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Influence of small amounts of rhodium on the structure and the reducibility of Cu/Al₂O₃ and Cu/CeO₂-Al₂O₃ catalysts.

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The influence of small amounts of rhodium on the structure and the reducibility of copper-based catalysts deposited on alumina and ceria-alumina supports has been studied by XRD and H₂-TPR techniques. For both supports, the addition of rhodium does not affect the reduction mechanism of copper, which has been shown to involve small clusters/isolated ions at lower temperatures and large particles at higher temperatures. However, rhodium addition inhibits the formation of large size copper particles in favor of small ones, thus making easier the reduction of the catalyst at low temperature.

1. INTRODUCTION

In the general framework of studying new types of three-way catalysts, copper has been studied as a substitute for automotive post-combustion [1] but seems not active enough without promoter. Considering that rhodium is a key component for the NO_x elimination, we have looked for the promotional effect of rhodium on the catalytic properties of copper. This study reports on the characterization of supported copper-alumina catalysts and specially on the influence of small amounts of rhodium on their reducibility by hydrogen. Since rhodium is easily reduced, with a reduction temperature lower than that of copper, it is expected to favor the reduction of copper. The influence of a redox support was also investigated by replacing alumina by ceria-alumina, since the surface of ceria is known to be reduced at low temperature in presence of metallic rhodium [2] and consequently may also favor the reduction of copper.

2. EXPERIMENTAL

The catalysts were prepared by co-impregnation with nitrate precursors of alumina (Al, 115m²/g) and ceria(20%)-alumina (CeAl, 95m²/g) supports supplied by Rhodia, and calcination at 400°C for 6 h under air. The copper content was 4.75 wt% and that of rhodium was 100, 500, 1000 and 2000 ppm. The corresponding Cu/Rh atomic ratio for the bimetallic samples were 760, 150, 76 and 38 respectively.

For the temperature programmed reduction (TPR) experiments, 50 mg of calcined sample were put in a quartz reactor and pretreated *in situ* under air at 400°C for 60 min and then under Ar at 500°C for 90 min, and finally cooled to room temperature (RT) under Ar. The reduction was then carried out under a 1% H₂/Ar mixture (total flow rate : 1.2 L.h⁻¹), using a 20°C/min heating rate. H₂ consumption was detected by thermal conductivity.

Before X-ray diffraction (XRD) experiments, samples were prerduced under H₂ at 500°C for 6 h, cooled under H₂ to RT, then put under N₂ and finally slowly exposed to air. Diffraction patterns were obtained with a D500 Siemens goniometer equipped with a diffracted-beam monochromator selecting the Cu K α radiation ($\lambda=1.5406 \text{ \AA}$).

The evolution of the crystalline phases during the reduction was followed by *in situ* XRD. The experiments were performed on a D500 Siemens diffractometer equipped with a high temperature camera using Mo K α Zr-filtered radiation ($\lambda=0.7107 \text{ \AA}$) and a positive sensitive proportional detector (Raytech). After the standard oxidizing pretreatment, the sample was heated at 20°C/min with a 5% H₂/He mixture flowing through the catalyst from RT to the first reduction temperature (total flow rate : 2.4 L.h⁻¹). After reaching the reduction temperature, the gas flow was changed to He and the sample was allowed to cool to RT. The diffractogram was then recorded. This reduction procedure was repeated on the same sample, increasing the reducing temperature stepwise for subsequent diffractograms.

3. RESULTS

Figures 1 and 2 show the XRD patterns for both series of catalysts. The peaks observed at $2\theta = 45.5^\circ$, 47.3° and 67.2° are characteristic of the alumina support and those at $2\theta = 33.0^\circ$ and 56.5° are due to the cubic CeO₂ phase. Metallic copper can be detected at $2\theta = 43.3^\circ$ (Cu (111)) and 50.4° (Cu (200)). Rh and Cu addition induces no detectable change in the structure of the supports but for each type of support the intensity of the two main Cu peaks decrease when Rh content increases. On Al supported catalysts, the Cu peaks were also clearly detected but only for Rh < 500 ppm.

