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Review (Special Issue in Memory of the 80th Birthday of Professor Jingfa Deng)

Research, development, and application of amorphous nickel alloy catalysts prepared by melt-quenching

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ABSTRACT

Raney Ni is one of the most widely used catalysts in the petrochemical industry. This material's intrinsic catalytic activity for hydrogenation may be enhanced by transforming the crystalline Ni-based alloy into an amorphous structure via melt-quenching. The meta-stability and low specific surface area of such amorphous alloys, however, can severely restrict their catalytic applications. Our work has demonstrated that the incorporation of rare earth (RE) elements increases the crystallization temperature of an amorphous Ni catalyst by 200 K. Related experimentation has determined that the specific surface area of such catalysts is dramatically increased by two orders of magnitude following alloying with Al and subsequent caustic leaching. In addition, by introducing a third metal as a promoter, the hydrogenation selectivity, corrosion resistance and magnetism of these materials may be precisely adjusted, giving rise to a family of skeletal amorphous Ni alloy catalysts, to which we apply the trade name SRNA. Among these catalysts, the SRNA-1 catalyst is used for the hydrogenation of pharmaceutical intermediates, SRNA-2 is employed for the hydrogenation of glucose into sorbitol, SRNA-3 is effective in the adsorptive desulfurization of gasoline and diesel and SRNA-4 is used for the purification of caprolactam. In addition, the SRNA-5 catalyst is useful in the hydrogenation of benzoic acid as a partial substitute for the costly Pd/C catalyst, reducing consumption of the latter during the hydrogenation process by almost 50%.

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The Raney Ni catalyst, developed by Murray Raney in 1925, is currently very commonly employed as a hydrogenation catalyst in the pharmaceutical, agrochemical, and petrochemical industries and has reached a level of significant technical maturity [1]. Thus, to achieve further significant improvements in the area of catalytic materials, great strides in catalytic performance are required, along with the development of associated advanced reaction engineering techniques suitable for use with new catalytic materials.

Amorphous metal alloys are a relatively new catalytic material which have structures with short-range order but long-range disorder and which exhibit useful catalytic proper-

ties. Since the pioneering paper on the catalytic performance of amorphous metal alloys appeared in 1981 [2], these materials have remained some of the most heavily researched catalysts. Although the intrinsic catalytic activity of amorphous metal alloys is usually higher than that of the corresponding crystalline metals, their meta-stability and low specific surface area have severely restricted their practical applications. To date, except that our research group has been successful in demonstrating the manufacture and application of various amorphous metal alloy catalysts on an industrial scale, most studies concerning these materials have been restricted to the laboratory or pilot-plant scale.

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Fig. 1. DSC traces for amorphous Ni-P and Ni-RE-P alloy catalysts. Cited from Ref. [3].

1. Improvement of thermal stability of amorphous Ni-P alloys [3]

1.1. Thermal stability of amorphous Ni-P and Ni-RE-P alloys

One shortcoming of amorphous alloys which limits their practical applications in catalysis is their meta-stability. However, if an alloy's crystallization temperature is sufficiently greater than the temperature of the reaction to which it is applied, it is possible for the amorphous alloy to maintain its high catalytic activity over a suitably long lifetime, without loss of the alloy's amorphous structure. In the case of the amorphous Ni-P alloy, its crystallization temperature is 629 K. One goal of our work was to further improve the thermal stability of this material by incorporating the rare earth (RE) elements Ce, Y or Sm into the alloy. This approach was adopted because it is known that the presence of RE atoms with large radii can retard the diffusion of Ni atoms, which is a prerequisite for the crystallization of the amorphous Ni-P alloy [4].

