

Cu/ZnO and Cu/ZnO/SiO₂ Catalysts Studied by Low-Energy Ion Scattering

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Low-Energy Ion Scattering (LEIS) was employed to study the surface of unsupported and silica-supported Cu/ZnO catalysts. It was shown that, by applying isotopic enrichment (⁶³Cu and ⁶⁸Zn), the copper and zinc signals can be separated. LEIS measurements showed a considerable amount of lead on the surface of the ⁶³Cu/⁶⁸ZnO catalyst. It was concluded that lead originated from the ⁶⁸ZnO raw material and segregated during catalyst reduction to the surface. In contrast, no impurities were detected on the surface of the ⁶³Cu/⁶⁸ZnO/SiO₂ catalyst. This seemingly contradictory observation was attributed to the higher degree of copper and zinc dispersion in the latter catalyst or interaction of lead with the support. It was shown previously, that catalytic activity of Cu/ZnO/SiO₂ catalysts in methanol synthesis and ester hydrogenolysis is proportional with the reduction temperature applied (600–750 K). A depth profile of copper and zinc obtained for the high-temperature reduced silica-supported catalyst revealed that the surface was enriched in zinc, whereas copper was more abundant in layers beneath the surface. In the low-temperature reduced catalyst, the zinc enrichment was less prominent. These results suggest that the reduction at high-temperature results in segregation of zinc oxide to the surface.

1. Introduction

Copper catalysts are used for many industrial processes. An important feature of copper is its high selectivity toward alcohols in hydrogenation reactions. For this reason, copper-containing catalysts are used in the production of, for examples, methanol from synthesis gas and fatty alcohols from fatty methyl esters. Usually, however, promoters are added to the catalyst to improve activity, selectivity, and/or chemical and physical stability. Zinc oxide is a common promoter for copper-containing catalysts in methanol synthesis.

Activity of the Cu/ZnO catalyst depends considerably on the reduction temperature. The active phase of Cu/ZnO methanol synthesis catalysts has been under debate for a long time. Hypotheses include Cu⁰,¹ ZnO on top of Cu⁰,² Cu⁺ in ZnO,³ and Cu⁰-Zn⁰ alloys.⁴ Part of the controversy regarding the nature of the active site may be explained by the dynamic behavior of copper in Cu/ZnO catalysts, which was recently reported by a number of authors. Topsøe et al., for instance, report wetting/nonwetting phenomena of copper particles in copper containing catalysts as a function of the reductive/oxidative potential of the gas phase.^{5–7} Yurieva et al., on the other hand, reported formation of flat metallic copper particles on top of a mixed oxide phase during reductive treatments at high temperature.⁸ These metallic copper platelets, which show high activity in hydrogenation reactions, show migratory behavior and redissolve into the mixed oxide phase upon removal of hydrogen at sufficiently high temperatures, yielding ionic copper dissolved in zinc oxide or chromium oxide. This result implies that, depending on the pretreatment procedure, the catalyst consists either of Cu⁰ on top of ZnO or Cuⁿ⁺ dissolved in ZnO; both

states have been reported to be present in methanol synthesis catalysts.^{1,3} Subsequently, it was substantiated that these phenomena can also be observed in supported catalysts. Cu/ZnO/SiO₂ catalysts show a similar increase of hydrogenation activity with increasing catalyst reduction temperature and dynamic behavior is also observed.^{9,10}

It is clear that for elucidation of the nature of the active phase, proper determination of the surface composition of Cu/ZnO catalysts is crucial. For elucidation of the dynamic behavior of copper, information on both the surface composition as well as the depth distribution of copper and zinc in the top atomic layers is required. Because layers of copper can be as thin as a few atoms, the analytical technique should preferably be sensitive to layers with atomic thickness.

