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Surface Analysis of Raney Catalysts

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Raney nickel and its variants are widely used as hydration catalysts. For surface analysis, e.g., scanning electron microscopy (SEM), electron spectroscopy for chemical analysis (ESCA), or micro-Auger electron spectroscopy (AES), it is necessary to transfer the samples from the reactor to the vacuum of the electron microscope or electron spectrometer unchanged. Appropriate experiments and results obtained for Raney Ni catalysts of several types (types doped with Cr, Mo, and Cu) and also for Raney Cu, which was examined for comparison, are described. Some of the samples were taken from catalysts that had already been used. These results provide a basis for industrial analysis, either in the development of catalysts or in the investigation of activity differences.

INTRODUCTION

Raney catalysts have been used for several decades, both industrially and in the laboratory, in numerous reduction and hydration reactions (such as the saturation of C–C multiple bonds and aromatic rings and the reduction of aldehydes and ketones to the corresponding alcohols and of nitro and nitrile groups to amines). They are distinguished by high activity and often by high selectivity and are therefore outstandingly economical. In most cases Raney nickel is used, but Cr-, Fe-, Mo-, and Cu-doped variants, and also Raney Cu and Raney Co catalysts, are available for special purposes. These catalysts were invented by Murray Raney (1885–1966), whose first patent (U.S. No. 1 563 587) was granted in 1925. They are produced by removing with an alkaline solution the aluminum from Ni–Al alloys (generally 50:50 wt%, or, if doped, $\mathrm{Ni}_{50-x}\text{-}Me_x\text{-}\mathrm{Al}_{50}$, where Me = Cr, Fe, Mo, Cu). The residue consists mainly of highly disperse Ni with a large specific surface area of 80–120 m^2/g. The catalysts are highly pyrophoric in the dry state and therefore have to be kept under water or some other suitable liquid.

Although Raney catalysts have been used industrially for a very long time, there are still numerous gaps in our knowledge of the processes involved in catalysis, e.g., of the hydrogen transfer and of ageing and poisoning phenomena. If the findings obtained by chemical, kinetic, and physical methods are to be interpreted, the fullest possible morphological and analytical characterization of catalysts is required. For this it is necessary to have preparation techniques which enable catalyst samples to be transferred from the reactor to the vacuum of an electron microscope or electron spectrometer without undergoing change.

EXPERIMENTAL

Catalysts. The catalysts investigated are listed in Table 1. According to the information available to us concerning catalysts 1, 5, and 7 in Table 1, they were produced by extracting with alkali the aluminum from alloys containing approximately 50% by weight of this metal. The starting alloy of catalyst No. 6 was Ni46 Al50Cu4. It was leached with excess NaOH. As Raney catalysts are pyrophoric, they have to be kept under water. Initially the water is generally

0021-9517/85 $3.00

TABLE 1

Designation and Description of Catalysts Investigated

Commercial Designation	Manufacturer	Description
1. Raney Ni fine No. 28-183	Strem	Raney Ni with large surface area
2. Raney 4200	Grace, Davison Chemical	Raney Ni with particle size range 73–350 μm
3. Raney 24	Grace, Davison Chemical	Raney Ni doped with Cr. Particle size range 70% <50 μm
4. Raney 4300	Grace, Davison Chemical	Raney Ni doped with Mo. Particle size range 74–350 μm
5. Raney 29	Grace, Davison Chemical	Raney Cu. Particle size range 70% <40 μm
6. Raney Ni–Cu	Laboratory sample	Raney Ni doped with Cu
7. Raney Ni, copperized	Laboratory sample	Raney Ni fine (No. 1) copperized electrochemically after production

saturated with air. To a small extent, therefore, the catalyst may be oxidized, consuming the oxygen dissolved in the water. Residual metallic Al may also decompose water, producing hydrogen.

The listed catalysts were first characterized in their initial state. In the case of the Raney 4200 catalyst, materials which had been used, e.g., to hydrate acetonitrile to ethyl amine, were also investigated.

Investigation methods. The prerequisites of Raney catalyst characterization are morphological investigation, bulk and surface analysis, and an investigation of spatial inhomogeneity. The surface was imaged in a Stereoscan 180 (Cambridge Instruments) scanning electron microscope, which was fitted with an energy-dispersive X-ray spectrometer and an Auger spectrometer (*1*). This combination provides good orientation with high lateral resolution, thus facilitating the choice of the areas to be analyzed. The X-ray microanalysis provides, in effect, a bulk analysis of the catalyst particles, the penetration depth of the primary electrons (2–5 μm) being relatively large, whereas the Auger microanalysis permits a genuine surface analysis in the nanometer range at the same place. In this procedure only the element information contained in the Auger spectrum is evaluated. In consequence of the partial overlapping of lines (e.g., those of Ni and Al in the low-energy range) and the electrostatic charging (of oxides) it is not possible to interpret chemical shifts.

A quantitative surface analysis of the elements present and a determination of the valence states of these elements from chemical shifts of the photoeffect lines were performed by ESCA in a Leybold-Heraeus LHS 10 system. The ESCA spectrum also contains the information contained in the Auger spectrum; since, however, the exiting X rays cannot be focused, a group of catalyst particles was averaged (the analyzed area was about 0.2 cm^2).

Preparation methods. Since, on the one hand, the fresh catalysts are kept under water and reactions promoted by catalysts occur mainly in aqueous or aqueous-alcoholic media, while, on the other hand, the investigation methods call for a high or even ultrahigh vacuum, a way of transferring the catalysts from the reactor to the spectrometer without undergoing changes when in contact with the laboratory air must be found. With Raney catalysts this air-lock problem can be solved in several ways:

(a) The samples are mounted on special sample-holders under water/alcohol and introduced directly into the vacuum of the measuring instrument or flange-connected preparation chamber, from which the liquid is then removed by pumping.

