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The Catalytic Activity and Selectivity of Some Metallic Glasses in the Hydrogenation of 1-Hexene

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The catalytic activity and selectivity of twenty one amorphous alloy ribbons were examined in the hydrogenation of 1-hexene. The amorphous alloys are of higher activity but of similar hydrogenation selectivity to the crystalline ones. Pd-based amorphous alloy ribbons, in particular $Pd_{80}Si_{20}$, are of a relatively high catalytic activity and of low selectivity towards hydrogenation. $Fe_{20}Ni_{60}P_{20}$ amorphous alloy is a highly hydrogenation selective catalyst. Incorporation of Pd in the Fe–Ni–B alloy doubled its activity and reduced its hydrogenation selectivity by 30%. Alloying P, instead of B, with Fe and Ni significantly increased the hydrogenation selectivity of this Fe–Ni based alloy; the hydrogenation selectivity was increased from 85% for $Fe_{20}Ni_{60}B_{20}$ to 93% for $Fe_{20}Ni_{60}P_{20}$.

Glassy metals are attractive subjects for study as heterogeneous catalysts because they differ substantially from their crystalline counterpart alloys in many of their mechanical, magnetic, electronic, and surface chemical properties.[1—4] Studies of Somorjai and others[5] demonstrating the sensitivity of some reaction rates to crystal structure and orientation suggest the possibility that the lack of crystalline order in glassy metals may confer upon them a catalytic behavior different from that of the crystalline materials. It appears that there is a relationship between the structure-sensitivity and alloying on reactions;[6] one may assume that reactions sensitive to alloying are even more strongly affected by the presence or absence of crystallinity in the alloys. Another feature of interest is that amorphous alloy catalysts can often be prepared as single phase alloys over a wider range of compositions than the corresponding crystalline alloys, because of the nonequilibrium conditions under which the formation of glassy metals takes place.[4]

There are some published reports on the catalytic behavior of metallic alloys in the glassy state. For example, the hydrogenation of carbon monoxide by amorphous alloys has been reported by several investigators.[7—15] Also, the catalytic activity and selectivity of many amorphous alloys were studied in the hydrogenation of some unsaturated hydrocarbons.[16—25] We have previously described a comparison of the catalytic selectivity of amorphous and crystalline $Pd_{80}Si_{20}$ in the hydrogenation of several organic substrates.[26—28]

We report here the results of a preliminary screening of a broad selection of metallic glasses for catalytic activity and selectivity, where these properties of the glassy alloys have been studied and compared to those of the crystalline ones. So that the effect of amorphousness or crystallinity on the surface structure, and thus on the catalytic behavior of these alloys is investigated. Most of the chosen alloy compositions contain the highly active Pd and/or Ni metals, and in some cases glass forming additive(s), such as B, Si, and P. The hydrogenation of 1-hexene in 1,4-dioxane at 50°C was chosen as a probe to study the catalytic activity and selectivity of these metallic glasses. 1-Hexene was chosen as a substrate for hydrogenation because of the many possibilities that it can undergo. For example, 1-hexene becomes saturated to hexane, or it may isomerize to the *cis*- and *trans*- 2 and 3-hexenes, depending on the reaction conditions, as well as the type of the active sites present on the surface of the catalyst. Therefore, the hydrogenation of 1-hexene would provide good information about the surface structure of the studied alloys. For our purposes, activity is defined as the reciprocal log time (min) required for conversion of 10% of 1-hexene to products, whether by hydrogenation, or isomerization to other hexenes. Selectivity for hydrogenation was also determined. Selectivity is defined here as the percentage of *n*-hexane among other products at the point of 10% conversion of 1-hexene to products.

Experimental

Glasses of a variety of compositions as listed in Table 1 were prepared in the form of ribbons of 20—30 μm thick, 1—4 mm wide and several meters long, by melt-spinning in a controlled protective atmosphere. The crystalline alloys were prepared by overnight heating of the amorphous ribbons in quartz tubes under vacuum at temperatures above their crystallization temperatures. The amorphous nature of the ribbons was checked before and after reaction by X-ray diffraction, and the chemical composition was confirmed by atomic absorption spectroscopy. Hydrogenation reactions were carried out in glass pressure bottles fitted with a teflon plug pierced by a stainless steel needle for hydrogen supply, and by a needle with a teflon valve for sample removal. Stirring was provided by a teflon-coated magnetic stir-bar. The standard reaction conditions were 0.40 g alloy ribbons cut into 4—5 mm long pieces, 5.0 ml 1-hexene and 5.0 ml 1,4-dioxane at 50°C and at constant H_2 pressures between 140 and 1500 kPa. Reaction progress was monitored by ^{13}C FT NMR spectroscopy of samples removed periodically, as described in detail in Ref. 29. Most of the ribbons were

Table 1. Catalytic Hydrogenation of 1-Hexene by Glassy Metal Ribbons (Compositions in Atomic Percent)