Low-Energy Ion Scattering (LEIS) is a surface-analysis technique with an extremely high sensitivity to the outermost atomic layer of a surface. LEIS is based on the elastic binary collisions of rare gas ions with outermost surface atoms. The high surface sensitivity is due to fact that the ions, which penetrate beyond the first atom layer, are almost all neutralized and, therefore, not detected. The energy of elastically scattered ions depends on the mass of the surface atoms and, hence, the energy spectrum of the ions represents the mass spectrum of the outermost atomic layer. However, that differentiation between target atoms with nearly the same mass, such as copper and zinc, is often quite difficult and depends on the mass resolution of the specific LEIS setup. In earlier reported LEIS studies of Cu/ZnO catalyst, these peaks remained unresolved and only the combined copper + zinc intensity was reported.^{11–14}

In this paper, an attempt was made to study with LEIS the effect of reduction temperature on the surface composition of

Cu/ZnO and Cu/ZnO/SiO₂ catalysts. To be able to separately detect copper and zinc signals, catalysts prepared with isotopically enriched ⁶³Cu and ⁶⁸Zn were studied. Information on the composition of the outermost atomic layers of Cu/ZnO catalysts obtained with LEIS may lead to a better understanding of the nature of the active phase of this highly interesting catalyst system.

2. Experimental Section

Isotopically enriched ⁶³Cu was obtained from Campro Scientific and was chemically >99.875 wt % and isotopically >99.87 wt % pure. Isotopically enriched ⁶⁸ZnO was obtained from Alfred Hempel GmbH and was chemically and isotopically >98.8 wt % pure. Both metals were converted into their nitrate forms by dissolution in 65% nitric acid (Acros Chimica, p.a.).

A ⁶³Cu/⁶⁸ZnO/SiO₂ (15 wt % Cu, 10 wt % ZnO) catalyst was prepared using homogeneous deposition precipitation as described elsewhere.⁹ The unsupported ⁶³Cu/⁶⁸ZnO (Cu:Zn = 2:1 mol/mol) catalyst was prepared by precipitation at pH = 7 according to the method described in ref 15. Subsequently, the precipitation mixture was aged for 140 min after which it was filtered and flushed with demineralized water. Both catalysts were dried overnight in air at 363 K.

The dried catalyst samples were pressed into a hole (2 mm diameter) in an aluminum disk (9.9 mm diameter). The silica-supported catalyst was calcined in a flow of 2 cm³·s⁻¹ of dry air at a temperature of 750 K for 12 h. Subsequently, the catalyst was reduced for 1 h at 600 or 700 K in a flow of 2 cm³·s⁻¹ hydrogen (Praxair, 99.999% pure and further purified using a copper catalyst and 5 Å molecular sieves). The unsupported catalyst was calcined in a flow of 2 cm³·s⁻¹ of dry air at 623 K for 6 h and reduced in 2 cm³·s⁻¹ hydrogen at 623 K for 1 h. The heating rate was in all cases 72 K·h⁻¹. The reduction procedures applied correspond to the ones described in refs 8–10 (and references therein), where remarkable changes in catalyst activities for acetone hydrogenation, ester hydrogenolysis, and methanol synthesis reactions are reported depending on the temperature of the reductive pretreatment. The resulting activated catalysts are extensively characterized in the cited references. Before transferring the samples to the LEIS setup, the samples were passivated at 363 K in a flow of 2 cm³·s⁻¹ 1% N₂O/99% Ar.

In the LEIS setup, the catalysts were rereduced in a pretreatment chamber at ≈25 K below the previously applied reduction temperature for about ≈15 min under a flow of hydrogen at atmospheric pressure.

The pure ⁶³Cu sample did not receive ex situ reduction or calcination and was only reduced under flowing hydrogen at atmospheric pressure in the LEIS pretreatment chamber at 573 K for 30 min. The pure ⁶⁸ZnO sample was outgassed in a vacuum (<10⁻⁴ mbar) for 30 min at 523 K preceding the measurements.

