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Modification of copper by redox reaction: location of Ru on Cu-Ru bimetallic catalysts

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Raney copper catalysts were modified by addition of ruthenium by means of an oxido-reduction reaction between copper surface and ruthenium chloride in aqueous solution. Energy dispersive spectroscopy fitted to a STEM unit allowed to conclude that the active sites for the selective conversion of glucitol into 1,4-3,6-dianhydroglucitol are composed of ruthenium and chlorine located on low coordinated copper atoms.

Keywords: Copper-ruthenium catalysts; EDS/STEM bimetals characterization; Ru/Cu decoration catalysts

1. Introduction

The catalytic properties in conversion of polyols on Raney copper and supported ruthenium catalysts have been described in recent papers [1,2]. On Raney copper [1] C–C and C–O bonds cleavages are slow and proceed by steps of dehydrogenation of alcoholic functions followed by nucleophilic attacks of carbonylated intermediates so formed. On the contrary, ruthenium catalysts [2] are very active for direct C–C and C–O bonds hydrogenolysis leading ultimately, in the same conditions, to C_1 molecules (methane).

Thus bimetallic catalysts Cu-Ru were prepared in the aim of increasing copper activity and selectivity. A ruthenium deposit on metallic copper particles was carried out following the redox reaction between metallic copper and ruthenium chloride solutions. On such bimetallic catalysts a distinct selectivity took place, i.e. formation of tetrahydrofuran from 1,4-butanediol and 1,4-3,6-dianhydroglucitol (isosorbide) from glucitol by S_N2 cyclodehydration mechanism [3].

It was thus worthwile to look at the origin of this selectivity by investigating the nature of the catalytic site(s). This was done by STEM (scanning transmission electron microscopy) fitted with elemental analysis by EDS (energy dispersive spectroscopy).

2. Experimental

2.1. CATALYSTS PREPARATION

Raney copper was elaborated by leaching a copper-aluminum (50-50) alloy with 10 M sodium hydroxide solution. After thoroughly water-washing the copper slurry was mixed, under nitrogen flow, with ruthenium chloride solutions. The metal deposit can be accounted for, in the case of ruthenium, by the following oxido-reduction reaction:

$$3Cu(s) + 2Ru^{3+}(aq) \rightarrow 3Cu^{2+}(aq) + 2Ru(s).$$

The Ru^{3+} concentration was adjusted so as to be equal to the number of surface copper atoms to be exchanged, taking into account, however, the stoichiometry of the redox reaction. The analysis of the solids made it possible to determine the extent of the exchange (number of surface atoms of copper exchanged by Ru^{3+}). It is to be noted that the exchange coverage is limited to 0.33 (Cu–Ru 0.33) [3].

The bulk chemical analysis gave the following composition (wt%): Cu: 97.1; Ru: 1.62; Cl: 0.63.

2.2. MORPHOLOGY AND COMPOSITIONAL ANALYSIS

Cu-Ru (0.33) catalyst as characterized by local analysis of Ru.

All the microanalysis work was done in a Jeol-100 CX electron microscope fitted with a STEM unit, an X-ray detector and a Tracor-Northern-5500 console. This system has a series of image processing routines such as filtering and particle recognition programs, as well as the standard programs and files for elemental analysis: STMF and MICRO Q.

The usual procedure for analysis and morphology studies consists in obtaining a scanning electron image in the cathode ray tube (CRT). The corresponding X-ray signals were recorded digitally in the Tracor system, then stored in a file.

2.2.1. SEM (scanning electron microscopy)

The scanning electron images were obtained directly from the powder samples, which are usually deposited onto graphite holders without any previous treatment. As Cu-Raney catalysts are good conductors, no coating was applied, then the scanning electron images correspond to the real outline.

In some cases, the scanning images were filtered out to get rid of scan defects or to enhance the particular features of interest. In other cases the original image was enlarged (zoom) in the screen in order to get some further details of the sample region.

2.2.2. EDS (energy dispersive spectrometry)

The compositional microanalysis is done by bombarding a sample region with an electron beam at 40 kV, thus provoking X-ray emission which carries out both the characteristic radiation and the continuous background from the region of interest. The X-ray signals which are generated in the microscope chamber are detected and transmitted by a Si/Li detector. The information is processed in the Tracor-Northern system. A typical spectrum is obtained in a couple of minutes from 0 to 40 keV; in this energy region all the primary (K lines) or secondary (L, M,... lines) emission lines appear sharply. As each element of the periodic table has its own emission line family, a straightforward qualitative analysis may be done. The quantitative analysis requires a further treatment of the data by means of the computer programs. This is usually done by use of the standard metallurgical thin film or the MICRO Q programs, which provide the atomic and weight percents.