Amorphous Ni-P and Ni-RE-P (RE = Ce, Y, and Sm) alloys were prepared via a melt-quenching technique, by which amorphous alloy ribbons 2 mm wide and 20 μm thick were obtained. Chemical analysis of the resulting alloys found atomic ratios of $\text{Ni}_{82.0}\text{P}_{18.0}$, $\text{Ni}_{82.0}\text{Ce}_{0.31}\text{P}_{17.7}$, $\text{Ni}_{82.0}\text{Y}_{0.25}\text{P}_{17.7}$ and $\text{Ni}_{82.0}\text{Sm}_{0.15}\text{P}_{17.8}$. Figure 1 shows the differential scanning calorimetry (DSC) traces obtained for the Ni-P and Ni-RE-P alloys and the data derived from the figure are summarized in Table 1. It can be seen that there was only one exothermic peak for the Ni-P alloy but three peaks for the RE-modified alloys, and that the initial crystallization temperature of the amorphous Ni-P alloy was 629 K, while those of the Ni-Ce-P, Ni-Y-P, and

Fig. 2. Schematic illustration of potential energy barriers during the crystallization of amorphous Ni-P and Ni-Ce-P alloys. Cited from Ref. [3].

Ni-Sm-P alloys were 88, 82, and 71 K higher, respectively. Furthermore, the peak maxima for the main exothermic peaks of the Ni-Ce-P, Ni-Y-P, and Ni-Sm-P alloys were 795, 787, and 742 K, respectively, and the corresponding enthalpy changes of crystallization (ΔH) were 2.10, 2.33, and 1.71 kJ/mol. These results unambiguously demonstrate that the addition of only a small amount of a RE element can lead to a remarkable increase in the crystallization temperature of the Ni-P alloy. This technique thus provides a simple and practical means of improving the thermal stability of the amorphous alloy, so as to avoid catalyst deactivation due to collapse of the amorphous structure.

1.2. The crystallization kinetics of amorphous Ni-P and Ni-RE-P alloys

To gain a better understanding of the beneficial effects of RE elements on the thermal stability of the Ni-P alloy, the activation energy of crystallization (E_a) was measured for different alloys, as a means to account for their differing thermal behaviors. To obtain these E_a values, a numbers of DSC curves were generated at different heating rates (β) and crystallization temperatures were recorded at the time at which the first formation of microcrystallites was observed through X-ray diffraction (XRD). Based on a sample's crystallization temperature (T_p) and β , E_a was calculated according to the Kissinger equation, as follows:

$$d(\ln T_p^2 / \beta) / d(1/T_p) = E_a / R$$

Here, E_a represents the potential energy barrier between two different phases. The larger the value of E_a is, the more difficult is the transformation between the two phases. As shown in

Table 1

Summary of DSC results for amorphous Ni-P and Ni-RE-P alloy catalysts. Cited from Ref. [3].

Catalyst	Peak I			Peak II			Peak III		
	T_p (K)	ΔH (kJ/mol)	E_a (kJ/mol)	T_p (K)	ΔH (kJ/mol)	E_a (kJ/mol)	T_p (K)	ΔH (kJ/mol)	E_a (kJ/mol)
Ni-P	629	1.83	225.7	—	—	—	—	—	—
Ni-Ce-P	717	0.60	415.2	795	2.10	326.4	860	0.19	345.6
Ni-Y-P	711	0.39	538.3	752	0.14	464.6	784	2.33	501.7
Ni-Sm-P	700	0.52	545.3	742	1.71	397.8	846	0.15	618.6

Table 1, E_a for the Ni-P alloy was 225.7 kJ/mol, while values for the Ni-Ce-P, Ni-Y-P, and Ni-Sm-P alloys were all greater, at 415.2, 538.3, and 545.3 kJ/mol, respectively. It is evident that, following the incorporation of RE elements, the E_a associated with the transformation between the amorphous phase and the crystalline phase was increased considerably, leading to improved thermal stability of the RE-modified alloys. Based on the data in Table 1, Figure 2 presents a schematic illustration of the potential energy barriers during crystallization of the Ni-P and Ni-Ce-P alloys (presented as a representative of the RE-modified alloys).

It has been noted that E_a correlates well with the apparent activation enthalpy for viscous flow, suggesting that viscosity is the rate-determining factor during crystallization [5]. When incorporating Ce, Y or Sm into the Ni-P alloy, it is reasonable to anticipate that these large RE atoms will effectively slow the diffusion of Ni and P atoms during thermal treatment, thus improving the thermal stability of the alloy.