The LEIS experiments were carried out using the NODUS setup, which is described elsewhere in more detail.¹⁶ A beam of monoenergetic rare gas ions (typically He⁺, Ne⁺, or Ar⁺, with energies of 1–5 keV) is directed perpendicularly onto the target. The energy distribution of the scattered ions is analyzed through a fixed angle (142°) with a kind of cylindrical mirror analyzer. The base pressure of the UHV system of the NODUS setup is ≈10⁻⁹ mbar. During the measurements, the pressure increases to the low 10⁻⁸ mbar range because of the ion beam.

In this study a 5 keV Ne⁺ beam was used to measure Cu and Zn. Because it is not possible to detect light elements such as O, F, Na, and Mg with a Ne⁺ beam, a 3 keV ⁴He⁺ beam

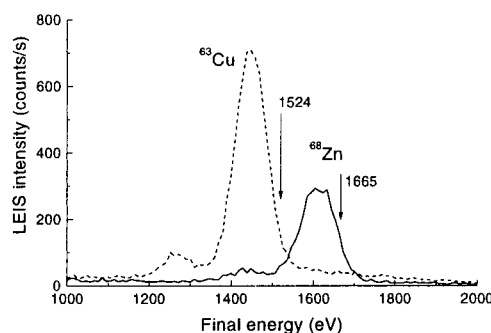


Figure 1. LEIS spectra of pure ⁶³Cu and ⁶⁸ZnO obtained with 5 keV Ne⁺ ions. Solid line: ⁶⁸Zn; dashed line: ⁶³Cu.

was used to check the purity of the surface. The average current density was 4.2 and 3.8 nA per mm² for ⁴He⁺ and Ne⁺, respectively.

As a consequence of the ion bombardment, atoms are sputtered from the target surface. This procedure allows determination of the depth distribution of the elements in the sample. The sputter yield — the number of target atoms sputtered from the surface of the catalyst per incident ion — for metallic copper for 5 keV Ne⁺ ions is 3 atoms per ion.¹⁷ For zinc oxide, to the best of our knowledge, no values of sputter yields for 5 keV Ne⁺ ions are available. When it is assumed that the sputter yield is 3 atoms·ion⁻¹ and the number of atoms in the surface of the catalysts is 1.3 × 10¹⁵ atoms·cm⁻² (the average of copper¹⁸ and zinc oxide¹⁹), an ion dose of 0.43 × 10¹⁵ ions·cm⁻² corresponds to the removal of approximately one atomic layer.

The LEIS spectra of the ⁶³Cu/⁶⁸ZnO/SiO₂ catalyst were measured as a function of the Ne⁺ ion dose (≈depth), and Cu and Zn peaks were fitted with two Gaussian peaks and a linear baseline with the aid of the PeakFit version 4 (Jandel scientific software) computer program. Peak height instead of peak area was used as a measure of the signal. Generally, however, peak heights and areas give equal results.^{20,21}

3. Results and Discussion

3.1. Pure Materials. In Figure 1 the LEIS spectra of the reference samples (pure isotopically enriched ⁶³Cu and ⁶⁸ZnO) are shown. Theoretically, the onsets of the ⁶³Cu and ⁶⁸Zn peaks measured with 5 keV Ne⁺ are expected at final energies of 1524 and 1665 eV, respectively, and hence the expected difference is 141 eV. This difference is much larger than would be obtained for nonenriched copper and zinc (56 eV). Furthermore, as both nonenriched Cu and Zn contain more than one isotope, an additional peak broadening occurs that results in a considerable overlap of the peaks, which impedes the copper–zinc peak separation.^{11–14} It is, however, clear from Figure 1 that enriched ⁶³Cu and ⁶⁸Zn can be individually detected and that the mass resolution of the NODUS LEIS setup is sufficient for the present study.

In the LEIS spectra of both ⁶³Cu and ⁶⁸ZnO, small peaks can be observed at final energies of ≈200 eV lower than the main LEIS peak. These peaks are due to scattering of the ²²Ne isotope. The spectra of ⁶⁸ZnO also showed an additional peak at ≈3500 eV, which is attributed to contaminant lead.

