JOURNAL OF CATALYSIS 56, 130–133 (1979)

Interaction of Antimony with Reduced Supported Nickel Catalysts

There recently has been great interest in the bulk and surface properties of both unsupported (*1*, *2*) and supported (*3*, *4*) alloy catalysts. Although it has been clearly established that alloying can dramatically alter catalytic and chemisorption properties, the relative importance of geometric to electronic effects is still largely unanswered. However, most reported studies are on slightly exothermic or endothermic alloys; i.e., systems in which the mutual perturbation of the alloy components is weak and no substantial changes in the electronic structure is expected. Ni–Sb alloys are interesting in that they represent a case in which the electronic interaction is expected to be large (heat of formation is −7.9 kcal/mol) (*5*). Another reason for interest in Ni–Sb alloys is that it has recently been shown that antimony compounds are effective agents for partially passivating metal contaminants, such as nickel, on cracking catalysts (*6*). Antimony apparently interacts strongly with the contaminant metals to effectively reduce their adverse hydrogen- and coke-producing reactions. The object of this note is to report preliminary results on the study of the interaction of Sb with supported nickel particles using x-ray diffraction (XRD).

The samples studied included groups containing 4.4, 2.7, and 1.9 wt% Ni and Sb:Ni atomic ratios (y) of 0.0, 0.06, 0.11, and 0.23. Samples prepared with 1 wt% Ni and lower did not have an observable XRD pattern, presumably due to the Ni crystallite size being less than about 40 Å. The supported nickel catalysts were prepared by impregnating a steam-aged Filtrol F-950 clay zeolite (surface area, 72 m^2/g) with nickel octanoate (Mooney Chemicals Inc.), going through two reduction/oxidation cycles, and calcining in air for 3 hr at 650°C. (Each cycle consisted of 5 min of Ar at 500°C, 5 min of H_2 at 500°C, 5 min Ar at 650°C, and 15 min of air at 650°C.) Antimony was impregnated on the supported nickel catalysts using antimony 0,0-dialkylphosphorodithioate (*7*), going through five additional reduction/oxidation cycles, and calcining in air for 3 hr at 500°C. The catalysts were then reduced in flowing hydrogen for 3 hr at 500°C. Thermogravimetric experiments indicate that this treatment was sufficient to reduce essentially all the nickel to the zero-valent state.

The x-ray diffraction data were collected in digital form by a computer-controlled diffractometer that was operated in a signal-averaging mode. The (200) peak of contaminant quartz in the catalyst support was used as an internal standard to measure the Ni (111) peak centroid, integral breadth, and area. Based on measurements of the lattice parameter of pure Ni at the 5% level for 11 separately prepared samples, the uncertainty in a_0 is estimated to be ±0.002 Å. Reduced specimens were measured without air exposure. A 0.25-mil Mylar covered holder

0021-9517/79/010130-04$02.00/0

TABLE 1

X-ray Diffraction Parameters Measured for Reduced $NiSb_x$ Solid Solutions on F-950 Support

Ni (wt%)	Sb (wt%)	Atomic ratio, Sb/Ni (y)	Unit cell size a_0(Å)	$NiSb_x$ stoichiometry (x)	Ratio $x{:}y$	XRD peak integral breadth (2θ)	$NiSb_x$ crystallite size (Å)[a]	N_{Sb}[b]
4.49	0.00	0.00	3.524	0.00	—	0.40	240	—
4.40	0.54	0.059	3.535	0.0155	0.26	0.41	230	1.4
4.34	1.02	0.11	3.554	0.0431	0.38	0.83	120	1.2
4.25	1.96	0.22	3.570	0.0696	0.31	0.60	160	3.4
4.43	3.80	0.41	3.569	0.0681	0.17	0.66	150	7.0
2.87	0.00	0.00	3.527	0.00	—	0.60	160	—
2.58	0.34	0.064	3.540	0.0217	0.34	0.35	360[c]	2.1
2.73	0.64	0.11	3.564	0.0599	0.53	0.86	110	0.80
2.71	1.28	0.23	3.575	0.0786	0.35	0.87	120	2.5
1.96	0.00	0.00	3.524	0.00	—	0.45	210	—
1.91	0.28	0.07	3.542	0.0248	0.35	0.74	130	0.83
1.93	0.52	0.13	3.549	0.0362	0.28	0.54	180	2.3
1.87	0.99	0.26	3.565	0.0611	0.24	1.40	70	1.9

[a] Crystallite size calculated from integral breadth using Scherrer equation (*8*) and assuming single-phase crystalline material.

[b] The number of monolayers of excess Sb on the surface. See discussion in text.