(b) The opportunities for oxidation by laboratory air can be further reduced by introducing the sample under ice on a refrigerated sample holder at the temperature of liquid nitrogen. The sample is then freeze-dried in the sample chamber of the SEM (10^{-8} mbar basic pressure) or of the ESCA instrument (10^{-10} mbar basic pressure) itself.

(c) The sample holders are placed in a glove box flooded with N_2 and transferred in the damp state to the measuring instruments with the aid of a specially developed UHV air-lock system (*2*).

Methods (b) and (c) are costly, but neces-

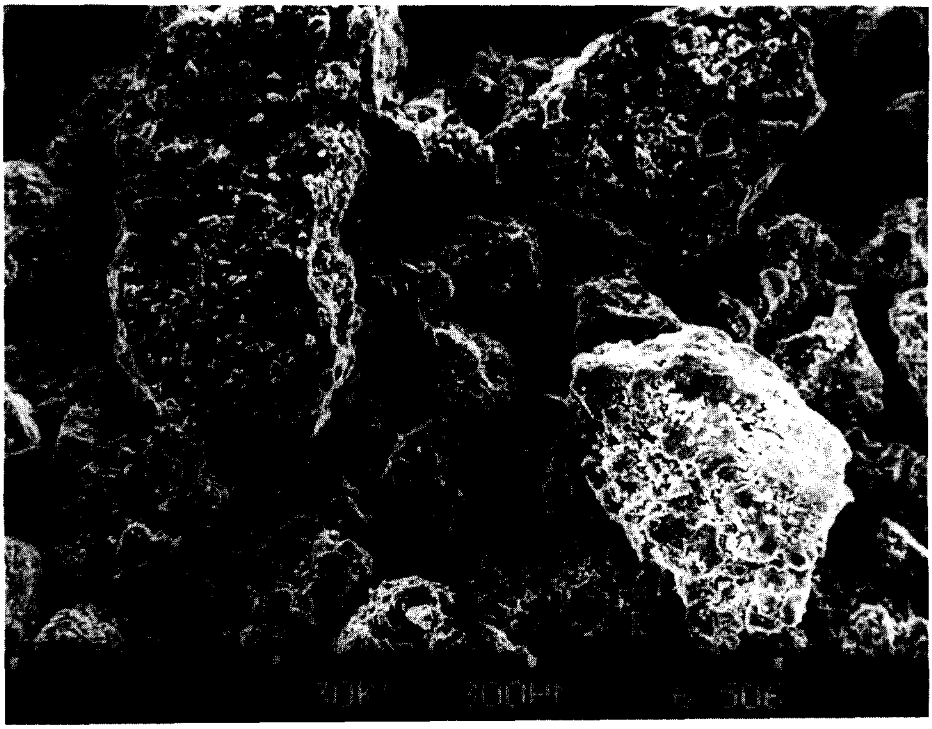

FIG. 1. Agglomerates in fresh Raney Ni fine (SEM).

sary when it is a matter of detecting slight oxidation of the Ni. Method (c) has the special advantage that the quantity of liquid covering the catalyst may be small. Where fresh catalysts are concerned no morphological differences are detectable by SEM, regardless of the method used. For used catalysts it is advisable to employ method (c) because in this case dissolved substances, which would form a surface deposit when the liquid evaporates, can be easily removed by rinsing with oxygen-free water.

When the above preparation techniques are used, the samples are oxidized, and displayed marked pyrogenic symptoms upon being removed from the instruments.

RESULTS AND DISCUSSION

Fresh Raney Ni Catalysts

The samples, both of Raney Ni fine and of Raney 4200, consisted of large (5–30 μm) particles (many of which were platelets with cracks), which, for their part, were more or less loosely agglomerated to form larger units (size up to 300 μm) (Figs. 1 and 2).

The structures of Raney catalysts are predetermined by that of the starting alloy. According to Freel *et al.* (*3, 4*), the following phases are present in a Ni–Al alloy containing 50% by weight of Ni: eutectic of Al with dissolved Ni and $NiAl_3$ approx. 2%, $NiAl_3$ approx. 40%, and Ni_2Al_3 approx. 58%.

In the alkaline medium mainly the eutectic and $NiAl_3$ are decomposed under mild conditions, whereas Ni_2Al_3 is attacked more slowly or only at higher temperatures and alkali concentrations. The dissolution of the eutectic leads to decomposition in individual grains, while the additional loss of Al causes shrinkage cracking, such as can be seen in Fig. 2, for example, to occur. The final development is the formation of the pore structure responsible for the large BET surface area (*3*). With the Raney Ni