2. Preparation of a high surface-area skeletal amorphous Ni-P alloy catalyst [3,6]

2.1. Physicochemical properties of skeletal amorphous Ni-P alloy catalyst

Because of the extremely low specific surface area of as-quenched amorphous Ni-P alloys ($\sim 0.1 \text{ m}^2/\text{g}$), these alloys are usually treated with subsequent pulverization, oxidation or reduction to increase their specific surface area and thus improve their catalytic activity. Such treated alloys, however, still exhibit a relatively low specific surface area of $2 \text{ m}^2/\text{g}$, which is much smaller than that of either the Raney Ni catalyst or the supported Ni catalysts. As a result, the prospects for industrial application of amorphous Ni-P alloy catalysts are currently limited and it would be highly beneficial to develop a simple, efficient method to increase the specific surface area of these alloys.

Based on existing methods for the preparation of Raney Ni catalysts with a sponge-like structure, we incorporated Al into the amorphous Ni-P alloy during the initial melt-quenching process. The Al in the resulting ternary alloy was then leached out with an alkaline solution to generate a porous structure. The amorphous structures of the ternary Ni-Al-P alloy and the resulting skeletal Ni-P alloy catalyst were confirmed by XRD. The results in Table 2 show that the specific surface area of the skeletal Ni-P alloy prepared in this manner increased dramatically to $106 \text{ m}^2/\text{g}$ (comparable with that of the Raney Ni catalyst), verifying the utility of our preparation method. The active surface area as determined by H_2 adsorption was $48.5 \text{ m}^2/\text{g}$, which is slightly higher than that of the Raney Ni catalyst, infer-

Table 2

Physicochemical properties of the skeletal amorphous Ni-P alloy catalyst. Cited from Ref. [3].

Catalyst	Bulk composition (atomic ratio)	A_{BET} (m^2/g)	V_{pore} (cm^3/g)	A_{act} (m^2/g)
Skeletal Ni-P	$\text{Ni}_{68}\text{Al}_{25}\text{P}_7$	106	0.10	48.5
Raney Ni	$\text{Ni}_{68}\text{Al}_{32}$	94	0.06	45.0

Table 3

Activities of catalysts for the liquid-phase hydrogenation of styrene to ethyl benzene. Cited from Ref. [3].

Catalyst	Specific activity (g/g)			
	353 K	363 K	373 K	383 K
Skeletal Ni-P	15.3	18.5	23.6	27.3 ^b
Ni-Sm-P	0.0	0.0	0.2	—
Raney Ni	15.9	18.7	21.2	26.5

Reaction conditions: 2.5 g catalyst, 50 ml 30 vol% styrene in cyclohexane, H_2 pressure 4 MPa, stirring at 29 r/min, reaction time 1 h.

^bUnder these conditions, styrene was completely hydrogenated in 1 h and 1.1% of the ethyl benzene product was further hydrogenated to ethyl cyclohexane.

ring that the catalytic activity of the skeletal Ni-P catalyst is potentially greater than that of the conventional Raney Ni catalyst.

2.2. The hydrogenation activity of the skeletal amorphous Ni-P alloy catalyst

Table 3 compares the catalytic activities for the liquid-phase hydrogenation of styrene between the skeletal Ni-P catalyst, the amorphous NiSmP catalyst treated under optimized oxidation-reduction conditions (which exhibited the greatest activity among the Ce, Y, and Sm-modified alloys) and the Raney Ni catalyst. The reaction conditions under which catalysis was measured are also given in this table. The specific catalytic activity for each material is expressed as the ratio of the mass of styrene converted to ethyl benzene per hour to the mass of catalyst employed. It is evident that the weight-normalized specific activity of the activated amorphous Ni-Sm-P catalyst is much lower than that of the Raney Ni catalyst, which we attribute to the amorphous catalyst's significantly lower specific surface area. The specific activity of the skeletal Ni-P alloy is similar to that of the Raney Ni catalyst at 353 and 363 K. At higher reaction temperatures, however, the skeletal Ni-P alloy is more active than the Raney Ni catalyst. Using the skeletal Ni-P at 383 K, all available styrene was converted to ethyl benzene and, in addition, 1.1% of the ethyl benzene was further hydrogenated to ethyl cyclohexane. Using the Raney Ni catalyst under the same conditions, unreacted styrene remained.

