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Morphological and Surface Studies of Ultrasonically Treated Raney Nickel Hydrogen-Deuterium Exchange Catalysts

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Previous surface studies of ultrasonicated Raney nickel catalysts have shown that ultrasonication leads to reduction of surface Ni species to the metallic state. Surface impurities that may poison the Raney nickel catalyst have also been removed during ultrasonication. Negligible increases in surface area are observed after ultrasound treatment of the catalysts even though their activities and selectivities in ^2H incorporation into carbohydrates and glycosphingolipids are markedly improved. The surface and morphological changes taking place during ultrasonic treatment are the focus of this paper. Cr^{3+} - and Mo^{6+} -doped Raney Ni catalysts have been studied before and after ultrasonication with scanning electron microscopy, X-ray photoelectron spectroscopy, and secondary ion mass spectrometry. Results of these studies indicate that the reason for enhanced selectivity is that fresh Ni surfaces are available after ultrasonication due to crack propagation of the Raney Ni catalysts. The surface Cr^{3+} content also increases after sonication, which may explain why these particular catalysts show the fastest rates of ^2H incorporation in carbohydrates and glycosphingolipids.

Introduction

Alloy and small metal particles are important in several areas of research including photography,¹ synthesis gas catalysis,² ethylene oxidation,³ reforming,⁴ olefin coupling,⁵ thin-film formation,⁶ alcohol synthesis,⁷ automobile catalysts,⁸ magnetic recording devices,⁹ and other areas. Alloying may also be important in the passivation of metal poisons.¹⁰

Alloys are important in catalysis since an active metal may be diluted with an inactive metal in order to control the activity and selectivity of the catalyst.¹¹ If the size and shape of the alloy particles influence the catalytic reaction, these reactions are called structure

sensitive.¹² One of the criteria of structure-sensitive reactions is that reactivity ought to decrease when inactive metals are alloyed with active metals.

Some alloys and mixed metal alloy systems actually show an increase in activity with respect to the pure monometallic active metal system.^{19a} Reasons for these increases in activity are not always clear, although the role of the extra metal may be in many cases due to smaller rates of side reactions.¹³ In addition, new structural properties may result.

We recently reported in this journal¹⁴ that ultrasonicated Raney Ni catalysts had purer surfaces than non-sonicated catalysts due to removal of contaminants like oxygen, carbon, and alkali ions. In addition, two distinct types of aluminum were observed by both Auger electron spectroscopy and X-ray photoelectron spectroscopy methods. These were assigned to zero-valent aluminum in nickel alloy phases and oxidized alumina. It was not clear from these studies whether the two types of aluminum species or the more pure surface was responsible for the increased activity and selectivity for deuterium incorporation into molecules such as carbohydrates and glycopyranosides.¹⁴

Further studies of transition-metal-doped Raney nickel catalysts show that the nature of the transition-metal dopant causes marked differences in catalytic activity and selectivity for deuterium exchange. For this reason, we have continued our studies of the surface properties of such catalysts in order to understand the effects of ultrasonication. For the surface studies reported here, we have focused on the effects of addition of molybdenum and chromium to the Raney nickel catalysts and what happens to these metals before and after sonication.

Another puzzling matter concerning our earlier sur-

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face studies of sonicated Raney nickel catalysts¹⁴ is that after sonication the surface area of the catalysts did not markedly change even though the metallic nickel surface area did increase. In order to understand this dilemma, scanning electron microscopy experiments were done to discern the nature of morphological changes that may occur during sonication.

This paper, therefore, concerns the morphological and surface changes that occur as a result of sonication of doped Raney Ni hydrogen-deuterium exchange catalysts. Scanning electron microscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry and catalytic experiments will be reported.

Experimental Section

Raney Nickel Doped with Transition Metals. Raney nickel catalysts were purchased (W-2 grade, Aldrich Chemical Co.) and used without further purification. Doped Raney Ni catalysts were obtained from Davison Division of W. R. Grace. The Cr sample is Raney 2400, and the Mo sample is Raney 3000, both of which have the general formula $\text{Al}_{58}\text{Ni}_{37-42}\text{M}_{0-5}$ and surface areas of about 250 m^2/g . The catalysts were always treated under an Ar atmosphere.