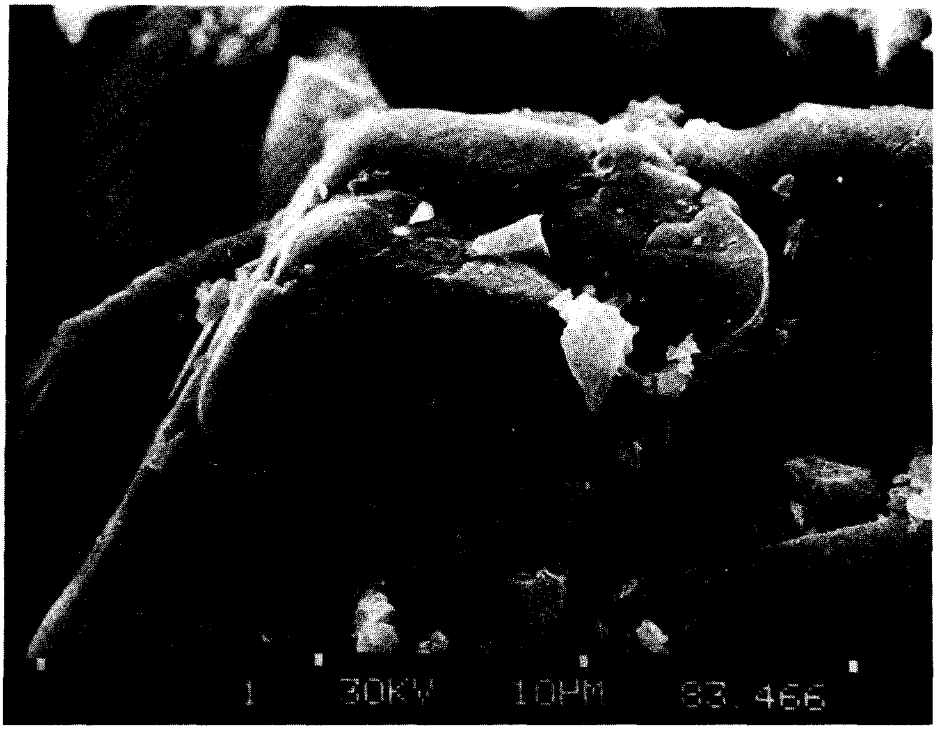

FIG. 2. Single particles of Raney Ni fine with shrinkage cracks (SEM).

catalysts this structure cannot be resolved in the SEM but it can be made visible in the TEM on a transirradiable particle (Fig. 3). In addition to being detected in the TEM (*5*), pores with diameters of less than 10 nm are expected in view of the results of X-ray diffractometry (*5*) and adsorption experiments (*3*, *6*). The pores of Raney Cu are wider (see below).

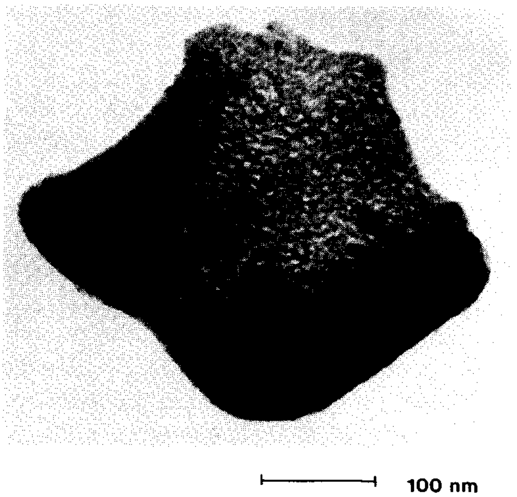

FIG. 3. TEM picture of a single particle of Raney Ni fine.

Energy-dispersive X-ray microanalysis (Fig. 4) reveals, in addition to Ni, approximately 5–10% of Al. The Auger microanalysis also shows small quantities of S in some cases (Fig. 4). Conspicuous features of these catalysts, especially of Raney Ni fine, are the variation of the Ni : Al intensity ratio from grain to grain (this is not shown by the bulk analysis) and the high Al (Al oxide) concentration at the particle surface, as given by the ESCA and AES spectra (Figs. 4 and 5) after application of appropriate sensitivity factors.

In the case of Raney Ni fine we detected not only particles with a more or less pronounced Al accumulation at the surface, but also needle- or platelet-shaped crystals (Fig. 6), in which only the elements Al and O were detectable by micro-AES. Probably they consisted of crystalline Al oxide or hy-

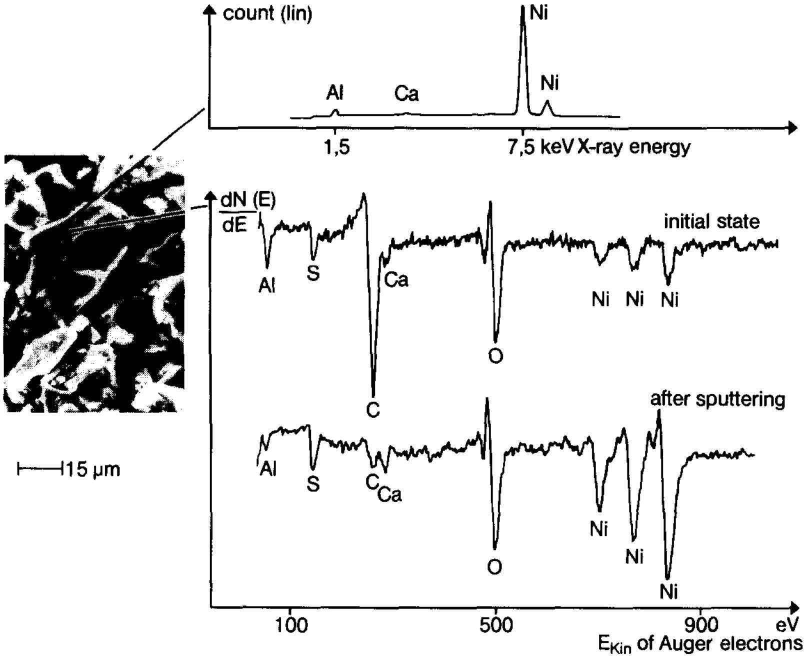

FIG. 4. Fresh Raney Ni fine. X-Ray and Auger microanalysis of the same particle.