Because the hydrogenation of styrene to ethyl benzene proceeded readily over both catalysts, the liquid-phase hydrogenation of toluene to methyl cyclohexane was examined to further differentiate their catalytic activities. The reaction conditions for these tests are given in Table 4. It was determined that, under these conditions, the catalytic activity of the skeletal

Table 4

Activities of catalysts for the gas-phase hydrogenation of toluene to methyl cyclohexane. Cited from Ref. [3].

Catalyst	Specific activity (g/g)			
	373 K	393 K	413 K	433 K
Skeletal Ni-P	1.9	2.5	4.8	9.3
Raney Ni	0.7	1.5	2.9	4.4
Skeletal Ni-La-P	2.3	3.1	5.0	10.9

Reaction conditions: 2.5 g catalyst, 50 ml 30 vol% toluene in cyclohexane, H_2 pressure 4 MPa, stirring at 29 r/min, reaction time 1 h.

Ni-P catalyst was more than twice that of the Raney Ni catalyst. A skeletal amorphous Ni-La-P alloy catalyst was subsequently prepared and its activity for the hydrogenation of toluene was also tested, with the results included in Table 4. The incorporation of La further improved the activity of the skeletal catalyst, possibly because of the improved thermal stability imparted by the La.

From the above results, it is evident that this new method of preparing the catalysts, involving the incorporation and subsequent removal of Al, can remarkably increase both the specific surface area and the catalytic activity of the amorphous alloy. Because no time-consuming oxidation-reduction activation procedure was required, this preparation method works ideally to remove one of the main obstacles currently limiting the application of amorphous alloy catalysts in industry.

3. The catalytic activities of skeletal amorphous Ni alloy catalysts

3.1. Hydrogenation of organic compounds on SRNA-1 and SRNA-2 catalysts

3.1.1. Hydrogenation of pharmaceutical intermediates on the SRNA-1 catalyst

The trade name we have applied to the skeletal amorphous Ni-P alloy catalyst is SRNA-1. Table 5 shows the reaction conditions and results for the liquid-phase SRNA-1 hydrogenation of five pharmaceutical intermediates containing several potential hydrogenation sites, including phenyl rings, C=C bonds, nitro groups and nitrile groups. The results show that the SRNA-1 catalyst exhibited higher activity than the Raney Ni catalyst. Under the same reaction conditions, the consumption of the SRNA-1 catalyst was 30% to 70% lower than that of the Raney Ni catalyst, showing that SRNA-1 is also more cost-effective. As a result of this improved performance, the current demand for the SRNA-1 catalyst for the hydrogenation of pharmaceutical intermediates is approximately 100 t annually.

Table 5

Comparison of the consumption of the SRNA-1 catalyst and Raney Ni.

Substrate	Reaction condition				Product	Cat. consump. (g/kg)	
	Solvent	T/K	P(H ₂)/MPa	t/h		Raney Ni	SRNA-1
NaOH-H ₂ O	323	9.0	2.0		100	50
NaOH-H ₂ O	303	1.0	3.0		75	25
H ₂ O	353	4.0	4.0		500	300
ethanol	303–323	7.0	4.0		200	90
ethanol	353–393	8.0	3.0		100	70

Table 6

Catalytic performance of the SRNA-2 catalyst and some commercial Raney Ni catalysts for glucose hydrogenation.