Ultrasonication. Ultrasonication of the doped Raney Ni catalysts was done with a Bransonic Model W-200-P sonicator with a titanium microtip immersed in the reaction mixture. About 30 W/cm^2 at 20 kHz was continuously applied during these experiments. The catalysts were washed to neutral pH prior to exchange with D_2O . Further details can be found elsewhere.¹⁵

Scanning Electron Microscopy and Energy-Dispersive X-ray Analyses. An ETEC Autoscan U1 scanning electron microscope with an ETEC energy-dispersive X-ray analyzer were used for all morphology experiments. The doped Raney Ni catalysts were mounted on the sample holder with conducting paint prior to analysis. SEM and EDX analyses were done on both sonicated and nonsonicated samples. All experiments were done with a primary beam voltage of 10 kV. The EDX analyses are accurate to within 10%.

Surface Science Experiments. X-ray photoelectron spectroscopy and static secondary ion mass spectrometry experiments were done on a Leybold Heraeus spectrometer. Samples were transported to the spectrometer under liquid nitrogen and loaded under a nitrogen gas stream in a glove bag surrounding the sample holder. Samples were immediately introduced into a preparatory chamber and evacuated to less than 1×10^{-8} mbar of pressure. Samples were then loaded into the analysis chamber and further evacuated to pressures as low as 1×10^{-10} mbar.

X-ray photoelectron spectroscopy experiments were done prior to any other experiments since this is the least destructive experiment. Static secondary ion mass spectrometry experiments were carried out on catalysts after XPS experiments.

The details concerning the experimental parameters used in these experiments can be found elsewhere¹⁴ for studies done on sonicated Raney nickel catalysts. Conditions such as the beam currents, voltages, spot sizes analyzed, types of radiation, etc., are available.¹⁴

Catalysis Studies. Comparative kinetic rate experiments were performed as described elsewhere.¹⁶ Samples were always kept under an inert gas atmosphere. Proton NMR experiments were performed to obtain kinetic rate information. Experiments were done on a 490-MHz home-built NMR spectrometer or on a 500-MHz Bruker WP-500 spectrometer. Ninety degree pulse widths and 20-s T_1 relaxation rates were used. About 64 scans were collected for each spectrum, and three spectra were collected for each experiment. Average integrated peak areas were internally referenced to average areas of nonexchanging protons with an accuracy of about $\pm 3\%$. Three-hour experiments were carried out for each doped Raney Ni catalyst prior to NMR analysis.

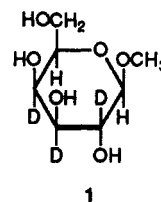
Table I. Deuteration of 1 in Various Positions

catalyst ^a	initial rate ^b			final % incorporated ^c		
	C ₂	C ₃	C ₄	C ₂	C ₃	C ₄
Cr,RN	50	67	62	21	97	98
Mo,RN	5	25	14	11	91	70
RN	13	70	69	40	72	88

^a Cr,RN = Cr³⁺-doped Raney Ni. Mo,RN = Mo⁶⁺-doped Raney Ni. RN = Raney Ni. ^b Percent ²H incorporated versus time (1 min). ^c After 3 h.

Results

Catalysis. A summary of catalytic results is given in Table I. The initial rate of substitution of 1-*O*-methyl- β -D-galactopyranoside (1) and the final percentage of ²H incorporated after 3 h are given there. The highest rate of incorporation of ²H is shown for the C₃ position of 1 when Cr³⁺-doped Raney Ni is used as a catalyst. Positions 2, 3, and 4 are labeled with deuterium in the following drawing of the molecule, with C₄ being closest to the C that has the HOCH₂ group (C₁) attached to it.



1

The rate of incorporation into the C₄ position for the Cr³⁺-doped Raney Ni catalyst is slower but finally levels off to about the same total amount (about 98%) for ²H incorporation into the C₃ position. Incorporation of ²H into the C₃ position is even slower over Mo⁶⁺-doped Raney Ni with a significantly lower amount incorporated (91%) after 3 h. Data for the Mo-doped system also show that incorporation into the C₄ position is markedly slower than all of the above materials as well as a much lower total amount (70%) of conversion after 3 h. Raney Ni itself is a better catalyst (88% incorporated) than the Mo-doped Raney Ni catalyst for the C₄ position, whereas the undoped material is the worst of the above materials for incorporation into the C₃ position (70% after 3 h).