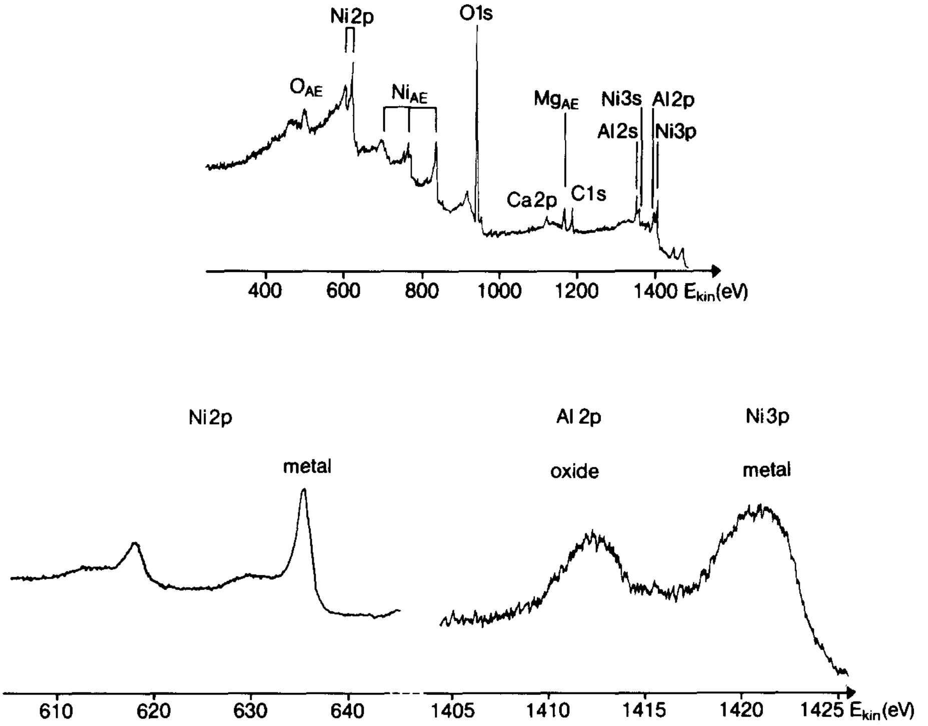

FIG. 5. ESCA spectra of fresh Raney Ni fine. Above: Wide scan spectrum. Below: Ranges of Ni 2*p* and Al 2*p*/Ni 3*p*; horizontal axis elongated to reveal the valence states of Ni and Al and, as evidence of the Al accumulation, the Ni 3*p* : Al 2*p* intensity ratio.

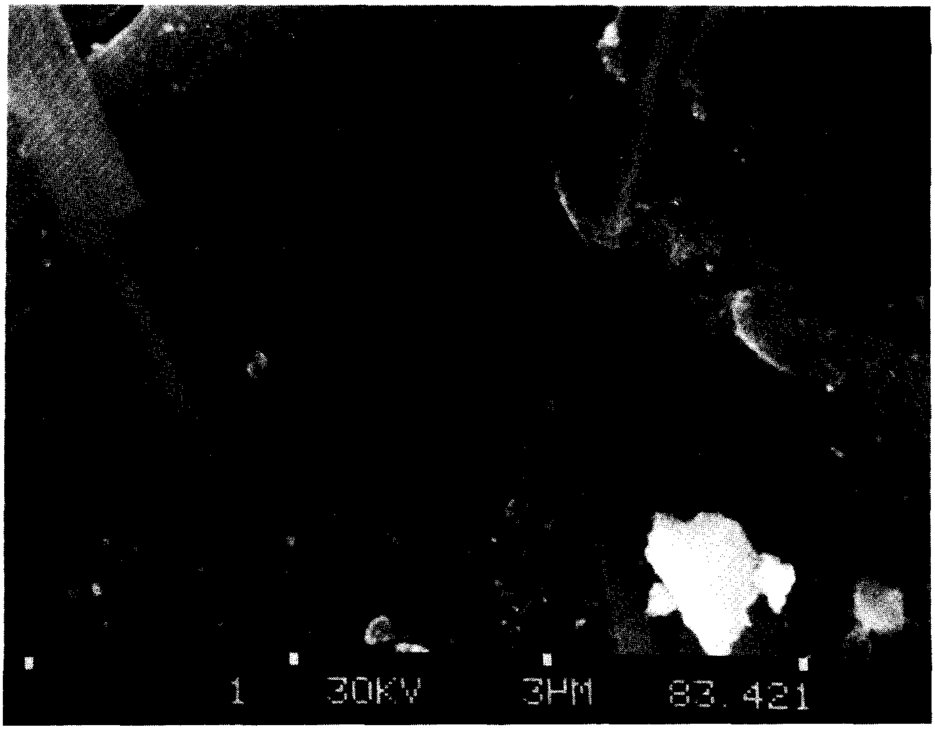

FIG. 6. Al oxide/hydroxide crystals on a single particle of fresh Raney Ni fine catalyst. SEM picture of the uncoated sample at 30 kV primary beam voltage.

droxide. Having a lower density than that of Ni, they appear translucent under the imaging conditions and are transirradiated in the X-ray microanalysis.

The ESCA spectrum (Fig. 5) shows a high O intensity, but it is clear from the Ni 2*p* spectrum that Ni is not present as oxide or hydroxide. The oxygen is thus bound only to the Al or the excess oxygen is present in the form of adsorbed molecules.

Commercial Raney Ni catalysts contain 5–12% of Al, according to their method of production. In discussing the residual Al content it is important to distinguish between metallic Al and Al oxide or hydroxide. Metallic Al may be present in the finished catalyst in consequence of insufficient dissolution of the Ni_2Al_3 phase, or, still more, of the $(NiMe)_2Al_3$ (*7*) phases of the doped catalysts, which are even more resistant to attack. As observed in the case of Ni–Al alloys, Al has a tendency—already at room temperature, but especially at higher temperatures—to diffuse to the surface of the particles within the depths encompassed by ESCA and AES, and to accumulate and possibly be oxidized there (*8–10*). This tendency could explain the occasional discrepancies between AES and ESCA with regard to the Al concentration. Intensive electron bombardment heats the sample, thus intensifying the migration and oxidation of the Al.