The EDS analysis may be done either from a relatively large region (average analysis) or from a 200 A-wide region (point analysis), therefore one can obtain the compositional fluctuation around an average value; for instance, the composition homogeneity, etc. All the analyses are based on the direct relationship between the intensity of the X-ray signal and the concentration of the element under analysis: $I(\mathrm{A})/I(\mathrm{B}) = K(\mathrm{AB})C(\mathrm{A})/C(\mathrm{B})$, but in most of the cases a further correction is applied for absorption and fluorescence effects [4–6].

2.2.3. X-ray mapping

The same EDS signal arising from the sample region is used for the formation of the X-ray maps, that is the video image formed in the Tracor system is energy filtered in a region of the spectrum of interest.

The selection of a specific window of energy (E, in keV) on the EDS system and its re-injection to the video system creates a bright spot region on the video image which indicates the spatial location of the element of interest. This is called the X-ray mapping.

Essentially the X-ray maps are displayed as a series of square maps (128 × 128 pixels) on the computer screen, together with the scanning image of the sample region of interest. From these pictures the spatial distributions of the elements are observed directly.

2.2.4. Linescan mappings

A distinct mode of microanalysis and mapping is the linescan mapping. This consists in the excitation of the sample in a starting point, then following a straight line across the sample region and finishing in another point. In this way