[c] The sample was taken through 10 reduction/oxidation cycles which may account for the large crystallite size.

was loaded with the sample in an oxygen-free glove box. Crystallite sizes were calculated using the Scherrer equation (*8*). The uncertainties in the reported crystallite sizes for the samples containing 4.4, 2.7, and 1.9 wt% Ni are approximately ±20, ±30, and ±40 Å, respectively.

Table 1 presents the XRD results for the reduced specimens. One effect of Sb was to increase the lattice dimensions (a_0). This increase is interpreted to be the result of the development of a $NiSb_x$ solid solution. Equation (1) gives the solid solution stoichiometry (x) in terms of the lattice dimension:

$$x = (0.4822a_0 - 1.6992)/(3.8892 - a_0). \quad (1)$$

This equation is an empirical fit to the data of Osawa and Shibata (*9*) between $x = 0.0$ and $x = 0.10$ and makes no provision for the small discontinuity near $x = 0.03$ which was interpreted to be due to the development of a $Ni_{15}Sb$ superlattice structure. From the column of solid solution stoichiometries in Table 1, the value of x increases with the atomic ratio of Sb to Ni (y) in the sample. The ratio $x{:}y$ represents the fraction of Sb in solid solution with Ni and shows no regular dependence upon total Ni or Sb content. Except for the sample with $y = 0.41$, the nine values of the $x{:}y$ ratio are approximately constant with an average of 0.34 and a standard deviation of 0.08. Thus, on the average, 66% of the Sb is not included in the solid solution (*vide infra*). Because the solid solution stoichiometry x is limited by the finite solubility of Sb in Ni [0.084 atom% Sb (*9*)], it is expected that the $x{:}y$ ratio should decrease for large values of y. This is indeed shown to occur for the 4.43-wt%

Ni and 3.8-wt% Sb sample ($x{:}y$ of 0.17 compared to 0.34 average).

Another effect of Sb is to decrease the apparent crystallite size (Table 1). This result, however, should be viewed with some caution. In a single-phase crystalline material the x-ray diffraction peak breadth can be used to calculate an average crystallite size. In the case of the solid solution there is the possibility of a distribution of stoichiometries that would also result in peak broadening and an apparent decrease in crystallite size. The variation in crystallite size may represent such a distribution in stoichiometry of the alloy crystallites.

The location of the excess Sb (i.e., the Sb not in solid solution) is important in understanding the interaction of Sb with Ni. If the excess Sb is assumed to be on the surface of the NiSb_x crystallite, the number of monolayers of Sb for a particle of cube edge length (or sphere diameter) L is given by

$$N_{\mathrm{Sb}} = (y - x)LD_{\mathrm{Ni}}/6(1 + x)M_{\mathrm{Sb}}, \qquad (2)$$

where D_{Ni} is the atom density of the crystallite (91.3 atoms/nm^3, assumed the same as Ni atom density) and M_{Sb} is the number of Sb atoms per unit area in a monolayer (11/nm^2). The values obtained for these specimens are listed in Table 1. The results suggest that the excess Sb is sufficient to form at least a monolayer on the surface. Some Ni may be reacted with the support as unreducable silicates or aluminates, making it unavailable to the Ni crystallites. The effect of such a Ni component would increase the estimate of the Sb coverage of the Ni crystallites.

Surface enrichment of Sb on bulk Ni metal has in fact been observed after hydrogen reduction (*10*). The low surface free energy and large difference in ionic radii provide a strong force for the surface segregation of Sb to the surface of Ni. On the other hand, the large negative heat of mixing indicates a strong interaction of Sb with Ni. Calculation of surface composition based on the four-layer model of Williams and Nason (*11*) modified to include strain energy (*12*) predicts a surface layer of Sb followed by a layer of Ni. These calculations assume a regular solution, but on the basis of the large volume effects observed (*13*), it is expected that Ni–Sb solid solutions are nonregular, and ordering at the surface may result (*14*, *15*).

For the samples studied here, it is probable that a high level of Sb is present on the Ni surface. Furthermore, the large volume and electronic effects that are observed (*13*) when Sb is added to Ni metal imply that the surface Ni–Sb interaction would also be strong. Therefore, Sb is expected to alter the catalytic behavior of Ni both because of geometric and electronic effects. In fact, in metals passivation, the addition of Sb does indeed decrease the effect of undesired reactions. The study of Ni–Sb alloys is also amenable to modern electron spectroscopic and gas adsorption techniques for characterizing the surface composition and electronic properties of alloy surfaces. Such measurements are in progress in our laboratory and will be reported in a future communication.

ACKNOWLEDGMENTS

The authors thank B. R. Hamilton for the sample preparation work and C. W. Krueger for help in the XRD measurements. The many useful discussions with J. P. Guillory are also appreciated.

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Received May 4, 1978