The ⁶³Cu and ⁶⁸ZnO reference spectra were used for quantification of copper and zinc signals. However, because the ⁶⁸ZnO reference sample is not pure, the actual concentration of Zn in the catalyst will be probably slightly lower than the quantified concentration. An earlier study has shown no preferential sputtering of oxygen.²² Using the reference LEIS signals of Cu and Zn, we can calculate the coverage of Cu and

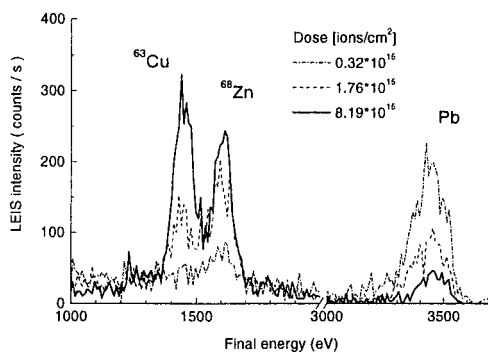


Figure 2. LEIS spectra of the unsupported ⁶³Cu/⁶⁸ZnO catalyst as a function of ion dose obtained with 5 keV Ne⁺ ions.

ZnO on the measured sample from the following equation

$$\text{Coverage \%} = S_i/S_{i,\text{ref}} \times 100\% \quad (1)$$

where S_i and $S_{i,\text{ref}}$ are the LEIS signals of element i in the catalyst and in the reference sample, respectively. However, to use this approach we have to assume that Cu on the catalyst is metallic Cu, whereas Zn is present as zinc oxide. Because the roughness of a sample surface decreases the intensity of the LEIS signal, the differences in surface roughness between sample and reference should be taken into account. It has been shown, however, that the influence of surface roughness is small and can be neglected when comparing pressed powders with not too different surface morphologies.²³

3.2. ⁶³Cu/⁶⁸ZnO. In Figure 2, the LEIS spectra of the unsupported ⁶³Cu/⁶⁸ZnO catalyst reduced at 623 K are shown. Although the signals are somewhat noisy, the separate ⁶³Cu and ⁶⁸Zn signals are still clearly recognizable.

As was explained previously, at a Ne⁺ dose of 0.43×10^{15} ions·cm⁻², approximately one atomic layer is sputtered away. This result implies that the spectrum collected below this dose contains mainly information on the first atomic layer of the catalyst (in this case, the spectrum that is collected with a dose of 0.32×10^{15} ions·cm⁻², see Figure 2). It can be clearly seen that both the copper and zinc signals are weak at low ion doses and that both increase with increasing ion dose, which would imply that the concentration of copper and zinc is low in the first atomic layer and increases in the layers directly beneath the surface. However, an increase in the LEIS signal at low dose is commonly observed and is normally attributed to adsorbed hydrogen or hydroxyl groups on the surface, which shield the underlying atoms and decrease their intensities. Further, the reduction of the samples under hydrogen prior to LEIS measurements could also suggest the presence of adsorbed hydrogen on the surface. Hydrogen is, however, sputtered very effectively and thus shielding by hydrogen can be excluded after a sputter dose of $\approx 0.4 \times 10^{15}$ ions·cm⁻².

In addition to signals of copper and zinc, an additional peak is observed at ≈ 3500 eV, which is attributed to contaminant lead. It can also be seen from Figure 2 that the Pb peak becomes less intense at higher ion dose whereas the copper and zinc signals increase. This result may suggest that copper and/or zinc are at least partly covered by lead. Experiments with polycrystalline Cu and Pb showed that with a 5 keV Ne⁺ beam, a lead atom gives about a 4.4 times higher signal than a copper atom. It is, however, evident that it is not only Pb which is shielding Cu and Zn, but most probably also hydroxyl groups.