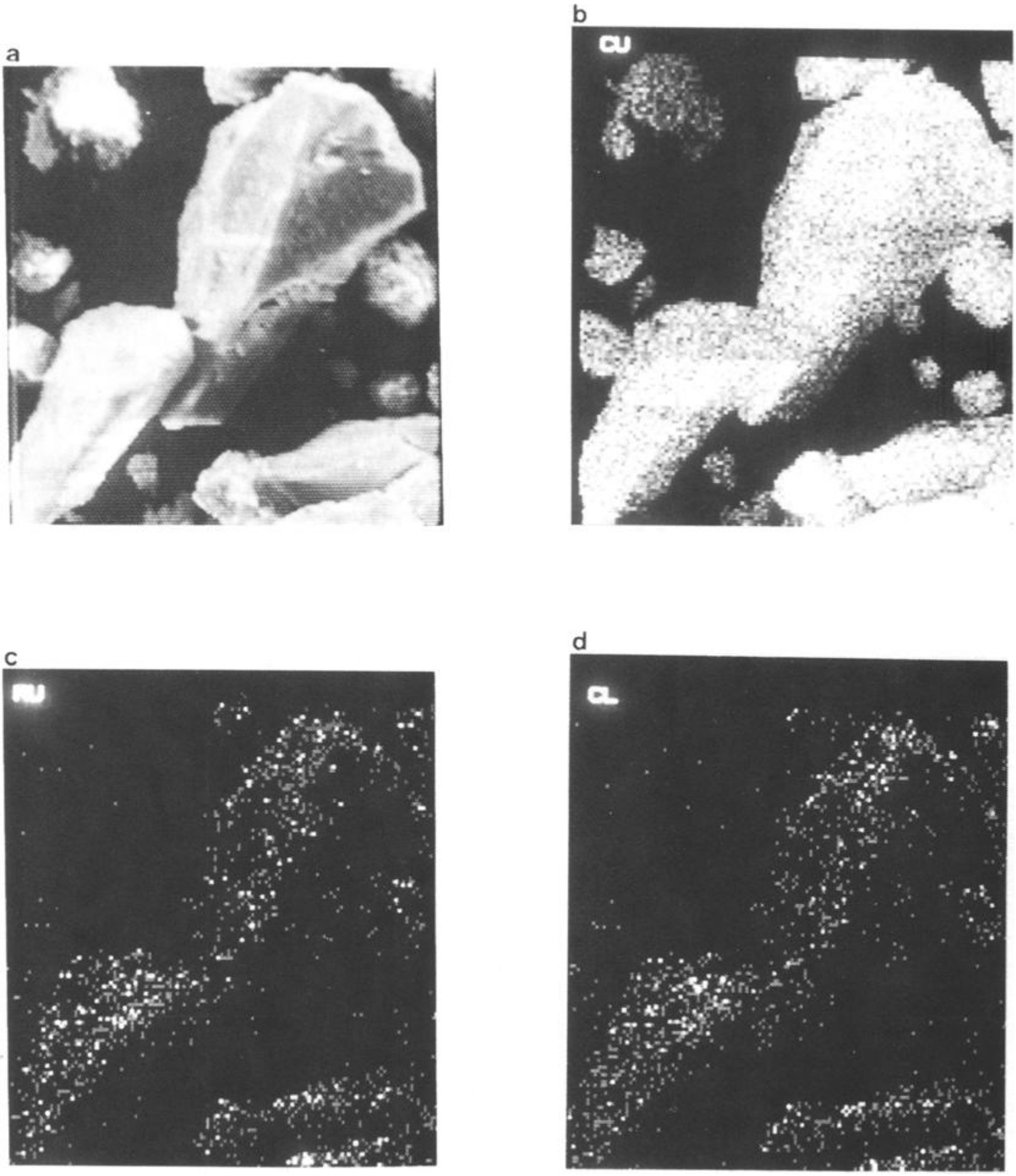


Fig. 1. (a) Copper particle, (b) Cu X-ray analysis, (c) Ru X-ray analysis, (d) Cl X-ray analysis. (Scale: 1 cm is 2.5 μm.)

a continuous emission of X-rays across the sample region of interest is obtained. This mode is useful for probing the composition in microdomains, grain boundaries, rims and faces, etc. In our case the linescan analysis was used for scanning the particle contour and flat faces which were found to form the Cu-Raney catalysts.

3. Results

Fig. 1a is a typical Raney copper particle, figs. 1b and 1c are the elemental Cu (K, 8.04 KeV) and Ru (K, 19.27 KeV) X-ray maps respectively, which correspond to the area 1a above. It appears from this analysis that ruthenium is preferentially deposited on high index planes while low index planes are totally free from deposited Ru atoms. The compositions of the particle contour and flat faces, which compose Cu-Ru catalysts, were analysed by linescan mapping. Figs. 3A and 3B are microanalyses for lines A and B (particle fig. 2). Along line B