Catalyst	Selectivity[a]	Activity[b]		H_2 pressure
	A&C	A	C	kPa
$Pd_{80}Si_{20}$	54	1.7	1.2	1400
$Pd_{80}Si_{20}$	42	1.0	0.56	700
$Pd_{80}Si_{20}$	32	0.67	0.35	140
$Zr_{65}Pd_{35}$	49	1.0	0.48	700
$Pd_{74}Cu_6Si_{20}$	31	0.67	0.35	140
$Pd_{86}Si_{14}$	30	0.59	0.32	140
$Fe_{20}Ni_{60}B_{20}$	85	0.31	—[c]	1200
$Fe_{20}Ni_{60}P_{20}$	93	0.34	—[c]	1250
$Fe_{18}Ni_{54}B_{16}Pd_{12}$	58	0.77	0.56	1200
$Fe_{40}Ni_{40}B_{20}$	63	0.32	—[c]	1100
$Fe_{80}B_{20}$	61	0.29	—[c]	1300
$Fe_{81}B_{13.5}Si_{3.5}C_2$	71	0.29	—[c]	1200
$Fe_{40}Ni_{40}Mo_4B_{16}$	67	0.28	—[c]	1300
$Fe_{67}Co_{18}B_{14}Si_1$	72	0.30	—[c]	1300
$Zr_{70}Ni_{30}$	57	0.33	—[c]	700
$La_{66}Ni_{34}$	40	0.30	—[c]	700
$Ni_{50}Ti_{40}Si_{10}$	56	0.46	0.32	700
$Zr_{49}Ti_{21}Ni_{30}$	—[c]	<0.28	—[c]	700
$Zr_{50}Cu_{50}$	—[c]	<0.28	—[c]	700
$Zr_{70}Cu_{30}$	55	0.42	0.34	1500
$Zr_{65}Co_{27}P_8$	61	0.34	—[c]	1400
$Co_{66.75}Cr_{28}Mo_5Co_{0.25}$[d]	58	0.38	0.32	1300
$Mg_{70}Zn_{30}$	57	0.33	—[c]	1500
Ni foil[e]	65	0.38	—[c]	1400
Pd foil[e]	57	1.1	—[c]	1400
Pd powder[e]	38	—[f]	—[c]	1400
Pd powder[e]	13	—[f]	—[c]	140

a) Selectivity=%Hexane×100, at 10% conversion of 1-hexene to other hexenes and hexane. A: Amorphous; C: Crystalline. b) Activity defined as 1/log time (min), from the time required for 10% conversion of 1-hexene to products. A: Amorphous; C: Crystalline. c) Conversion level too low for accurate comparison. d) Partly crystalline. e) Crystalline reference materials. f) Too active to compare quantitatively to similar amount of ribbon.

quite ductile and either did not fragment further or gave only small amounts of powder under the reaction conditions; the one exception was $La_{66}Ni_{34}$ which was completely converted to powder during reaction.

Results and Discussion

The results of our survey are presented in Table 1. The survey included a variety of Pd or Ni based alloys, and a few other readily glass forming alloys. A comparison with unalloyed Pd and Ni is made by including results of commercially available metal foils of Pd and Ni (Alfa Inorganics) and Pd powder (Strem Chemical, Alfa). Pd and the Pd-containing alloys were the most active catalysts. The $Pd_{80}Si_{20}$ ribbon was slightly more active than Pd foil; this difference may be partly due to the lower surface area of the foil (ca. 0.06 $m^2\,g^{-1}$) than that of the ribbon (ca. 0.15 $m^2\,g^{-1}$). Activity remained high even at the lower Pd levels in $Zr_{65}Pd_{35}$ and $Fe_{18}Ni_{54}B_{16}Pd_{12}$. At H_2 pressures between 700 and 1400 kPa, all Pd based materials showed low hydrogenation selectivity where hydrogenation was at 30—60%. $Pd_{80}Si_{20}$ and Pd foil were similar in selectivities. Both selectivity and activity are dependent on H_2 pressure in the usual way, with activity and selectivity towards hydrogenation increasing at increasing H_2 pressure.

All Ni based amorphous alloys were considerably less active than the Pd based alloys and were slightly less active than Ni foil. However, the hydrogenation selectivity of Ni alloys is higher than that of the Pd alloys, with hydrogenation in most cases at the 55—70% level. Hydrogenation selectivity was significantly high for two alloys, $Fe_{20}Ni_{60}P_{20}$ and $Fe_{20}Ni_{60}B_{20}$, which gave 93 and 85% hydrogenation, respectively. These alloys can be considered as high hydrogenation selective catalysts. Incorporation of Pd in the $Fe_{20}Ni_{60}B_{20}$ alloy to form $Fe_{18}Ni_{54}B_{16}Pd_{12}$ resulted in significantly increasing the activity and decreasing the hydrogenation selectivity of that alloy. For instance, the activity was increased from 0.31 to 0.77, whereas the selectivity was decreased from 85 to 58 upon incorporation of Pd to the Fe–Ni–B alloy. Three amorphous alloys containing Co were more active than the corresponding Ni based alloys, but were of similar, moderate selectivity, with hydrogenation at 60—70%. It is noteworthy that the $Mg_{70}Zn_{30}$ alloy was also moderately selective. $Zr_{50}Cu_{50}$ and $Zr_{49}Ti_{21}Ni_{30}$ both were the least active alloys, even compared to $Zr_{70}Ni_{30}$ which was examined at the same H_2 pressure.