Unsupported catalysts reduced at higher temperature (≈ 700 K) were also measured. They showed also a considerable amount of lead on the surface. Interestingly, the surface com-

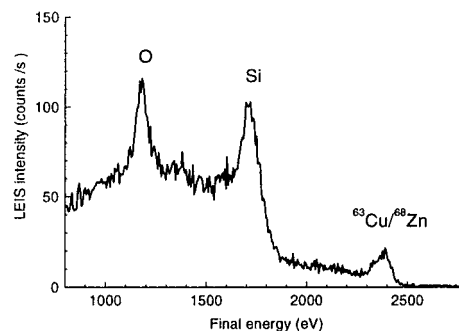


Figure 3. LEIS spectrum of ⁶³Cu/⁶⁸ZnO/SiO₂ catalyst obtained with 3 keV ⁴He⁺ ions. Catalyst reduction temperature: 700 K.

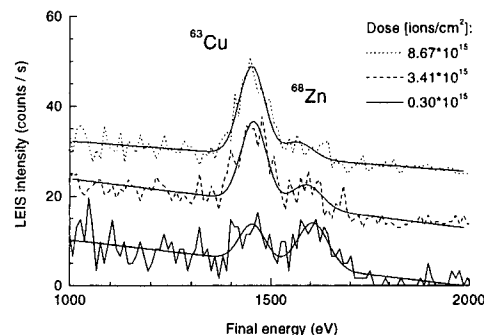


Figure 4. LEIS spectra of the ⁶³Cu/⁶⁸ZnO/SiO₂ catalyst obtained with 5 keV Ne⁺ ions (spectra have been vertically shifted for clarity). Catalyst reduction temperature: 700 K. Solid lines: fitted Gaussian peaks.

position of the high- and low-temperature-reduced catalysts differed clearly. However, because of the presence of lead on the surface, no quantitative analysis nor conclusions were made from these measurements.

Careful analysis of all materials used revealed that the ⁶⁸ZnO raw material is the source of the lead contamination. Apparently, lead segregates from ⁶⁸ZnO particles to the surface of the catalyst during the reduction.

Lead is present in zinc ore²⁴ and cannot be easily removed; even high purity zinc oxide contains lead in the ppm range.²⁵ In view of this phenomenon, contamination and segregation of lead should also be taken into account when analyzing the surface of industrial Cu/ZnO catalysts.

3.3. ⁶³Cu/⁶⁸ZnO/SiO₂. In Figure 3, a LEIS spectrum of the ⁶³Cu/⁶⁸ZnO/SiO₂ catalyst reduced at 700 K is shown. This spectrum is measured with 3 keV ⁴He⁺ ions, so the signals of ⁶³Cu and ⁶⁸Zn cannot be separated as the energy difference is only 15 eV. In addition to copper, zinc, silicon, and oxygen, no other elements are observed, indicating the relatively high purity of the catalyst surface. Even lead, which was seen on unsupported catalysts, is not detected. With a 3 keV ⁴He⁺ beam, lead is expected at 2800 eV. In the previous section we concluded that lead originates from ⁶⁸ZnO raw material. Therefore, the absence of lead on the supported catalyst seems contradictory. This result might be caused by the different method of catalyst preparation (pH, metal concentration, time) or interaction of lead with the silica carrier (e.g. through formation of lead glass, PbSiO₂ during reduction), but most probably is due to the much higher degree of copper and zinc dispersion in the supported catalyst with respect to the unsupported catalyst.

In Figure 4, LEIS spectra of the catalyst reduced at 700 K, obtained with a 5 keV Ne⁺ beam, are shown as a function of the ion dose. Although fairly noisy, this figure still shows separate copper and zinc signals, indicating that LEIS can also

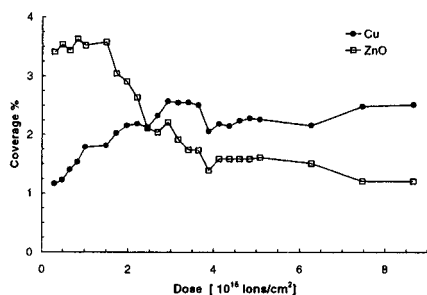


Figure 5. The coverage percentage of Cu and ZnO on the silica-supported catalyst reduced at the high temperature (700 K) as function of ion dose. The estimated error of the coverages is $\approx 10\%$ of the indicated value.