The TPR profiles of the CuRh/Al catalysts are given Fig. 3. The Cu/Al catalyst exhibits two main peaks at 270°C and 375°C, followed by a small shoulder at about 500°C. The calculation of the H₂ consumption up to 800°C shows a complete reduction of the deposited copper. The same type of profile was obtained with the Cu/CeAl catalyst with two main modifications (Fig. 4) : i) the first peak is broader, because the CeO₂ surface in contact with reduced copper is simultaneously reduced [3] and ii) a low H₂ consumption is observed from approximately 550°C until the end of the test at 800°C, which is attributed to the reduction of the bulk ceria [4]. As for Cu/Al, a complete reduction of copper may be assumed on Cu/CeAl, although the contribution of the ceria reduction makes difficult a precise calculation.

For both supports, the presence of rhodium does not seem to lower the temperature of the beginning of the reduction and does not change the temperature of the peaks. Its main effect is clearly to increase the intensity of the first TPR peak at about 270°C, whereas the intensity of the second peak at 375°C decreases with the Rh content (Figs. 3 and 4). With the CeAl support, the additional broadening of the first peak on the low temperature side can be attributed to the reduction of both rhodium oxide and the ceria surface in contact with rhodium [4]. Note however that for the CuRh/Al catalysts where no ceria surface reduction occurs, the contribution of Rh to the H₂ consumption is too low to be detected with our

apparatus. The small H_2 consumption obtained at about $500^\circ C$ for Cu/Al, which decreases with the Rh content, could be attributed to the reduction of a surface Cu aluminate [5]. Finally, with the CuRh2000/Al catalyst, a broad but limited H_2 consumption is observed near $600^\circ C$. Its origin is not elucidated yet, but the experiments indicate that it could be linked to the Rh content.

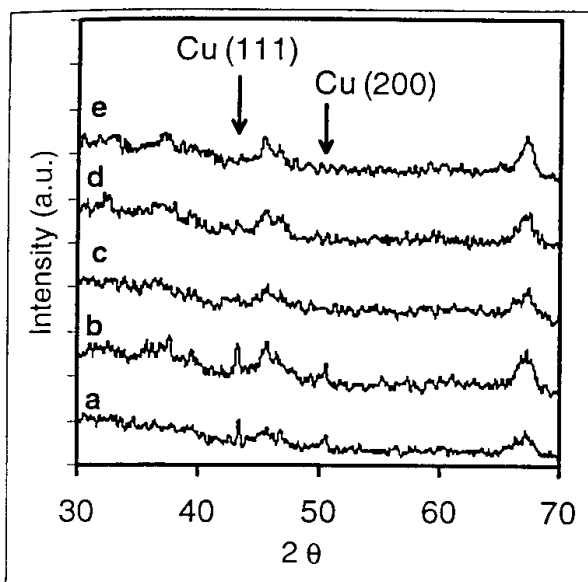


Fig. 1. XRD patterns of the CuRh/Al catalysts : (a) Cu, (b) CuRh100, (c) CuRh500, (d) CuRh1000, (e) CuRh2000.

