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Amorphous and Crystalline FeNiCrPB Alloys as Catalysts for Acetylene Hydrogenation

Beyond the sole chemical aspects, the wide range of factors affecting catalytic efficiency calls for progressive improvement of already proven catalysts as well as for the development of new materials. Examples of these attempts are the recent use of bimetallic alloy catalysts in a number of reactions (*1–4*) and exploitation of metal catalysts alloyed with nonmetallic partners to improve upon the selectivity of the classic metallic catalysts (*5*).

In designing heterogeneous metallic catalysts, structural conditions and morphology, type of compounds, and proper stoichiometry, catalytic stability, and efficiency are some of the factors depending on and constrained by new methods of preparation. Evaporated alloy films (see review papers in (*6*)), which allow a range of metastable solid solutions to be obtained with almost any required chemical composition, are attractive guidelines for testing adsorptive and catalytic behavior but, unfortunately, they are not practical as technology replacements (*7*). Conversely, ultrarapid quenched metallic glasses (see review papers in (*8*)) appear the most versatile approach for obtaining "polyelement" catalysts with mechanical, physical and chemical properties suitable for practical catalytic purposes.

Spurred by these interesting prospects, a growing attention has been paid in the last few years to the surface reactivity of these recent materials (*9, 10*).

Our concern both in metallic glasses (*11, 12*) and hydrogenation reactions (*13*) suggested testing $Fe_{44-x}Ni_{37}Cr_xP_{15}B_4$ ($0 \leq x \leq 10$) amorphous and/or crystalline systems in acetylene hydrogenation.

Master alloys, prepared at some selected compositions, were induction-melted under a protective atmosphere of purified argon, then rapidly quenched into ribbons about 2 mm wide and 30–40 μm thick using a single-roll melt-spinning apparatus.

X-Ray analysis (Co*Kα*) showed that the as-quenched samples were completely amorphous; the interference functions (Mo*Kα*) and related reduced atomic distribution functions behaved according to the usual general features distinctive of metallic glasses (*8*). Differential Scanning Calorimetry (DSC) tests were performed under hydrogen flow to check amorphous alloy stability against crystallization and to identify the glass-working temperature ranges. By increasing the Cr content, shifts were observed in glass-transition temperatures (370–390°C) paralleled by increases in crystallization temperatures (425–470°C), evidencing the stabilizing effects of Cr. Complete crystallization led to a fcc (FeNiCr) solid solution and a tetragonal (FeNiCr)PB phosphoboride. The possibility of applying the Vergand role to cell parameters of precipitated phases indicates the diadochy of metals as well of metalloid components (*12*). On this basis, catalytic runs were performed within the 50–290°C temperature range where the amorphous state of samples was maintained. Further tests were performed on the same specimens annealed under a protective atmosphere up to the relevant DSD crystallization peak and then rapidly quenched in liquid nitrogen. A highly defective crystalline condition pertained to these treated alloys as shown by relevant X-ray diffraction patterns, which appear smeared out.

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Column 1 of Table 1 shows the concentrations of the catalysts used: the as-quenched and annealed samples are coded A and C, respectively.

Hydrogenation experiments were carried out with the apparatus shown in Fig. 1 which allows control of temperature, H_2 and acetylene fluxings. A weighted amount of catalyst was introduced as packed strips into the 10-cm × 4-mm cylindric microreactor. A relatively mild H_2 pretreatment (3 h at 290°C) was chosen to avoid possible structural relaxation phenomena (*14*) and nucleation; then, the reaction temperatures were adjusted to the operating values. These pretreatment conditions do not affect the subsequent catalytic runs. The reacted acetylene/H_2 gas mixture was continuously monitored using a Shimadzu-CR1B gas chromatograph. Catalytic activity data, expressed as percentage acetylene conversion, were averaged over 2 h working time. During this time no detectable modifications of activity were observed, therefore excluding poisoning phenomena or catalytic activity loss. For each catalyst, conversion was measured at 50, 80, 110, 140, 170, 200, 230, 260, and 290°C; the individual activation energies were calculated from relevant Arrhenius plots.