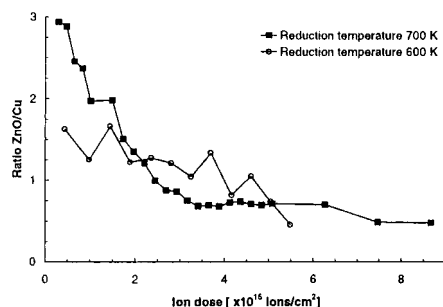


Figure 6. The ratio of ZnO and Cu coverage as a function of ion dose, obtained for $^{63}\text{Cu}/^{68}\text{ZnO}/\text{SiO}_2$ with 5 keV Ne^+ ions.

be applied for analysis of supported catalysts. It is apparent that the LEIS signals of copper and zinc change as a function of ion dose. At a low dose ($0.3 \times 10^{15} \text{ ions}\cdot\text{cm}^{-2}$), the signals of copper and zinc show equal intensity, whereas at higher ion dose, the copper signal increases and the zinc signal decreases in intensity.

By fitting Gaussian curves through the LEIS spectra and using eq 1, the coverage percentage of Cu and ZnO can be obtained. In Figure 4 an example of a fit with Gaussian peaks and linear baseline is shown. Figure 5 shows the coverage percentages for the catalyst reduced at 700 K. It seems that the ZnO coverage remains constant up to a dose of $\approx 1.5 \times 10^{15} \text{ ions}\cdot\text{cm}^{-2}$, whereas the Cu coverage increases up to a dose of $\approx 3 \times 10^{15} \text{ ions}\cdot\text{cm}^{-2}$. As explained in the previous section, the adsorbed hydrogen or hydroxyl groups on the surface shield the underlying atoms and reduce the LEIS signal at low ion dose. As a consequence, the observed LEIS signal underestimates the amount of the elements present on the surface at low ion dose. Therefore, it is reasonable to expect that both the Cu and ZnO coverages at low ion dose are in fact higher than the obtained 1.2% and 3.5%, respectively. Further, it can be seen in Figure 5 that the ZnO coverage decreases at least 2.3%, whereas the Cu coverage increases at most 1.3%. This result suggests that ZnO covers partly not only Cu but also the silica support.

The coverage ratio ZnO/Cu as a function of ion dose for both the low- and high-temperature-reduced catalyst is shown in Figure 6. At a low ion dose, the ZnO/Cu coverage ratio for the high-temperature-reduced catalyst is ≈ 3 , and at higher ion dose, the ratio decreases and reaches a constant level. The value is ≈ 0.5 at a dose of $4 \times 10^{15} \text{ ions}\cdot\text{cm}^{-2}$. Assuming that no preferential sputtering of Cu nor Zn occurs, we can conclude that the surface of the high-temperature-reduced catalyst is enriched in Zn.

The low-temperature-reduced catalyst shows a less prominent decrease with ion dose in the ZnO/Cu coverage ratio than the high-temperature-reduced catalyst. By comparison, it seems that

the reduction of the Cu/ZnO/SiO₂ catalyst at a higher temperature results in a larger ZnO enrichment.

The LEIS results suggest, thus, that ZnO is enriched on the surface and forms a thin layer, partly covering Cu and the silica support. The ZnO enrichment can be justified by considering the total free energy of the system, which is minimized in the thermodynamical equilibrium. During the reduction at high temperature where the species are mobile, the species with the lowest surface energy will segregate to the surface. Because ZnO has lower surface energy than Cu and SiO₂,²⁶ it will segregate to the surface and spread over Cu and the silica support in order to minimize the surface energy.