Catalyst	T (K)	P (MPa)	t (min)	Cat./glucose (53 wt% in water)	Conversion (%)
Raney Ni-1	408	6.5	70	1.6 g/150 ml	99.1
Raney Ni-2	393	4.76	300	2 g/60 ml	99.2
Raney Ni-3	408	7.0	70	1.1 g/150 ml	94.3
SRNA-2	408	5.0	70	1.1 g/150 ml	100.0

3.1.2. Hydrogenation of glucose on the SRNA-2 catalyst

The trade name of our skeletal amorphous Ni-B alloy catalyst is SRNA-2. This catalyst was prepared in a manner similar to the skeletal amorphous Ni-P alloy catalyst, with the exception of the replacement of the metalloid P by the metalloid B. The data in Table 6 show that, compared with several commercial Raney Ni catalysts, the use of the SRNA-2 catalyst results in the complete conversion of glucose to sorbitol, while also allowing the application of lower H₂ pressure, shorter reaction time and a lower catalyst-to-glucose ratio. The current demand for the SRNA-2 catalyst for the hydrogenation of glucose is around 200 t annually, corresponding to a market share above 20%.

3.2. APR of ethylene glycol on the SRNA-3 catalyst [7]

H₂ is considered to be a potential source of clean energy because its use does not emit greenhouse gases, either during direct combustion or during the operation of a H₂ fuel cell. The current methods for the industrial-scale production of H₂ are primarily based on the use of non-renewable fossil fuels [8–11], and thus a process for obtaining H₂ from renewable sources is highly desirable. Dumesic et al. [12,13] have demonstrated that H₂ can be produced from sugars and sugar alcohols over either a Pt/Al₂O₃ catalyst or a Sn-modified Raney Ni catalyst at temperatures near 500 K in a single-reactor aqueous phase reforming (APR) process.

Table 7

Comparison of the catalytic behaviors of SRNA-3 catalyst and Raney Ni for APR of a 5 wt% ethylene glycol solution. Cited from Ref. [7] with permission from Elsevier.

Item	Raney Ni [14]	RQ Ni ^a	Raney Ni [14]	RQ Ni ^a
Temperature (K)	498	498	538	538
Pressure (MPa)	2.58	2.58	5.13	5.13
LHSV (h ⁻¹)	4.13	3.60	8.26	3.60
Conversion of C to gas (%)	97	92	104	102
H ₂ selectivity (%)	35	35	28	21
Alkane selectivity (%)	44	47	47	59
Gas products (mol%)				
H ₂	47.6	47.4	41.4	34.9
CO ₂	30.4	30.8	31.9	27.2
CO	0.02	n.d.b	0.03	n.d.b
Methane	20.7	22.8	25.6	36.4
Ethane	0.97	1.12	0.92	1.43
Propane	0.28	0.23	0.18	0.15
Butane	0.02	0.00	0.01	0.00
Liquid products (mol%, excluding unreacted EG)				
Methanol	10.2	85.1	34.3	95.1
Ethanol	48.3	12.9	2.5	3.5
Acetic acid	30.2	0.0	63.2	0.0
Acetaldehyde	7.3	0.0	0.0	0.0
Glycolaldehyde	4.0	0.0	0.0	0.0
2-Propanol	0.0	0.2	0.0	0.2
Acetone	0.0	1.8	0.0	1.2

^a 0.5 g of catalyst.

^b Below the detection limit.

3.2.1. Comparison between the SRNA-3 catalyst and Raney Ni

SRNA-3 is the trade name of a skeletal amorphous Ni catalyst which has a lower atomic coordination number and a bulk composition with an atomic ratio of Ni₈₄Al₁₆. Because of the absence of a metalloid, the SRNA-3 catalyst is partly crystalline. Table 7 compiles the H₂ and alkane selectivities and gas and liquid product distributions at 498 and 538 K over the SRNA-3 and Raney Ni catalysts [14]. SRNA-3 exhibited comparable or lower H₂ selectivity and higher alkane selectivity as compared with the Raney Ni catalyst. However, SRNA-3 produced less CO in the effluent gas, which is especially significant when considering applications in the field of H₂ fuel cells, because the cell anode materials are usually vulnerable to CO poisoning [15].