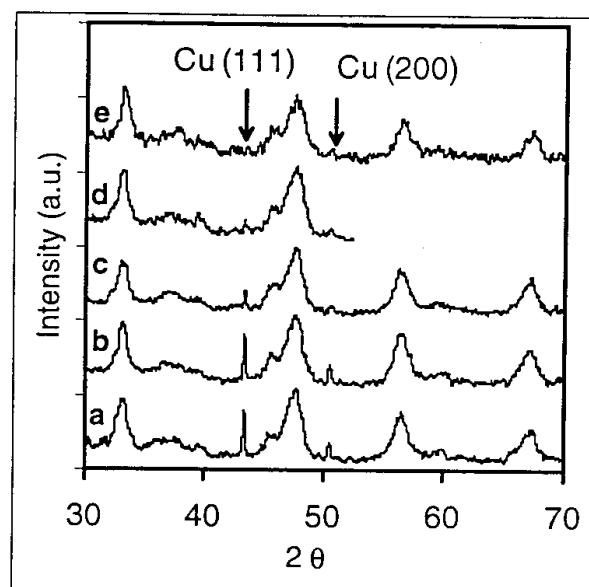


Fig. 2. XRD patterns of the CuRh/CeAl catalysts : (a) Cu, (b) CuRh100, (c) CuRh500, (d) CuRh1000, (e) CuRh2000.

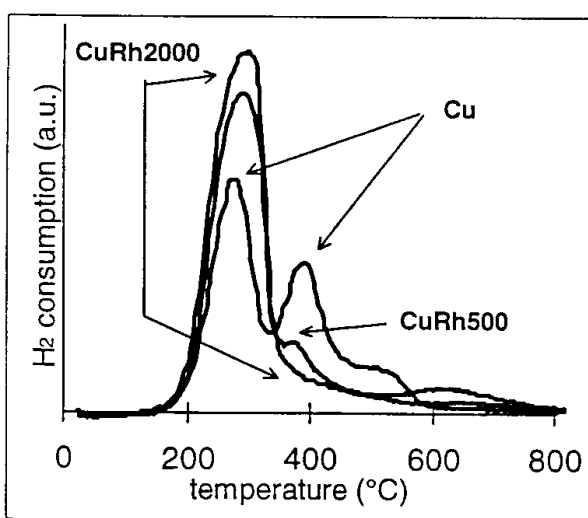


Fig. 3. TPR profiles of the CuRh/Al catalysts.

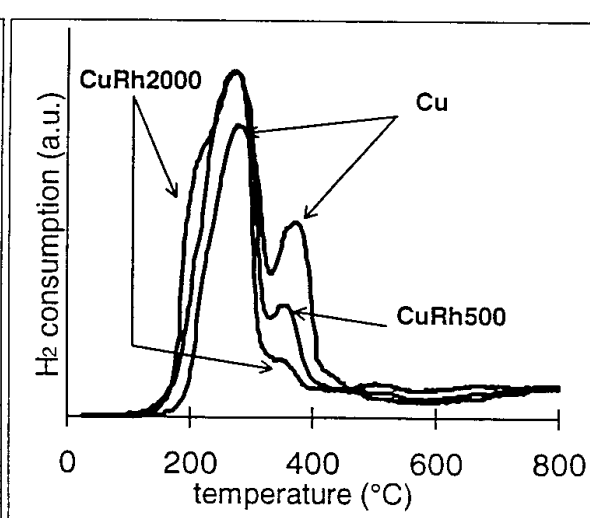


Fig. 4. TPR profiles of the CuRh/CeAl catalysts.

Figure 5 shows XRD patterns during *in-situ* reduction of the Cu/Al sample. The quantitative evolution of the phases CuO and Cu are given Fig. 6. No change in the diffraction pattern is noted between the calcined sample and after reduction at 200°C, with only CuO being detected. After reduction at 220°C, Cu⁰ peaks are coming out with CuO peaks still remaining but with a lower intensity. No formation of Cu₂O is evidenced. After reduction at 250°C, peaks of CuO totally disappear while those of Cu⁰ increase. Cu₂O is still undetected. Upon increasing the reduction temperature above 250°C, only the increase of the Cu⁰ peaks is observed, smoothly between 250 and 500°C, more abruptly between 500 and 680°C. This increase in the copper peaks intensity can be assigned to the sintering of metallic copper particles initially not detected.