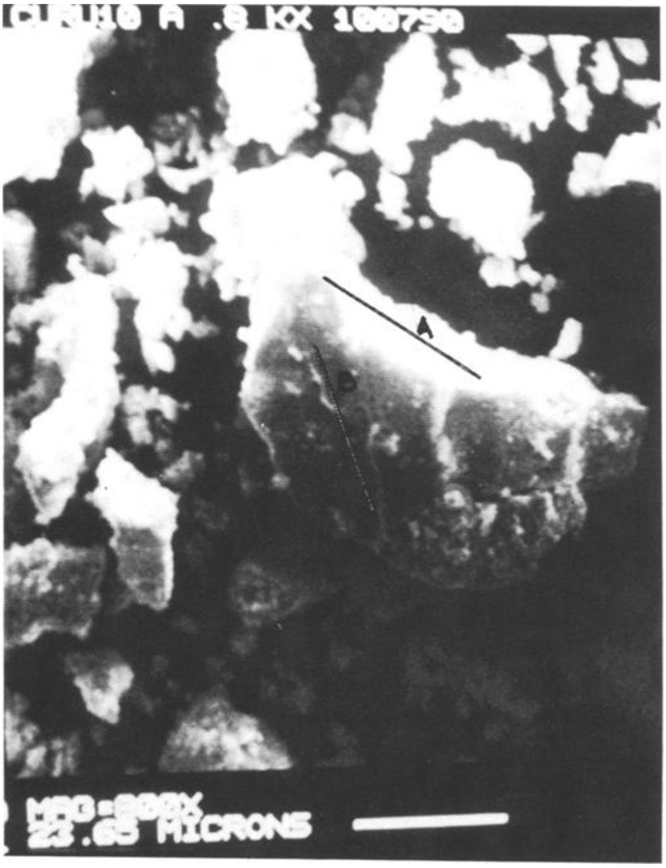
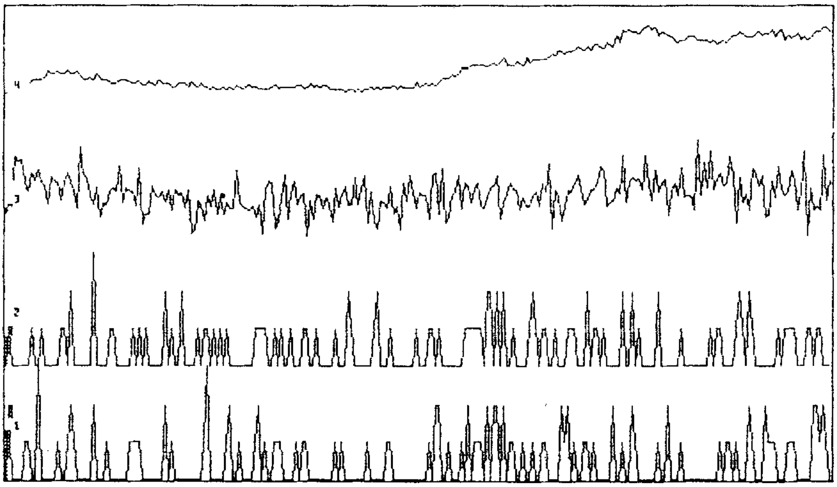
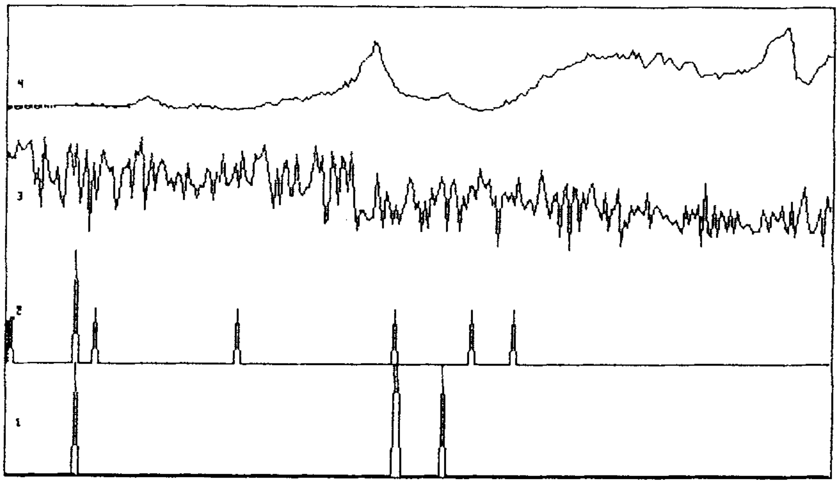


Fig. 2. Raney copper particle.



Line A



Line B

Fig. 3. Microanalysis for lines A and B (particle fig. 2). (1) Ru, (2) Cl, (3) Cu, (4) video.

ruthenium concentration is very low (2B) while along line A a high ruthenium concentration is pointing out (2A) that Ru is deposited in decoration on particle contours.

On the other hand microanalysis of chloride (K, 2.62 KeV although overlapping with Ru transition (L, 2.55 KeV)) points out that chloride deposition does not occur on low index planes of Cu (line B, figs. 2 and 3). Thus chloride and ruthenium revealed by chemical analysis, were deposited on the same sites of Raney Cu catalyst.

In conclusion, the preparation of bimetallic catalysts in which the two metals are in interaction was carried out by using a specific redox method where the basic metal itself (Cu) is used as the reducer of the additive (Ru^{3+}). Such direct redox reaction is easily conceivable in the case of a noble metal deposit (like Ru) on a less noble metal (like Cu). It appears that in the case of the Cu-Ru couple, redox reaction, like all corrosion reactions, occurs on particular sites of the oxidizable metal. So Ru is deposited on high index planes of Cu.

In the case of glucitol conversion on Cu-Ru catalysts only cyclodehydration reactions occur [3]. The catalytic sites would be $Cu_x\ Ru_y\ Cl_z$ on the high index planes of Cu. On Raney copper, only degradation reactions (C–C and C–O cleavages) occur [1,3] from nucleophilic action of OH group on dehydrogenated species. These OH groups would be located on the same high index planes.

Additional experiments will be performed to determine the role and the nature of the noble metal (by extension to Ag, Au, Pd, Pt, Ir and Rh) and the role of the remaining chloride (by using chloride free precursors) on cyclodehydration reactions.

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