The content of Al oxide is largely dependent on the preparation technique (*4*). If an excess of NaOH is added, Al is reacted and washed out according to

$$\mathrm{Al} + \mathrm{NaOH} + 3\mathrm{H_2O} \rightarrow \mathrm{Na[Al(OH)_4]} + 1.5\mathrm{H_2}$$

and possibly

$$\mathrm{Na[Al(OH)_4]} + 2\mathrm{NaOH} \rightarrow \mathrm{Na_3[Al(OH)_6]} \quad (1)$$

If, however, only a substoichiometric quan-

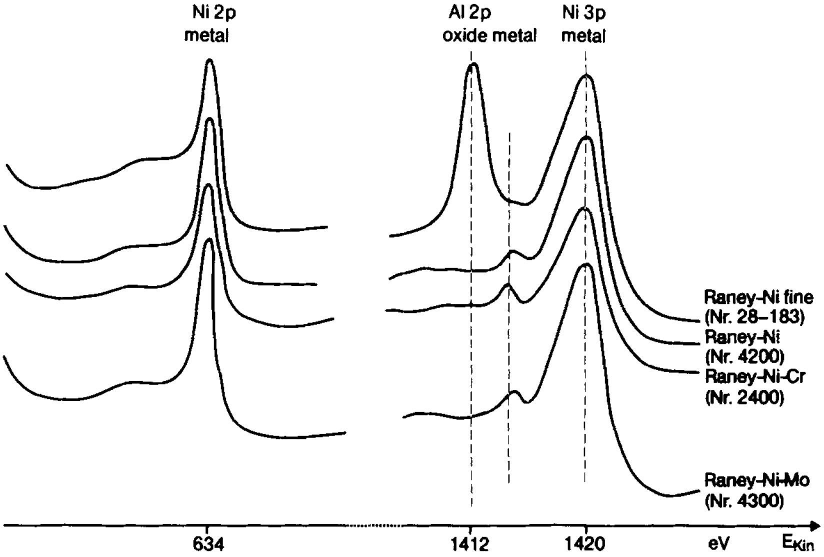

FIG. 7. Ni 2*p* and Al 2*p*/Ni 3*p* ESCA spectra of the investigated Raney Ni catalysts for comparison.

tity of NaOH is provided, the alkaline solution continuously released in the washing-out process as a consequence of the hydrolysis of sodium aluminate according to

$$Na[Al(OH)_4] \rightarrow Al(OH)_3 \downarrow + NaOH \quad (2)$$

is able to react with the residual Al. The $Al(OH)_3$ ages rapidly through the formation of various oxo compounds, e.g., the crystalline substance $Al_2O_3 \cdot 3H_2O$. It is safe to assume that the translucent crystals in Fig. 6 consist of this substance. Because of its crystallinity the $Al_2O_3 \cdot 3H_2O$ makes practically no contribution to the pore volume and BET surface area (*6*).

The ESCA spectra of the investigated Raney Ni catalysts are compared in Fig. 7. In view of what has just been stated, Raney Ni fine was produced with a substoichiometric amount of NaOH and the remaining catalysts with excessive NaOH. However, also in the latter case, an admittedly smaller quantity of Al_2O_3 may be formed according to Eq. (2) or through a direct reaction between Al and entrained oxygen or with H_2O according to

$$Al + 3H_2O \rightarrow Al(OH)_3 + 1.5H_2 \quad (3)$$

However, in this case, instead of being crystalline, the Al_2O_3 is either a thin deposit on the Ni particles or fills the pores (*5*). The "redistribution," discussed by Allgeyer (*11*), of Ni and Al on the surface of Raney Ni catalysts in use is probably attributable mainly to the processes described by Eqs. (2) and (3). Commentaries on this effect will also be found in Refs. (*6, 8–10*). Equation (3), incidentally, makes the formulation of a balance for the hydrogen transfer problematical.

Quantification of the metallic residual aluminum content according to the ESCA spectra (Fig. 7) is difficult because the line of the metallic Al overlaps the satellite structure of the Ni. Delannay *et al.* (*12*) discuss various models for the incorporation of the Al, but are not able to distinguish clearly between a homogeneous solution of the Al in Ni, an accumulation of Al at the surface of the Ni grains, and an envelopment of Al by a thin layer of Ni.

Cr-, Mo-, Cu-Doped, and Copperized Raney Ni Catalysts

In special cases it has been found advantageous to use doped Raney Ni, e.g., to increase the selectivity or durability of the

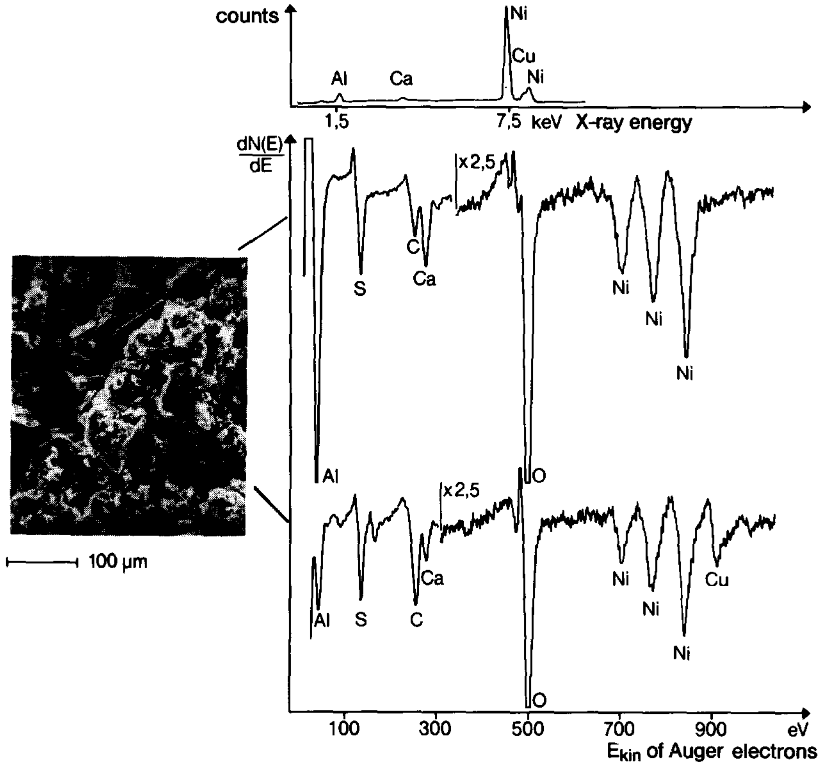

FIG. 8. X-Ray and Auger microanalysis of several single particles of fresh Raney Ni–Cu catalyst (starting alloy doped already).

catalyst. Doping has practically no influence on the morphology of the catalysts. Its order of magnitude is 5–10% and it can be easily detected by the analytical methods. Even X-ray microanalysis provides evidence that the doping elements are not uniformly distributed. This also applies to the surface composition of the individual grains. In Fig. 8 this may be seen for the Cu-doped catalyst: the Auger microanalysis shows that there are surface particles with a certain Cu accumulation and others practically without Cu, whereas the X-ray microanalysis shows the same Cu content in both cases. The ESCA binding energies and Auger parameter reveal that the doping elements are present in the metallic form (Fig. 9).