3.2.2. The promoting effect of Sn on the SRNA-3 catalyst

Figure 3 shows the trends in H₂ and alkane selectivities as increasing amounts of Sn are incorporated into the SRNA-3 catalyst. As can be seen, the selectivity of the catalyst for H₂ increased when the Sn content was increased, with the H₂ selectivity exceeding 90% at Sn/Ni molar ratios above 4.4%. The alkane selectivity showed the opposite trend to that of H₂. At a Sn/Ni ratio of 15.7%, the alkane selectivity was less than 1%, whereas the H₂ selectivity reached as high as 98%. Kinetic data suggest that the addition of Sn not only decreases the turnover frequencies (TOF) for the alkanes, but also steadily increases the TOFs for H₂ and CO₂, thus leading to higher selectivity for H₂.

3.3. Chemoselective hydrogenation of 2-ethylanthraquinone (eAQ) on the SRNA-5 catalyst [16]

Fig. 3. Effect of Sn/Ni molar ratios in Sn-modified SRNA-3 catalysts on H₂ and alkane selectivities during APR of ethylene glycol. Reaction conditions: 0.5 g catalyst, 5 wt% ethylene glycol aqueous solution, LHSV 3.60 h⁻¹, temperature 498 K, pressure 2.58 MPa. Cited from Ref. [7] with permission from Elsevier.

The hydrogenation of eAQ is a key step in the industrial production of H₂O₂ [17]. As shown in Scheme 1, the hydrogenation produces 2-ethylanthrahydroquinone (eAQH₂) and 2-ethyltetrahydroanthrahydroquinone (H₄eAQH₂), the “active quinones” [18], which can then be oxidized to produce H₂O₂. Other more fully hydrogenated and hydrogenolysis products (degradation products) are not desirable, because they can neither produce H₂O₂ nor be regenerated, which leads to the loss of expensive eAQ. In industry, Pd catalysts are used in eAQ hydrogenation because of their high selectivity for active quinones [17]. These Pd catalysts, however, are highly expensive. We therefore developed the SRNA-5 catalyst for the chemoselective hydrogenation of eAQ. SRNA-5 is the trade name of a skeletal amorphous Ni catalyst promoted by Cr and Fe, with an atomic ratio of Ni_{74.6}Fe_{2.4}Cr_{4.3}Al_{18.6}.

Figure 4(a) shows the percent yield of H₂O₂ as a function of time for both catalysts. Over the SRNA-5 catalyst, the yield of H₂O₂ initially increases and then levels off, with X ($X = n_{\text{H}_2\text{O}_2}/n_{\text{eAQ}} \times 100\%$, which also represents the selectivity for active quinones) plateauing at approximately 97%. In comparison, the yield of H₂O₂ over Raney Ni reaches a maximum of only 67% and drops after prolonged reaction times. These results clearly demonstrate the higher selectivity of the SRNA-5 catalyst in the hydrogenation of eAQ to active quinones, as

Scheme 1. Reaction products in the hydrogenation of eAQ. Cited from Ref. [16] with permission from Elsevier.

Fig. 4. H₂O₂ yield (a) and the evolution of eAQ and H₄eAQ (b) over the SRNA-5 and Raney Ni catalysts as a function of the reaction time. In (b), solid lines are for SRNA-5 and dotted lines for Raney Ni. Cited from Ref. [16] with permission from Elsevier.

compared with the conventional Raney Ni catalyst.