Data of catalytic activity, selectivity at 170°C, and the values of activation energy are reported in Table 1. Results suggest that the NiFe(Cr)PB amorphous and/or annealed alloys behave as hydrogenation catalysts with substantial conversions in the explored temperature interval. This fact is interesting since the surface area of the ribbons used is very low; indeed Yokoyama *et al.* measured surface area of ~0.4 m^2 g^{-1} for analogously prepared catalysts (*10*).

TABLE 1

Catalyst[a]	Catalytic activity[b]	Selectivity[c]	Activation energy[d]
$Fe_{44}Ni_{36}P_{14}B_6$ *A*	60	86	8.6 ± 1.6
$Fe_{44}Ni_{36}P_{14}B_6$ *C*	48	82	9.5 ± 0.2
$Fe_{39}Ni_{36}Cr_5P_{14}B_6$ *A*	22	91	13.2 ± 1.8
$Fe_{39}Ni_{36}Cr_5P_{14}B_6$ *C*	30	86	12.5 ± 1.4
$Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ *A*	22	87	12.7 ± 0.9
$Fe_{34}Ni_{36}Cr_{10}P_{14}B_6$ *C*	35	85	13.1 ± 1.4
$Fe_{30}Ni_{36}Cr_{14}P_{14}B_6$ *A*	24	87	11.9 ± 1.2
$Fe_{30}Ni_{36}Cr_{14}P_{14}B_6$ *C*	33	85	13.0 ± 1.1

[a] *A*, amorphous; *C*, annealed.

[b] Expressed as % conversion of acetylene: experimental conditions: 170°C, 1 atm, 1 g of catalyst, flux = 7.6 cm^3 min^{-1} at 25°C with $H_2/C_2H_2 = 2$.

[c] Expressed as % ethylene of total acetylene conversion.

[d] From Arrhenius plots in 50–290°C temperature interval, units: kcal/mol.

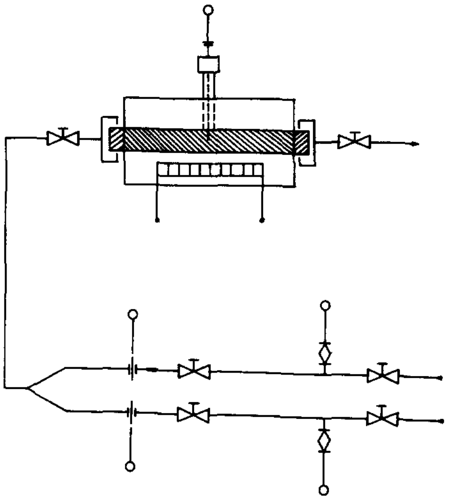

FIG. 1. Scheme of acetylene hydrogenation apparatus.

Activation energies are substantially identical for both amorphous and crystalline catalysts: this seems reasonable in view of the fact that hydrogenation of unsaturated hydrocarbons, according to the classic Horiuti–Polanji mechanism (*15*), does not strictly imply the presence of metallic catalysts in crystalline form. On the other hand, activation energies for Cr-containing catalysts are ~3.5 kcal/mol greater than FeNiPB catalysts. Actually, Cr is considered a very poor hydrogenation catalyst even if it may stabilize metallic catalysts against poisoning and corrosion in industrial operative conditions (*16*).

The effect of the presence of Cr on catalytic behavior seems particularly important even for catalytic activity. To have an immediate view of the dependence of catalytic activity on Cr content, the data of Table 1 are reported in Fig. 2. It is noteworthy that catalytic activity is strongly affected by Cr presence; however, catalytic efficiency is independent of Cr content, at least for the explored concentration range. Thus, Cr introduction modifies the original organization of FeNiPB in the elemental catalytic site, resulting in a lowering of catalytic activity which is insensitive to further increase of Cr. This is probably due to averaging contribution of other elements present in our polycomponent alloys. Lacking appropriate analysis, we do not exclude possible Cr oxidation at the surface, owing also to the mild H_2 pretreatment of samples; this possibility may also further account for the observed lower activity in the presence of Cr.