Incorporation of Cr³⁺ or Mo⁶⁺ into Raney Ni leads to a substantial decrease in ²H incorporation at the C₂ position of 1 although the initial rate (as long as 10 min) of incorporation for the Cr³⁺-doped material is the highest of all of the catalysts studied.

Morphological Studies. A scanning electron micrograph of the Cr³⁺-doped Raney Ni catalyst before sonication is given in Figure 1a. The surface of this material has several cracks, and the average particle size is about 80 μm . An SEM photo of the Cr³⁺-doped Raney Ni catalyst after sonication is given in Figure 1b for comparison. After sonication, the average particle size is about 30 μm , although the particle size distribution ranges from about 10 to about 80 μm now.

Energy-dispersive X-ray analyses of the Cr³⁺-doped Raney Ni are given in Figure 2. The upper curve represents Cr³⁺-doped Raney Ni before sonication, and the lower curve is for after sonication. Notice that the amount of detected chromium increases after ultrasonic treatment.

Figure 3 is a scanning electron micrograph of Mo⁶⁺-doped Raney Ni after sonication. This photo shows similar cracks and small particles as the sonicated Cr³⁺-doped sample. The corresponding energy-dispersive X-

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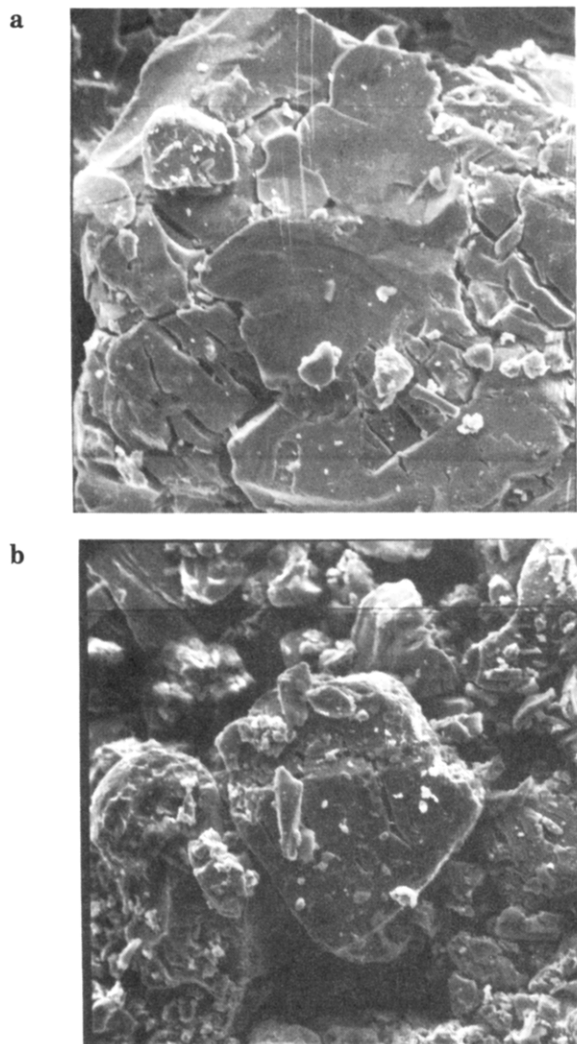


Figure 1. Scanning electron micrographs of Cr³⁺-doped Raney Ni at 1000× magnification: (a) before sonication; (b) After 30 min of sonication.

