtained from a high purity monoclinic zirconia sample (CERAC

Chem.) described in Ref. (8). The very sharp Raman doublets are centered at 310, 360, 500, 550, and 625 cm^{-1} , with a peak at 475 cm^{-1} as the most intensive one.

The spectra of a precipitated zirconia sample, which was subsequently calcined for 3 h, are shown in the top traces of Fig. 1. The XRD scan of this sample contains signals which might be assigned to either tetragonal or cubic zirconia (11). From the Raman spectrum, it becomes apparent that the sample consists of tetragonal zirconia, with characteristic bands at 255–265, 310–320, 475, and $625\text{--}640\text{ cm}^{-1}$.

For reference, the Raman frequencies of the zirconia samples under investigation are listed in Table 1 and compared to the results with the metal/zirconia catalysts described below.

The spectra of the palladium/zirconia catalyst obtained from the precursor $\text{Pd}_{25}\text{Zr}_{75}$ (Fig. 2) exhibit the same peak

TABLE 1

Raman Frequencies Observed with Zirconia and Metal/Zirconia Catalysts	
Compound	Raman shift (cm^{-1})
Zirconia	
Amorphous	550–600 (broad)
Monoclinic	300, 330, 340, 380, 475, 500, 535, 555, 615, 635
Tetragonal	255–265, 310–320, 475, 625–640
Cubic (not shown)	490 (cf. Ref. (8))
Pd/zirconia	
Activated $\text{Pd}_{25}\text{Zr}_{75}$	315–330, 360–370, 460–475, 545–555, 615–640 (monoclinic zirconia, broadened)
Cu/zirconia	
Precipitated (Cu 70)	\approx 550 (broad)
Precipitated/calcined (Cu 50)	295, 340–355, 635 (tetragonal, shifted)
Activated $\text{Cu}_{70}\text{Zr}_{30}$	210, 300, 410–430, 490–515, 650 (contributions from monoclinic and tetragonal zirconia modifications)

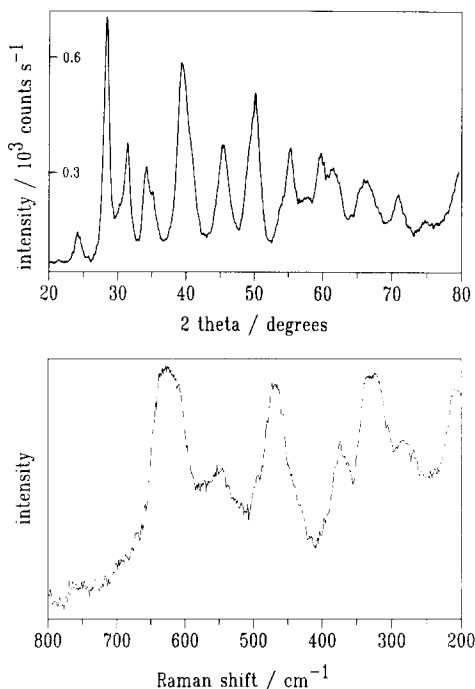


FIG. 2. XRD and Raman spectra of a palladium/zirconia catalyst obtained by *in situ* activation of a glassy $\text{Pd}_{25}\text{Zr}_{75}$ alloy under CO_2 hydrogenation conditions. Peaks observed in both spectra correspond to the monoclinic modification of zirconia (cf. Fig. 1, middle trace).

positions as those of monoclinic zirconia. The signals are, however, substantially broadened. Several factors can contribute to this broadening, i.e., (i) the presence of tetragonal zirconia and (ii) most importantly, poor crystallinity of the zirconia component. Additional peaks in the X-ray diffractogram were assigned to a palladium/hydrogen solid solution (2), which leads to an increase of the Pd lattice constants.

Results obtained with copper/zirconia catalysts are presented in Fig. 3. For the uncalcined catalyst (prepared as described above), only signals from copper and copper oxides are detected in the XRD scan; these components are present in crystalline form in this catalyst, and are marked by the corresponding symbols in Fig. 3. The Raman spectrum reveals that the zirconia support is predominantly amorphous, with a weak, broad feature around 550 cm^{-1} (Fig. 3, bottom traces). (For reference, we note that crystalline Cu_2O has optical phonon modes at 609 and 148 cm^{-1} , which are not Raman active (12). For CuO mixed with KI, an infrared absorption at 510 cm^{-1} has been reported (13); the corresponding Raman feature has been observed at 524 cm^{-1} in particles from smoke (12).)