The LEIS results obtained for the Cu/ZnO/SiO₂ catalyst do not confirm the previously reported model for this catalyst of thin layers of copper on top of a mixed copper–zinc oxide phase.¹⁰ The high-temperature-reduced catalyst not only showed remarkably enhanced activity in the methanol synthesis and ester hydrogenolysis reactions,^{9,10} but also substantial coverage by ZnO, suggesting that this geometry is promoting catalytic activity, as proposed in refs 2 and 4. However, several factors may complicate the interpretation of LEIS data especially at low ion dose. First, the adsorbed hydroxyl groups, which shield the underlying atoms, make the interpretation of the spectra difficult. Therefore, further improvement of the cleaning procedure for these catalysts prior to LEIS measurements would be useful. Moreover, to make a reliable quantitative analysis of the topmost layer, a good signal to noise ratio of the data obtained at low ion dose is required. In this study, an ion dose of $0.3 \times 10^{15} \text{ ions}\cdot\text{cm}^{-2}$ was already used when the first spectrum (see Figure 4) was completed. At such an ion dose, before one atom layer is sputtered away, it would be preferable to have better signal to noise ratio of the data. Therefore, research of this catalytic system will be pursued in the more sensitive Calipso LEIS setup.

4. Conclusions

In contrast with previous studies on copper–zinc catalysts, LEIS allows for separate detection of copper and zinc on the surface of both unsupported and silica-supported $^{63}\text{Cu}/^{68}\text{ZnO}$ catalysts. On the surface of the unsupported $^{63}\text{Cu}/^{68}\text{ZnO}$ catalyst, a considerable amount of lead was detected. It was concluded that lead originates from the ^{68}ZnO raw material and segregates to the surface during catalyst reduction. Because lead is a common impurity in zinc ore and removal is difficult, surface contamination of lead in industrial Cu/ZnO catalysts must also be considered. Lead surface contamination rendered quantitative analysis of the surface of the unsupported $^{63}\text{Cu}/^{68}\text{ZnO}$ catalyst difficult. It is clear, however, that both copper and zinc are present in the outermost surface of the catalyst.

With the $^{63}\text{Cu}/^{68}\text{ZnO}/\text{SiO}_2$ catalyst, LEIS revealed also that both copper and zinc are present in the outermost surface. In addition to copper and zinc, only silicon and oxygen were observed, indicating the relatively high purity of the catalyst surface. The reason that no lead could be observed in this case is probably the higher degree of copper and zinc dispersion with respect to the unsupported sample or the interaction of lead with the support.

A depth profile of copper and zinc concentrations of the $^{63}\text{Cu}/^{68}\text{ZnO}/\text{SiO}_2$ catalyst was obtained by fitting the raw LEIS spectra with Gaussian peaks. Based on these profiles, it appears that zinc enrichment exists in the first few atomic layers of the surface of the high-temperature-reduced catalyst. In the low-temperature-reduced catalyst, the ZnO enrichment is less obvious. This image does not confirm the models previously

put forward for this catalyst that propose thin layers of copper on a zinc oxide phase. The high temperature reduced catalyst proved remarkably active in methanol synthesis and ester hydrogenolysis reactions, so the results are in agreement with a model in which ZnO coverage is beneficial for catalytic conversion.

The zinc enrichment on the catalyst surface is supported by the fact that the surface energy of ZnO is lower than that of Cu and SiO₂. Therefore, in conditions where the species are mobile enough, such as during high-temperature reduction, ZnO will segregate to the surface to minimize the total free energy.

Several factors may, however, complicate the interpretation of the LEIS data, like nonuniform distribution of copper and zinc in the catalyst or a too high ion dose for detection of small metallic platelets. In view of these potential complications, research on these catalytic systems was pursued in the Calipso LEIS setup, which is 1000 times more sensitive than the NODUS setup.

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