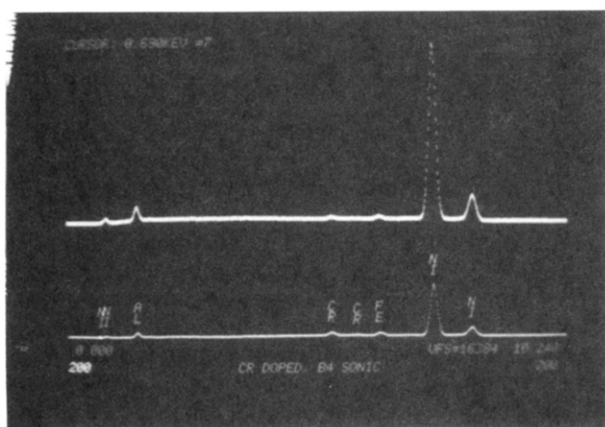


Figure 2. Energy-dispersive X-ray analysis of Cr³⁺-doped Raney Ni catalysts: top curve, before sonication; bottom curve, after 30 min of sonication.

ray analysis of the Mo⁶⁺-doped Raney Ni before sonication is given in the upper curve of Figure 4, whereas the lower curve shows the EDX analysis after sonication. The level of molybdenum detected is very small in both cases.

Surface Studies. X-ray photoelectron spectra for the Ni 2p_{1/2} and Ni 2p_{3/2} transitions for the nonsonicated and sonicated molybdenum-doped Raney nickel catalysts are shown in parts a and b of Figure 5, respectively.

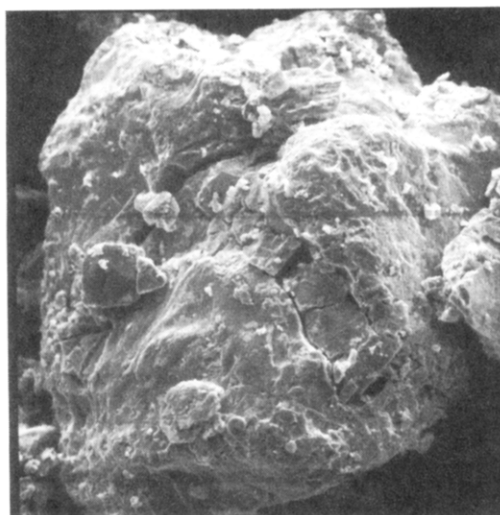


Figure 3. Scanning electron micrograph of Mo⁵⁺-doped Raney Ni after 30 min of sonication at 1000× magnification.

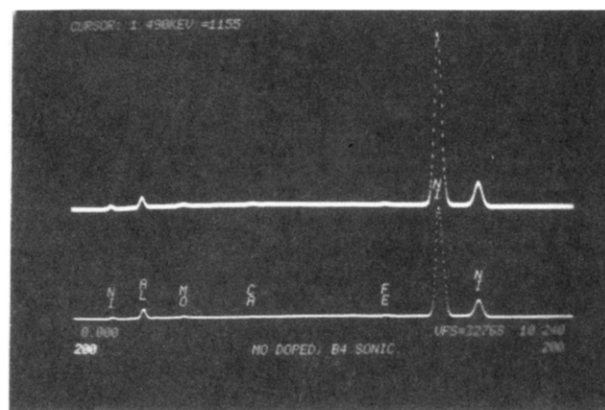


Figure 4. Energy-dispersive X-ray analysis of Mo⁵⁺-doped Raney Ni catalysts: top curve, before sonication; bottom curve, after 30 min of sonication.

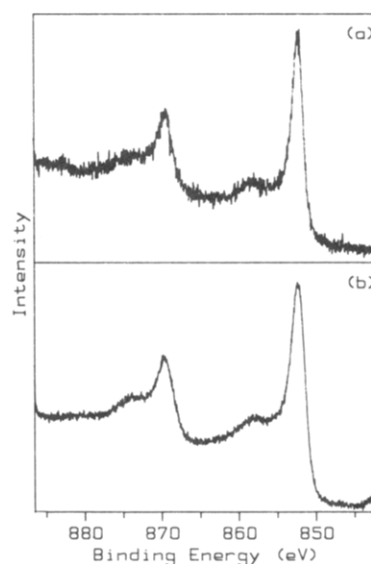


Figure 5. X-ray photoelectron spectrum of Ni 2p_{1/2} and Ni 2p_{3/2} regions of Mo⁵⁺-doped Raney Ni catalyst: (a) before sonication; (b) after 30 min of sonication.

These transitions occur in the binding energy range 877.6–845.0 eV. Note that these two spectra are very similar.