4. DISCUSSION

The presence of two peaks in the TPR profiles and their modifications upon addition of rhodium have to be discussed in relation to the XRD results and literature data. The *in-situ* XRD experiment has clearly shown that for the Cu/Al sample, only the peaks of metallic Cu have appeared simultaneously with the vanishing of the CuO phase, without the formation of Cu₂O. Thus, the CuO particles which are large enough to diffract have a reduction process that occurs in a single step. The formation of Cu^I species as an intermediate step has been proposed for Cu/zeolite solids [6], for some Cu/SiO₂ [7] or Cu/Al₂O₃ catalysts [8]. It is not evidenced in the present study, although it is not possible to completely discard that highly dispersed copper not detected by XRD could be reduced through the formation of a Cu⁺ intermediate.

A two/three peaks reduction TPR profile has often been found in literature for supported copper catalysts and is generally interpreted as due to the successive reduction of small clusters and/or isolated ions at low temperature, followed by the reduction of larger particles at higher temperature [5, 9-11 and references therein]. Increasing the Cu content so that excess copper formed bulk CuO particles evidenced by XRD or STEM/EDX increased the high temperature peak intensity [10,11]. We can interpret our results in the same way by attributing the second TPR peak at 375°C to the reduction of bulk CuO whereas the first one at 270°C corresponds to the reduction of small CuO clusters and isolated Cu²⁺ ions, undetectable by XRD. This attribution is in agreement with the results of Dumas et al. who observed on a 6 wt% Cu/alumina catalyst a similar profile with peaks at 242 and 312°C [5]. Increasing the Cu loading to 10% was accompanied by a much higher reduction peak at 312°C [5]. The fact that higher temperatures are found in the present study may be attributed to a higher heating rate during the TPR (20°C min⁻¹ instead of 5°C min⁻¹). The differences in the operating conditions used can also explain the shift in the temperature range observed for the *in situ* XRD reduction of CuO particles which occurs at about 250°C (H₂ partial pressure five times higher, double flow rate and cumulated heating times above 200°C corresponding to several minutes, whereas the heating rate was 20°C min⁻¹ in the TPR experiments).

The attribution of the second peak to the reduction of CuO particles and its decrease when the rhodium content increases is supported by XRD data on the initial calcined samples. As shown in Fig.7, a CuO phase could be evidenced on the Cu/CeAl while it could not be detected with the CuRh1000/CeAl, showing that rhodium addition limits the formation of CuO particles.

This is also in line with the XRD spectra of the reduced catalysts. As evidenced in Fig. 8 for the CuRh/CeAl catalysts, there is a linear relationship between the intensity of the (111)

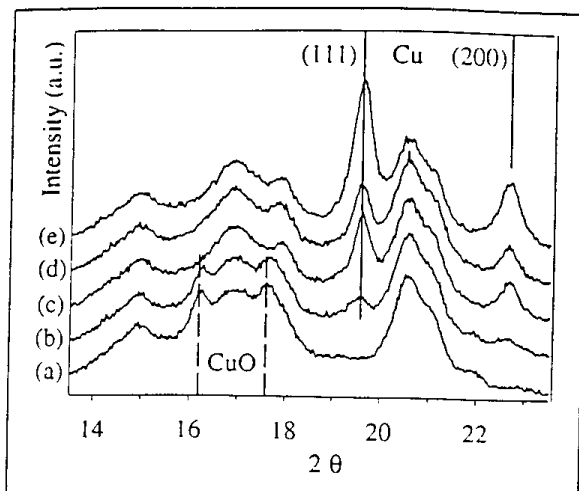


Fig. 5. *In-situ* XRD patterns of the Cu/Al sample reduced at (a) 200°C, (b) 220°C, (c) 240°C, (d) 260°C and (e) 680°C.