To assess the effect of structure as well as composition on the observed catalytic properties, activity and selectivity were also examined for some alloys in the crystalline state. The catalytic activity of the amorphous state was higher than that of the crystalline one for each of the studied alloys (Table 1). This observed higher activity of the amorphous alloys could be due to the surface structural differences between the amorphous and the crystalline states. Where the amorphous alloys possess more surface defects and irregularities, and different electronic properties than the crystalline alloys.[1—6] This observation is in an agreement with results of similar studies.[7—10,12,15,20—28] Whereas, the selectivity was the same for both the amorphous and crystalline forms of each of the studied alloys. For example, $Fe_{18}Ni_{54}B_{16}Pd_{12}$ and $Fe_{20}Ni_{60}P_{20}$ each showed the same selectivity for the amorphous and the crystalline states, with the latter alloy being more hydrogenation selective than the former one. Figures 1 and 2 show the selectivity characteristics for $Fe_{18}Ni_{54}B_{16}Pd_{12}$ and $Fe_{20}Ni_{60}P_{20}$, respectively, with data points in the composition vs. hydrogenation of 1-hexene for both the amorphous and the crystalline catalysts.

This observed independence of the catalytic selectivity on crystallinity is to be considered in the light of

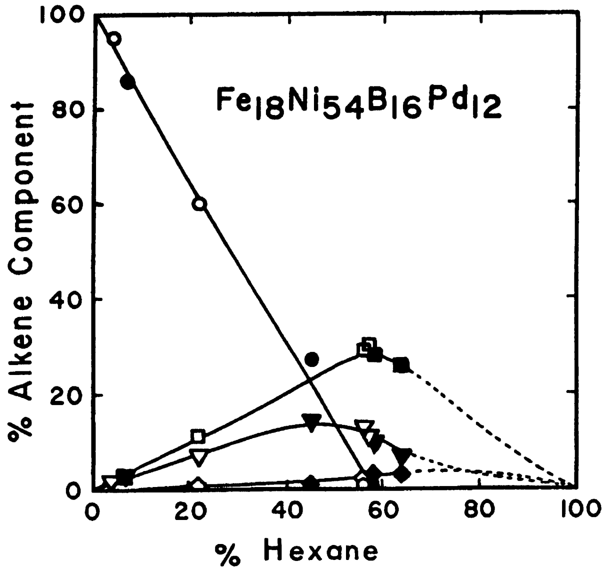

Fig. 1. The catalytic selectivity of amorphous (filled points) and crystalline (open points) $Fe_{18}Ni_{54}B_{16}Pd_{12}$ alloy ribbons in the hydrogenation of 1-hexene: ○,● 1-hexene; □,■ *trans*-2-hexene; ▽,▼ *cis*-2-hexene; ◇,◆ *trans*-3-hexene.

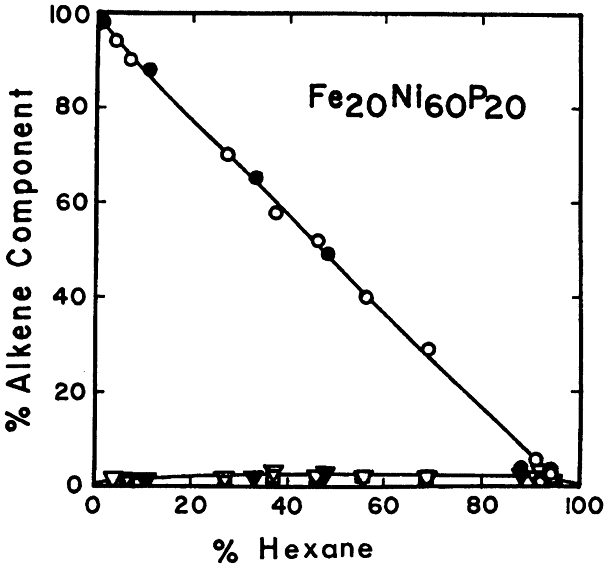

Fig. 2. The catalytic selectivity of amorphous (filled points) and crystalline (open points) $Fe_{20}Ni_{60}P_{20}$ alloy ribbons in the hydrogenation of 1-hexene: ○,● 1-hexene; □,■ *trans*-2-hexene; ▽,▼ *cis*-2-hexene; ◇,◆ *trans*-3-hexene.

the experience,[5] that is hydrogenation of alkenes is not a structure-sensitive reaction, this feature apparently carries over to insensitivity to the presence or absence of crystallinity. The alternative explanation is that the glassy alloys form crystalline surfaces during hydrogenation reaction is unlikely since the test temperatures are much lower than the crystallization temperatures ($T_{\text{test}}/T_{\text{cryst}}$ or 323 K/664 K $=0.5$ for $Pd_{80}Si_{20}$) and bulk crystallization did not occur over the test period, as confirmed by XRD.

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