Secondary ion mass spectrometry data for the nonsonicated and sonicated molybdenum-doped Raney nickel catalysts are shown in parts a and b of Figure 6, respec-

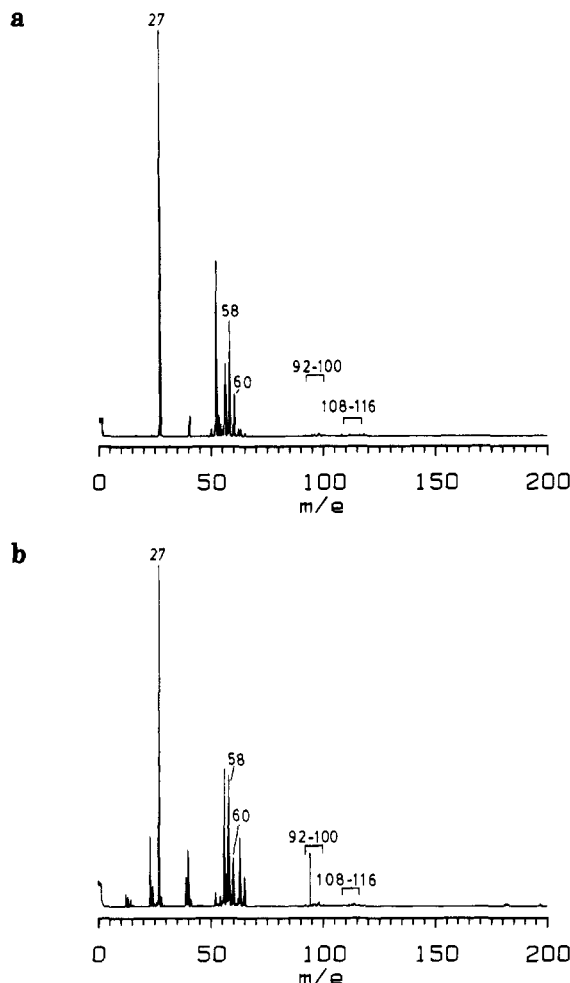


Figure 6. Secondary ion mass spectra for Mo^{5+} -doped Raney Ni catalysts: (a) before sonication; (b) after 30 min of sonication.

tively. Peaks at 23, 27, 39, 40, 56, 58, 60, 63, 65, between 92 and 100, and between 108 and 116 m/e are observed in both spectra, although the relative intensities of these peaks are somewhat different. The peaks at 39 and 40 m/e in the sonicated sample are somewhat diminished in relative intensity with respect to the other observed peaks in comparison to the nonsonicated catalyst.

The other XPS and SSIMS data for the nonsonicated and sonicated catalysts are very similar to what we have previously reported for sonicated and nonsonicated Raney nickel catalysts¹⁴ with the exception that molybdenum dopants are observed. That is to say that two types of aluminum species are observed in the X-ray photoelectron spectrum of the sonicated molybdenum-doped Raney nickel catalyst.

For the chromium-doped Raney nickel catalyst, the surface data are quite different. First of all, the Al 2p region of the nonsonicated chromium-doped catalyst has two types of aluminum species; one occurs at 74.9 eV and the other occurs at 71.7 eV, as shown in Figure 7a. The sonicated chromium-doped Raney nickel catalyst primarily shows one type of aluminum species, as shown in Figure 7b.

The Ni 2p_{1/2} and Ni 2p_{3/2} transitions for the nonsonicated and sonicated chromium-doped Raney nickel catalysts are shown in parts a and b of Figure 8, respectively. The shakeoff features for the sonicated catalyst are less intense than those for the nonsonicated catalyst.

The chromium 2p_{1/2} and 2p_{3/2} transitions for the nonsonicated and sonicated chromium-doped Raney nickel

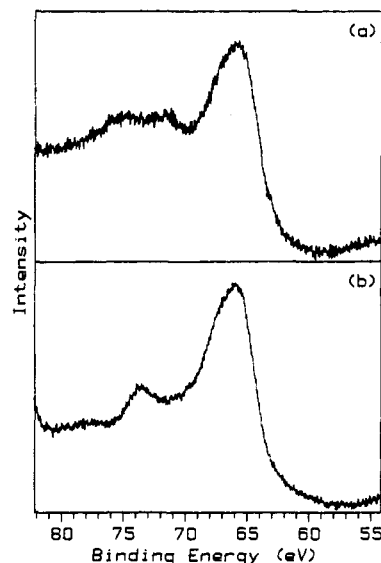


Figure 7. X-ray photoelectron spectra of Al 2p, Ni 3p_{1/2}, and Ni 3p_{3/2} regions of Cr^{3+} -doped Raney Ni catalysts: (a) before sonication; (b) after 30 min of sonication.