As regards Al there are certain discrepancies between micro-AES and ESCA: in the micro-AES investigations most of the grains showed a higher Al intensity than would have been expected from the integral ESCA analysis. It is noteworthy that the Al detected by ESCA was mainly metallic. Grains having Cu at their surface showed less enrichment of Al.

For comparison purposes a Raney Ni fine catalyst was chemically copperized. This did not affect the morphological coarse structure of the catalyst. However, both when the samples are introduced into the SEM under ice and when they are introduced under water, oxide pustules are found on the individual particles (Fig. 10). ESCA (Fig. 11), too, shows marked oxidation of the Ni. Cu, on the other hand, is present in the metallic form.

In view of the production method this is quite understandable:

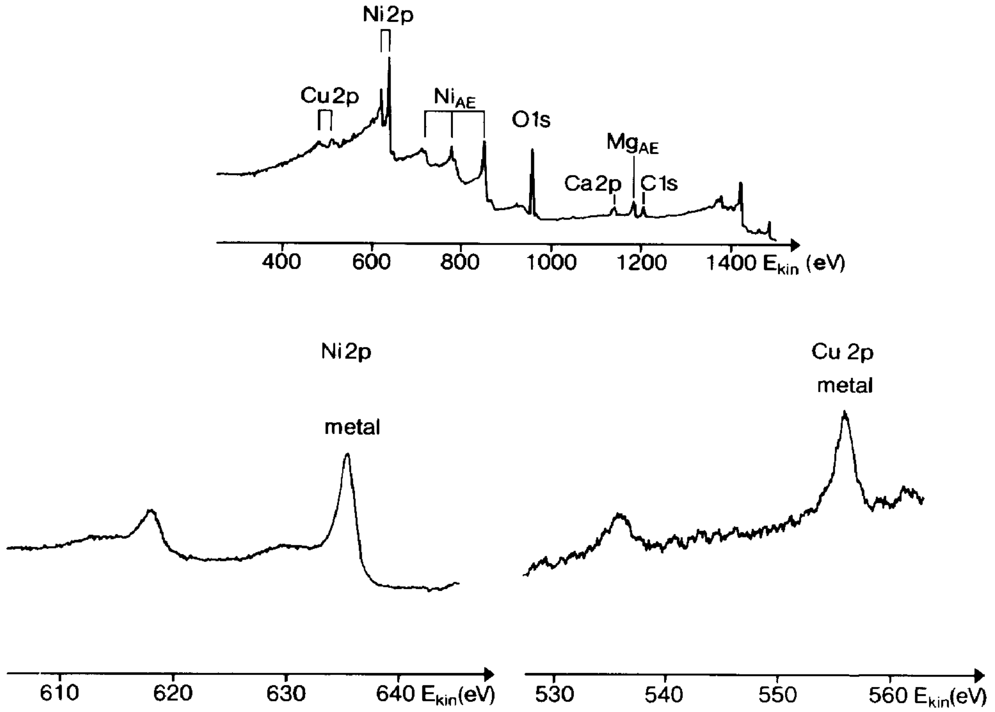

FIG. 9. ESCA spectra of fresh Raney Ni–Cu catalyst (starting alloy doped already). Above: Wide scan spectrum. Below: Details of the Ni 2*p* and Cu 2*p* spectrum at various degrees of magnification to reveal the valence states (through the Auger parameter).

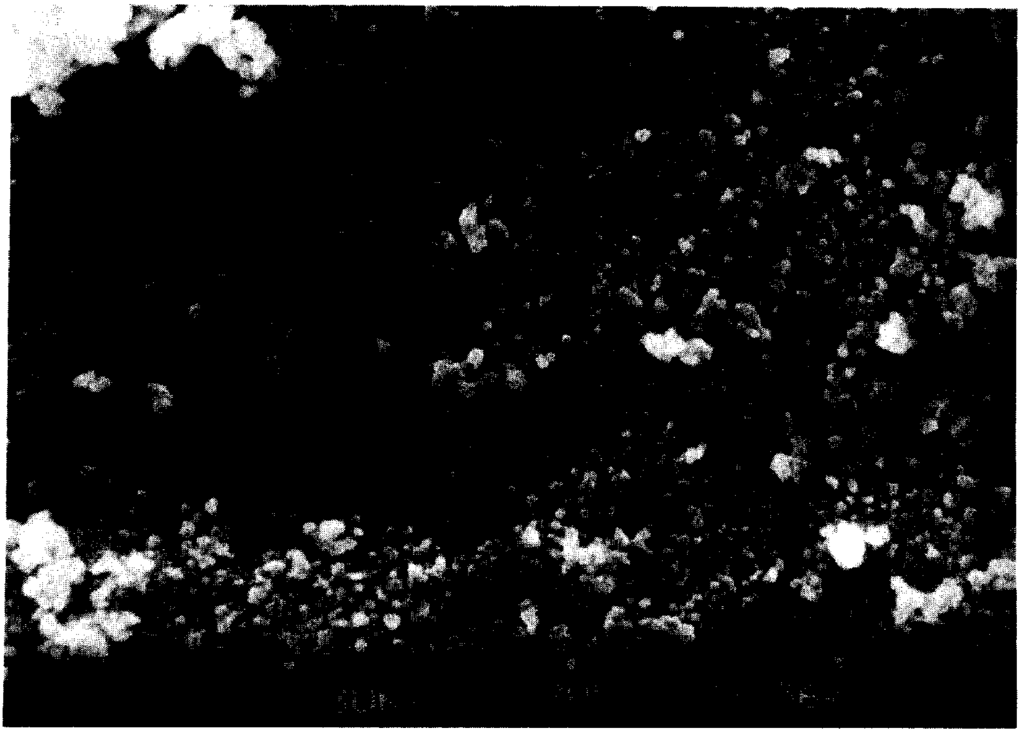

FIG. 10. Oxide pustules on a Raney Ni catalyst after deposition of Cu (SEM).