In order to gain further insight into variations in the selectivity of these two catalysts, the outputs of both eAQ and H₄eAQ were monitored and plotted in Fig. 4(b). It should be noted that the plotted values for eAQ in Fig. 4(b) denotes the sum total of unreacted eAQ and eAQ hydrogenated to eAQH₂, while the values for H₄eAQ equal the quantity of H₄eAQH₂, as can be seen by referencing the reduction-oxidation cycles shown in Scheme 1. Using the SRNA-5 catalyst, no H₄eAQ was generated during the first 20 min, which is indicative of the catalyst's high selectivity for eAQH₂. In contrast, when using Raney Ni, H₄eAQ was produced as soon as the hydrogenation commenced. Based on gas chromatography-mass spectrometry (GC-MS) analysis, H₈eAQH₂ was also immediately generated over Raney Ni. We can therefore conclude that the SRNA-5 catalyst exhibits higher selectivity than Raney Ni for carbonyl group hydrogenation in the presence of an aromatic ring, thus leading to higher yields of H₂O₂ and lower consumption of H₂ and expensive eAQ, which is highly preferred for an industrial process.

4. Adsorptive desulfurization of transportation fuels on skeletal amorphous Ni alloys

Most transportation fuels currently in use contain 100 to 1000 µg/g of organosulfur compounds. These S-containing molecules not only react with oxygen during combustion to produce the SO_x species which lead to acid rain [19], but also act to poison catalytic converters and thus create additional pollutants as well [20,21]. The EU and United States have both announced plans to reduce the allowable S content in gasoline and diesel fuels to 10 µg/g [22–24]. In addition, for fuel cells using gasoline as feedstock, a S content below 0.2 µg/g is pre-

ferred [25]. The desulfurization of transportation fuels by adsorption is a promising means to allow such fuels to meet these stringent environmental regulations [25–27]. Adsorptive desulfurization has the benefits of low investment cost and simple technology, minimal reduction in both the yield and octane number of gasoline, no consumption of H₂ and no need for extreme reaction conditions such as high temperature and pressure. To date, however, the use of metallic adsorbents in this process has not attracted significant attention, even though Raney Ni has seen widespread use in the desulfurization of organic and organometallic compounds [28–30].

4.1. In situ XPS study on the desulfurization of thiophene over SRNA-3 [31]

4.1.1. Adsorption and dissociation of thiophene

Following the addition of thiophene to SRNA-3 at 103 K, the S 2p_{3/2} binding energy (BE) of physisorbed thiophene at 165.1 eV was identified during subsequent XPS analysis [32]. After heating to 173 K, about one half of the physisorbed thiophene was desorbed, although only about 17% of the thiophene retained on the catalyst surface underwent sulfur abstraction, while the rest remained intact. Further annealing to 273 K induced scission of the C–S bonds of the residual thiophene and the surface concentration of atomic S reached a maximum and the formation of nickel sulfide commenced. At 473 K, there was only one doublet peak located between 160 and 165 eV, due to sulfur in the form of nickel sulfide [33,34]. The total sulfur intensity remained constant from 173 to 473 K.

On Raney Ni, thiophene in direct contact with the metallic Ni readily decomposes upon thermal annealing to give carbonaceous species and atomic sulfur. The C–S bonds of thiophene undergo scission at approximately 173 K on Raney Ni, close to the scission temperature of approximately 150 K observed on a Ni(111) surface [35]. It is consistent with experimental observations that the (111) diffraction peak is the dominant feature in the diffractogram of Raney Ni [36]. On the SRNA-3 alloy, however, most chemisorbed thiophene remained intact at 173 K and did not dissociate until 273 K, a temperature significant higher than the dissociation temperatures observed on Ni single crystals and Raney Ni.

4.1.2. Interpretation of differences in surface chemistry

We determined that the unit-cell dimension in SRNA-3 alloy is 0.3548 nm, which is significantly larger than in either Raney Ni or crystalline Ni [36]. This difference in unit cells may be attributed to the effect of quenching, which may cause atoms in the Ni–Al alloy to deviate from their equilibrium positions. It is known that the dissociation of an activated molecule is generally possible only when there is a good match between the interatomic distances in the molecule and the atomic arrangement of the surface metal atoms [37]. The increased Ni–Ni distance in the SRNA-3 alloy may therefore not be conducive to the scission of C–S bonds. The melt-quenching technique thus presents new possibilities for the design of metallic adsorbents with tunable bonding strengths towards thiophene or thiophenic compounds. As an example, by further increasing the

Table 8

Adsorptive desulfurization of gasoline by SRNA-3 alloy. Cited from Ref. [39].