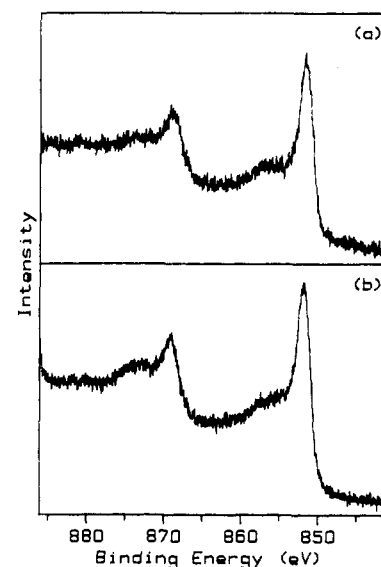


Figure 8. X-ray photoelectron spectra of Ni 2p_{1/2} and Ni 2p_{3/2} regions of Cr^{3+} -doped Raney Ni catalysts: (a) before sonication; (b) after 30 min of sonication.

catalysts are given in parts a and b of Figure 9, respectively. The relative intensities of these transitions are 4 times greater for the sonicated catalyst than for the nonsonicated catalyst. This trend of increased amount of chromium ions at the surface of the sonicated chromium-doped Raney nickel catalyst is also apparent in the SSIMS data shown in Figure 10. The SSIMS data of Figure 10a for the nonsonicated chromium-doped Raney nickel catalyst show peaks at 23, 27, 39, 52, 56, 58, and 60 m/e . Similar peaks are observed in the SSIMS data shown in Figure 10b although the relative intensities of the peaks at 23, 39, and 52 m/e are lower than the other peaks with respect to the nonsonicated catalyst.

Discussion

Catalytic Studies. Catalytic data of Table I clearly show that the rate of ^2H incorporation into 1 is dependent on the position of substitution and the type of dopant of the Raney Ni. Deuterium exchange at the C₃ and C₄ positions is much more facile than at the C₂ position for

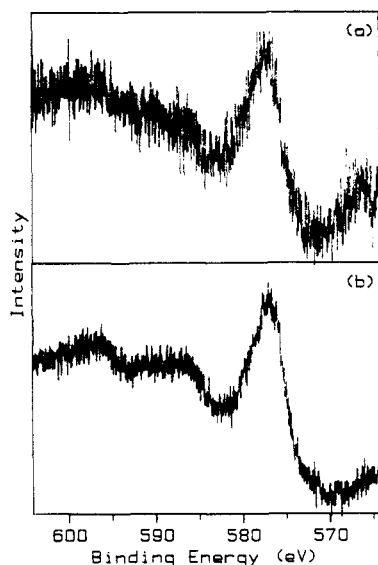


Figure 9. X-ray photoelectron spectra of Cr $2p_{1/2}$ and Cr $2p_{3/2}$ regions of Cr^{3+} -doped Raney Ni catalysts: (a) before sonication; (b) after 30 min of sonication.