The reactivity of crystalline alloys is moderately greater than the amorphous one except for the NiFePB alloys. Changes in catalytic activity due to phase separation and crystallization events are not unexpected (*9, 10*). However, only tenuous assumptions can be put forward to account for the observed catalytic features. In FeNiCrPB glass the thermally activated path leading to the final crystallization occurs through separation of metastable states, resulting in different crystalline morphologies and chemical compositions (*17*). P and Cr diffusion appear to dictate the initial stage of the process, sustaining the view of specific affinities between transition elements themselves or with nonmetallic components. Moreover, primary or eutectic crystallization reactions have been shown to occur, depending on the nominal composition of this system (*12, 17*). A fine structure of precipitated crystals characterize the eutectic-separated phases of FeNiPB (*18*); on the other hand, for this composition, P-enriched zones have been observed, responsible for some induced properties on heating (*19*), which possibly affect the ultimate structural conditions. Although the complexity of the involved mechanisms hinders a correlation between bulk and surface features—always a difficult task in metallic glasses—a different outermost texture can be coherently inferred in crystalline FeNiPB and FeNiCrPB alloys. In catalytic terms, this framework implies different surface makeups, i.e., terraces, ledges, kinks, which determine the population and reactivity of active ensembles. With conventional catalysts titration of active sites is a current test to substantiate these assumptions; unfortunately this approach is impractical for our polycomponent alloys since the sorption stoichiometry is still a debated question even for more simple metallic systems, apart from the small surface area.

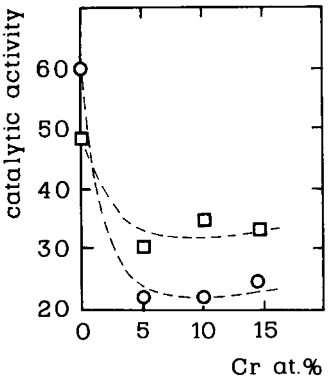

FIG. 2. Catalytic activity vs % Cr: ○, amorphous; □, crystalline.

For amorphous and crystalline FeNiPB catalysts, catalytic experiments with variable flux of H_2/acetylene = 2 were performed in order to follow changes of gas composition as a function of different contact times: results are shown in Fig. 3 for both amorphous and crystalline FeNiPB. The trends are the best fitting curves from experimental compositions of gaseous phases found for 10 different reagent fluxes in the interval 5.0–59.0 $cm^3\ min^{-1}$, corresponding to the interval 70–900 ms of apparent contact times. In general, amorphous catalysts are more selective vs the half-hydrogenation of acetylene than the corresponding annealed systems. The same results also appear in the selectivity data of Table 1 measured at constant reagent flux. The selectivity differences, albeit small,

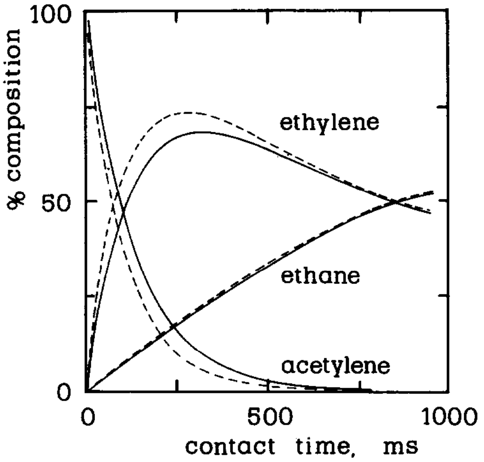

FIG. 3. Acetylene hydrogenation with amorphous (---) and crystalline (—) FeNiPB catalyst.

may be important for practical exploitation, considering the simplicity of preparation, easy handling, and low cost of these alloys.

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