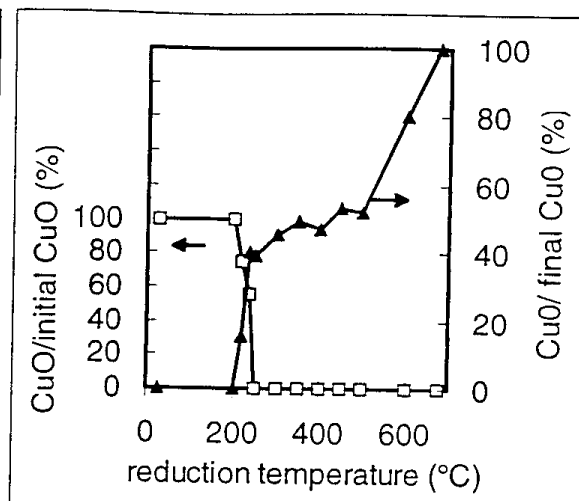


Fig. 6. Cu/Al: evolution of the CuO/initial CuO (calined sample) (□) and the Cu⁰/final Cu⁰ (sample reduced at 680°C) (▲) determined by integration of the XRD peaks of CuO and Cu⁰.

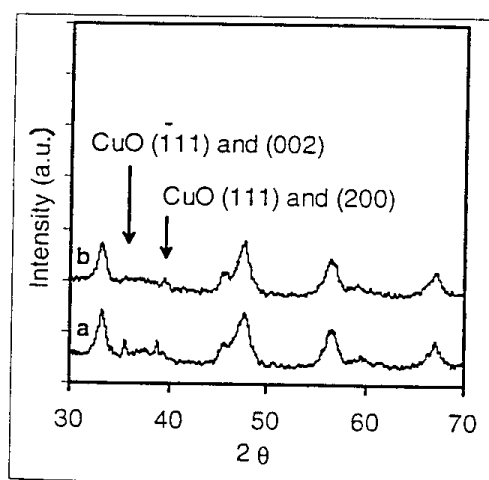


Fig. 7. XRD patterns of the calcined CuRh/Al catalysts: (a) Cu, (b) CuRh1000.

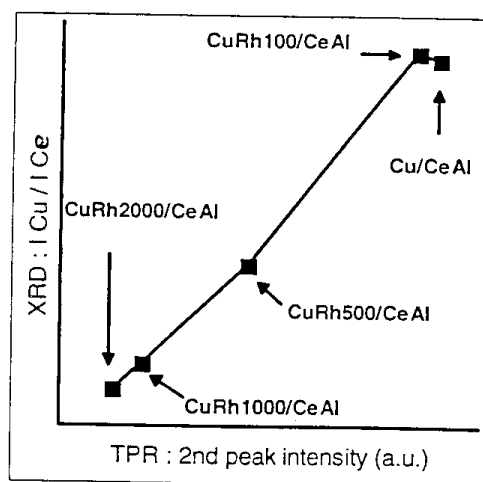


Fig. 8. Relationship between the height of the (111) Cu diffraction line (CeO₂ as internal standard) and the intensity of the 2nd TPR peak for the CuRh/CeAl catalysts.

Cu diffraction line and the intensity of the second TPR peak at 375°C. The same tendency is observed with the CuRh/Al catalysts, for which no Cu diffraction peaks are detectable for [Rh] >100 ppm in agreement with the low intensity of the second TPR peak observed for these catalysts. Since no variation of the breadth of the XRD Cu peaks could be measured, this decrease of the Cu diffraction peaks indicate a decrease in the number of large Cu particles.

These results clearly show that addition of small amounts of rhodium inhibits the formation of CuO particles expely to give large size copper particles by reduction. It favours the formation of small clusters which are more easily reduced at lower temperatures.

4. CONCLUSION

The addition of small amounts of rhodium to a copper-alumina catalyst does not basically modify the reduction mechanism based on the successive reduction of i) the isolated ions and small clusters and then ii) the bulk copper oxide. However, the structure of the catalyst is deeply changed since the presence of rhodium decreases the number of large size copper oxide particles. In this sense, it can be said that rhodium assists in the reduction because it favors the formation of small clusters which are reducible at lower temperature. This effect of rhodium addition resulting in a more dispersed structure of copper is more easily observed when copper is supported on ceria-alumina than on alumina. The redox nature of ceria does not deeply modify the reduction process at low temperature.

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