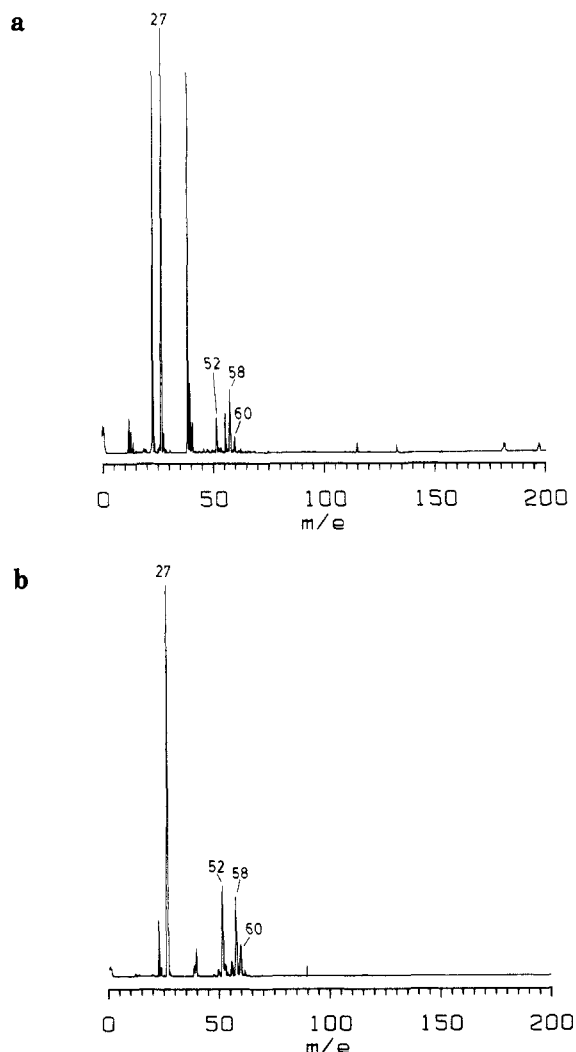


Figure 10. Secondary ion mass spectra for Cr^{3+} -doped Raney Ni catalysts: (a) before sonication; (b) after 30 min of sonication.

all catalysts studied.^{15,16} This is also true for silver- and copper-doped Raney Ni catalysts prepared in our laboratories. This may be explained by steric constraints

induced by neighboring groups on C_1 . In general, the Cr^{3+} -doped Raney Ni catalyst allows deuteration at higher rates and to greater extents than the Mo^{6+} -doped or undoped Raney Ni catalysts. Even the initial rate of exchange in the C_2 position for the Cr^{3+} catalyst is faster than the rate for all other catalysts. It is not clear what causes certain catalysts to level off before they reach 100% exchange. The purpose of the morphological and surface studies is to try to elucidate what geometric factors may account for such behavior.

Morphological and Bulk Analysis Studies. The data of Figures 1 and 3 clearly show that on sonication the doped Raney Ni catalysts break up and form smaller particles. Large particles are also still present, and it appears that the main effect of the sonication is to sever the cracks originally present in the material. This would account for the slight increase in the surface area noted after sonication.¹⁴ This also accounts for the increased activity after sonication since new fresh metal surfaces that are not oxidized are now available for reaction. Studies concerning Ni powder, on the other hand, have shown that the particle size is significantly decreased and that Ni particles aggregate after 2 h of ultrasonication.¹⁷

The energy-dispersive X-ray analysis data of Figure 2 show that the Cr^{3+} -doped Raney Ni sample has a larger amount of Cr^{3+} in the top micron of the sample after sonication than before. It should be stressed that the EDX analysis represents data from about 1 or 2 μm within the sample, and as such these are considered bulk analyses. EDX data of Figure 4, on the other hand, do not show significant amounts of Mo in the top 1–2 μm of the Mo^{6+} -doped Raney Ni either before or after sonication. The amount of Ni detected after sonication, however, does appear to be relatively small compared to data before sonication. This suggests that less nickel surface is available for reaction on this sample after sonication.

Surface Science Data. Surface science data for the molybdenum-doped Raney nickel catalyst, whether sonicated or nonsonicated, are very similar, as shown by comparing data of Figures 5 and 6. XPS data suggest that the nickel is oxidized on both the nonsonicated and sonicated Mo^{6+} -doped Raney Ni catalyst surfaces. The SIMS data conclusively show that molybdenum oxides are present on the surface of the Raney nickel catalysts regardless of treatment with ultrasound. Molybdenum has several isotopes¹⁸ between 92 and 100 m/e , and peaks observed at 16 m/e units with the same relative ratios between 108 and 116 m/e are due to Mo O^+ species. This is not surprising given the tendency for molybdenum to oxidize. Impurity ions like Na^+ ($m/e = 23$) and K^+ ($m/e = 39$) on the catalyst surface are lowered on sonication, as was previously discovered with non-transition-metal-doped Raney nickel.¹⁴ In addition, the Ni/Al ratio stays about the same from the SSIMS data before or after sonication. Both the XPS and SSIMS data suggest that the relative amounts of Mo at the surface of both the nonsonicated and sonicated materials are quite low. These results are in good agreement with the EDX data discussed above.