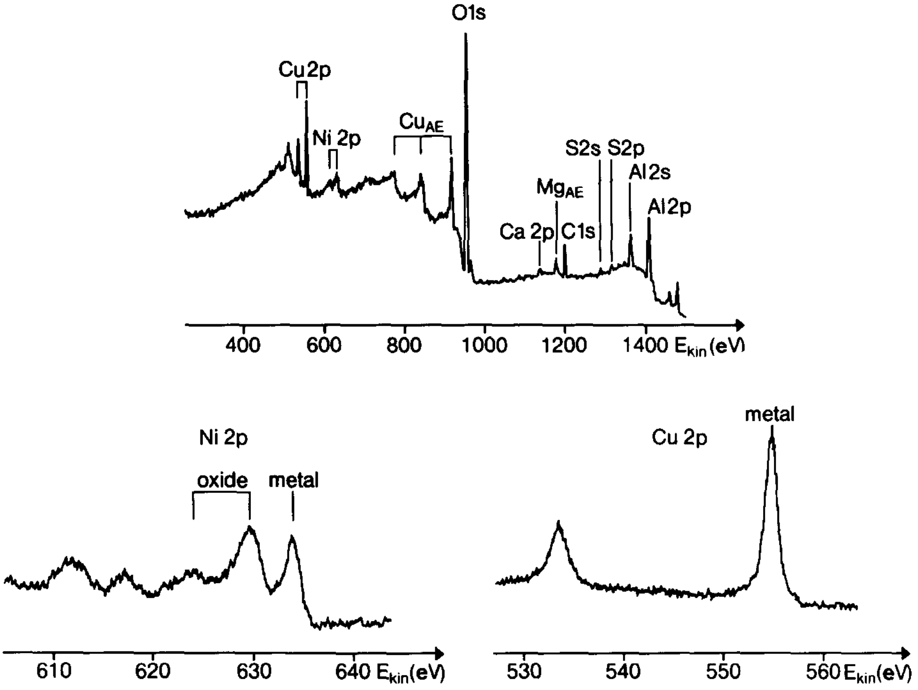

FIG. 11. ESCA spectra of a chemically copperized Raney Ni catalyst. Above: Wide scan spectrum. Below: Details of the Ni 2*p* and Cu 2*p* spectrum at various degrees of magnification.

$$Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$$

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$$

The already present Al accumulation is affected by the copperization to a small extent only.

That this sample consists of Raney Ni coated with Cu can be demonstrated for the individual grain by micro-AES (Fig. 12) and integrally by ESCA independently of one another. The micro-AES sputtering profile reveals that Cu is uppermost and Ni and Al below. The maximum Cu intensity is reached after a layer thickness of about 20 nm has been removed; thereafter, however, it does not fall as rapidly as would be expected for an ideal layer structure. This may be attributable either to properties of the investigated location (microroughness, partial interdiffusion of Cu and Ni during preparation) or to artifacts formed during the investigations (interdiffusion as a consequence of sample heating by electron and ion bombardment). The interpretation of an ESCA depth profile is more difficult still. In this case, although the sample is not heated by electron bombardment, the most widely differing zones of the sample are averaged. However, here also the highest Cu intensity occurs after the removal of about 20 nm.

Raney Cu

This catalyst has a coarse structure similar to those of the Raney Ni catalysts (Fig. 13). At high magnification (Fig. 14), however, pores with a diameter of around 50 nm are seen on the platelets. A noteworthy analytical finding is that the catalyst contains considerably less Al. Probably it could be leached more completely as a consequence of the coarser structure of the initial alloy.

Used Raney Catalysts

When a Raney catalyst is used normally in a liquid medium the grain size is continu-

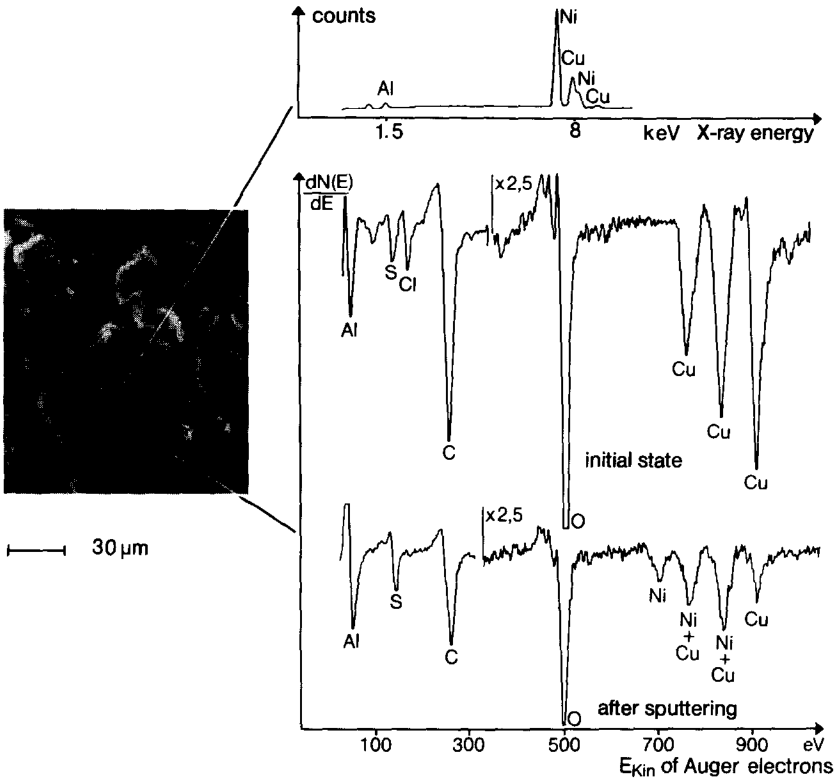

FIG. 12. X-Ray and Auger microanalyses of a single particle of the chemically copperized Raney Ni catalyst.