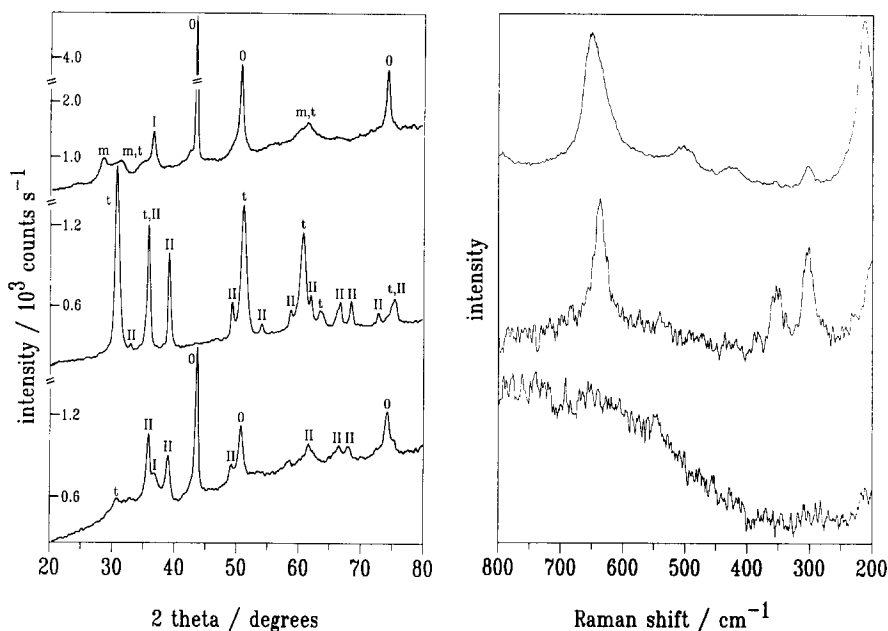


FIG. 3. XRD and Raman spectra of copper/zirconia catalysts. The bottom traces correspond to a catalyst containing 70 at.% of Cu, prepared by co-precipitation of copper and zirconium hydroxides, drying, and reduction in H_2 . Second, a catalyst containing 50 at.% of copper was prepared by the same procedure, followed by calcination at 970 K (2 h) and rapid quenching. This sample is characterized by the middle traces. Finally, a catalyst obtained by *in situ* activation of a glassy $Cu_{70}Zr_{30}$ alloy under CO_2 hydrogenation conditions is characterized by the spectra shown in the top traces (3). X-ray reflections corresponding to metallic copper, copper(I) oxide, and copper(II) oxide are labeled by 0, I, and II, respectively. XRD signals arising from the monoclinic and tetragonal modifications of zirconia are designated by m and t, respectively.

The X-ray diffractogram of the catalyst containing 50 at.% copper on zirconia (Fig. 3, middle traces) exhibits reflections which would match those assigned to cubic zirconia (14). As these reflections are quite close to those of tetragonal zirconia (11), the two metastable modifications can hardly be distinguished by X-ray diffraction, as mentioned above. The Raman spectrum, however, clearly reveals that the only metastable modification present in significant amounts is tetragonal zirconia, with bands around 295, 345, and 635 cm^{-1} . No signals from cubic ZrO_2 , which is characterized by a single band at 490 cm^{-1} (8), are detected with appreciable intensity. Note that the doublet of ZrO_2 bands, observed at 295 and 345 cm^{-1} on the copper-containing catalyst, is shifted to higher

frequencies by $\approx 30 cm^{-1}$, as compared to the reference spectra of tetragonal zirconia recorded by us (Fig. 1, top trace) and other authors (8, 15).

Another striking feature is the strong decrease to almost zero intensity of the 480 cm^{-1} Raman signal in the middle trace of Fig. 3. A Raman loss at this frequency was assigned to the tetragonal phase of zirconia (cf. Fig. 1 and Refs. (8, 15)). From the present results, we may attribute both the absence of this signal and the frequency shifts mentioned above to the influence of copper.

The Raman spectrum of the catalyst prepared by *in situ* activation of $Cu_{70}Zr_{30}$ (Fig. 3, top traces) shows several broad bands in the range between 200 and 700 cm^{-1} , but the relative intensities are quite differ-

ent from those recorded with all the reference samples investigated in this study. Zirconia appears to be present as a mixture of different modifications, but no definite assignments are feasible at present. The same conclusion is reached from the X-ray diffractogram, where strong signals due to crystalline copper and copper (I)-oxide are the dominating features.

The present investigation has confirmed that Raman spectroscopy is a powerful tool for distinguishing between the metastable modifications of ZrO_2 . Summarizing our results we can state that for none of the samples investigated has any indication for a presence of the cubic modification in significant amounts been obtained. In the catalysts prepared by *in situ* activation of a glassy $Pd_{25}Zr_{75}$ precursor, the crystalline fraction of the zirconia is mainly present in the stable monoclinic form. In contrast, the presence of copper appears to stabilize the tetragonal modification. In particular, an exclusively tetragonal zirconia matrix is obtained by rapid quenching of a co-precipitated sample (Cu 50) after calcination at 970 K. The influence of the zirconia crystal modification on the catalytic properties of the copper catalysts will be the subject of further investigations.

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