In summary, there are very few differences between the nonsonicated and sonicated molybdenum-doped Raney nickel catalysts at least with respect to surface composition. This is in contrast to the differences between nonsonicated and sonicated Raney nickel catalysts previously reported.¹⁴ The present data, therefore, suggest

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that incorporation of transition-metal dopants into the Raney nickel catalysts can markedly affect the surface composition of these materials.

Surface data for the chromium-doped Raney nickel catalysts also suggest that transition-metal dopants of Raney nickel can cause differences in surface composition, although in this case an entirely different picture appears. The XPS data of Figure 7 show that there are two types of aluminum species on the nonsonicated chromium-doped Raney nickel catalyst. These data are in direct opposition to those previously reported for the undoped sonicated Raney nickel catalyst which had two types of aluminum with respect to one type for undoped nonsonicated Raney Ni.¹⁴ All these data suggest that the differences in the types and number of aluminum species on the surface may not be important in the hydrogen-deuterium exchange reactions. This conclusion is supported by the data of Figure 7b for the sonicated chromium-doped Raney nickel catalyst where one major aluminum species is observed.

Data of Figure 8 for the Ni 2p regions of the nonsonicated and sonicated chromium-doped Raney nickel catalysts show that there is less oxidation of the nickel after sonication as expected from previous work.¹⁴ The data of Figure 9, however, may be the key to the reason why the sonicated chromium-doped Raney nickel catalyst is such a good hydrogen-deuterium exchange catalyst. After sonication, there is an appreciable increase in the amount of chromium on the surface of the catalyst. The binding energies of the chromium peaks before and after sonication both indicate that Cr^{3+} ions are on the surface of the catalyst.

This assertion is supported by the SSIMS data of Figure 10. The nonsonicated chromium-doped Raney nickel catalyst has a smaller amount of chromium on the surface than the sonicated catalyst. In addition, the relative amount of impurity ions such as K^+ and Na^+ has decreased after sonication. Sputtering of the sonicated sample results in SSIMS spectra that show a little less chromium on the surface than before sputtering.

The increased rate of hydrogen-deuterium exchange with the Cr^{3+} -doped Raney Ni catalysts is likely due to the increased amount of metallic Ni and Cr^{3+} ions on the surface after sonication rather than due to the aluminum portion of the Raney Ni. The increased transition-metal and ion surface concentrations are due to crack propagation of the porous Raney Ni. The catalytic activ-

ity of the Cr-doped sample is always greater than the other materials, which also lose alkali metal ions after sonication. These data suggest that the enhanced Cr^{3+} ion content at the surface after sonication is responsible for enhanced catalytic activity. Different dopants result in different chemical compositions at the surface and therefore to different rates of hydrogen-deuterium exchange. Several chromium-doped samples have been studied, and surface and microscopic experiments consistently show a surface enrichment of chromium.

It is possible that Cr^{3+} ions migrate to the surface during sonication and are active scavengers for oxygen, consequently protecting the surface Ni from oxidation. Co/Mn solvated metal atom dispersion catalysts have been shown to be excellent hydrogenolysis catalysts since the inactive manganese component serves as an oxygen scavenger allowing active Co particles to remain reduced.¹⁹

Conclusion

Results of surface science studies of molybdenum-doped Raney nickel catalysts show that the surface composition before and after sonication is roughly the same although alkali ion impurities are diminished after sonication. In the case of chromium-doped Raney nickel catalysts, the surface science and EDX data clearly show increased amounts of nickel metal and Cr^{3+} ions on the surface of the sonicated catalyst with respect to the nonsonicated catalyst. This increased metal content at the surface may be responsible for the high selectivity and activity of the sonicated chromium-doped Raney nickel catalyst. Morphological studies of these catalysts show that the particles crack apart during sonication, which exposes more surface of the material. The type of surface exposed critically depends on the nature of the starting doped Raney Ni material. The overall particle size is not markedly changed, and small increases in surface area are due to crack growth along crevasses initially present in the nonsonicated precursor.

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Registry No. Ni, 7440-02-0; Cr, 7440-47-3; Mo, 7439-98-7.

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