ously reduced by abrasion. The SEM pictures of the fresh contacts explain this at once: first the agglomerates break apart and then the platelets break up, mainly along the shrinkage cracks. As the particles become progressively smaller there comes a point at which, because of filtration difficulties, the catalyst can no longer be used. The catalyst has to be renewed, not because it has become inactive, but because particles of it would otherwise enter the product.

The possible causes of a premature loss of catalyst activity are leaching out of the residual Al or Al oxide, oxidation of the Ni, and the deposition of reaction products or poisons on the catalyst particles. In comparison with these factors the growth of the Ni crystallites and consequent reduction of the BET surface area, which have been observed in gas reactions promoted by Raney Ni (*13*), are probably of little importance.

There is no doubt that the activity of Raney Ni catalysts is influenced by the residual aluminum content, since it can be predetermined within certain limits by controlling the Al_2O_3 formation in accordance with Eqs. (2) and (3).

Oxidation of Ni appears to be impossible at first sight in the presence of H_2 in hydration reactions. Nevertheless, oxidation of the Ni may occur at an elevated temperature in the presence of oxidizing agents, e.g., in the hydration of compounds containing nitro groups. As demonstrated in the case of the copperized catalyst, ESCA enables surface oxidation processes to be detected.

In some cases, e.g., the reduction of nitriles to amines, a loss of activity is observed as a consequence of a deposition of organic layers on the catalyst (*2*, *14*). The presence of such deposits can be clearly

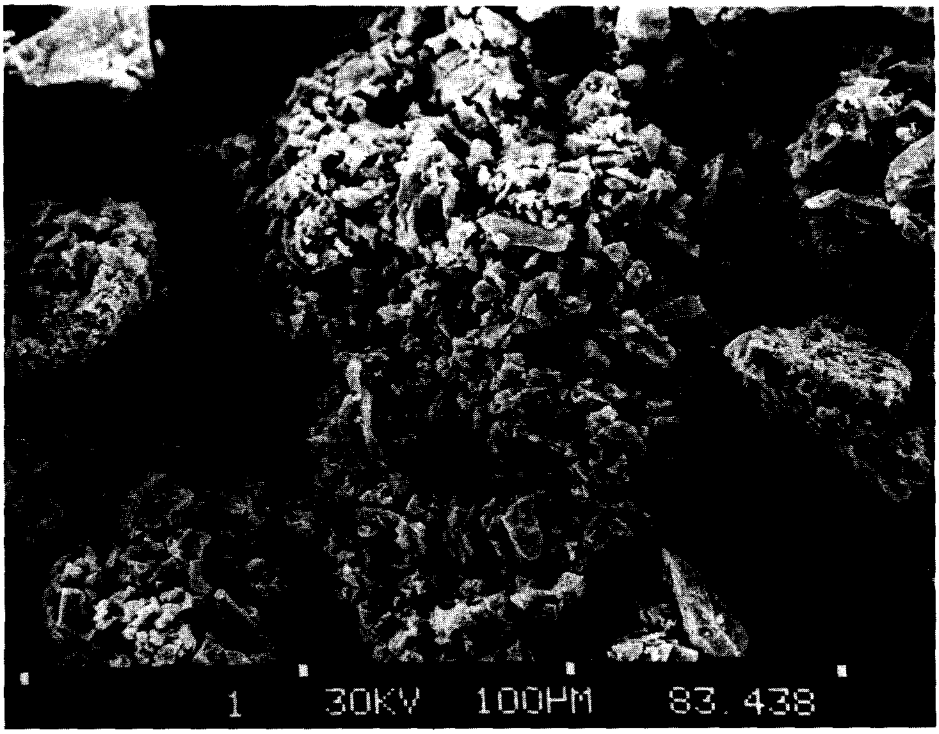

FIG. 13. Agglomerates in the fresh Raney Cu catalyst (SEM).

FIG. 14. Single particle of the fresh Raney Cu catalyst, with pore structure visible (SEM).

seen from the N 1*s* and C 1*s* ESCA signals. However, unambiguous differentiation of Ni oxides and hydroxides from organic Ni compounds is very difficult since these compounds often have Ni 2*p* spectra with very similar chemical shifts and satellite structures (*15*).

Oxidation and formation of surface deposits should not be regarded exclusively from the aspect of catalyst poisoning. Controlled oxidation and surface coating has enabled pyrophoric catalysts to be rendered nonpyrophoric, with the result that the powder does not have to be stored and transported in water (*16, 17*). Under reaction conditions the active state can be quickly restored.

CONCLUSIONS

The results obtained show that the described preparation methods enable fresh Raney catalysts to be investigated morphologically and analytically without significant additional oxidation through exposure to air.

It is thus possible to draw conclusions from the Al enrichment of the surface as to the methods used in the production of commercial catalysts and to make statements regarding the distribution and binding states of dopants.

Oxidation and organic contamination layers on catalysts are detectable by surface analysis methods as causes of losses of activity. However, difficulties in the quantitative determination of the Ni compounds present may arise from line overlapping in the Ni 2*p* spectrum.

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