Gasoline	Amount of adsorbent (g)	T (K)	Residence time (min)	S (10^{-6})		Desulf. ratio (wt%)
				In feed	In product	
Feed-1	40	293	5	1800	470	73.9
Feed-2	10	333	5	335	17	94.9
Feed-3	20	313	10	265	< 1	> 99.6

Adsorption conditions: 250 ml gasoline, alloys particle diameters 60–80 μm , stirring rate 280 r/min, blanketed by N_2 at ambient pressure.

quenching rate it is possible to obtain Ni adsorbent on which thiophene does not decompose even at room temperature. The intact thiophene molecules can consequently be removed via supercritical CO_2 extraction [38], thus simplifying the regeneration of the Ni adsorbent.

4.2. Adsorptive desulfurization of gasoline and diesel [39,40]

4.2.1. Adsorptive desulfurization of gasoline

Three different gasoline feedstocks were used in these studies. Feed-1 was a full-range gasoline derived from fluidized catalytic cracking (FCC), with a density of 0.7200 g/cm³ and a S content of 1800 $\mu\text{g/g}$. Feed-2 was a heavy fraction of hydro-treated FCC gasoline, with a density of 0.7800 g/cm³ and a S content of 335 $\mu\text{g/g}$. Feed-3 was a light fraction of FCC gasoline, with a density of 0.6600 g/cm³ and a S content of 265 $\mu\text{g/g}$. The S content in gasoline after adsorption by the SRNA-3 alloy in a slurry-bed reactor was measured by a microcoulometric technique. The results summarized in Table 8 show that the S content in the resulting product can be readily controlled by varying the adsorbent/gasoline ratio and the adsorption conditions. The S contents of Feed-1 and Feed-2 were decreased to below 500 $\mu\text{g/g}$ and 50 $\mu\text{g/g}$, respectively, which would meet Chinese gasoline regulations. In the case of Feed-3, when using 20 g of the SRNA-3 alloy as the adsorbent at an adsorption temperature of 313 K and a residence time of 10 min, less than 1 $\mu\text{g/g}$ of S was left in the gasoline, demonstrating that SRNA-3 alloy is a promising adsorbent for the production S-free gasoline under mild adsorption conditions.

4.2.2. Adsorptive desulfurization of diesel

Although adsorptive desulfurization over alloys is also applicable to straight-run diesel, FCC diesel or coker diesel, wherein the S content may range from 500 to 10000 $\mu\text{g/g}$, considering that the majority of the organic sulfides in diesel (in-

Table 9

Adsorptive desulfurization of diesel by SRNA-3 alloy. Cited from Ref. [40].

Adsorption temperature (K)	S content after adsorption (10^{-6})
293	20
313	15
333	10
353	9

Adsorption conditions: 100 ml diesel, 1 g alloy with particle diameter of 60–80 μm , stirring rate 300 r/min, adsorption time 10 min, blanketed by N_2 at ambient pressure. Sulfur in the raw feed is 70×10^{-6} .

cluding thiols, thioethers, and thiophenes) can be readily removed by hydrosulfurization (HDS), we used HDS diesel for adsorptive desulfurization testing, for economical and practical purposes. Heterocyclic sulfur compounds such as benzothiophenes, dibenzothiophenes, and their derivatives are difficult to remove by the conventional HDS process, and so we monitored for these compounds using a gas chromatograph equipped with an atomic emission detector (GC-AED). The diesel sample had a density of 0.8400 g/cm³ and a distillation range of 477–644 K. The S content in the diesel after adsorption in a slurry-bed reactor was determined by GC-AED and is given in Table 9. From these results, we see that higher adsorption temperatures produce lower S content following adsorption.

5. Examples of commercial applications of skeletal amorphous Ni alloy catalysts

A 30 t per year prototype unit for the manufacture of SRNA catalysts was commissioned in 1993, with the aim of both improving the production technology and reducing costs. The melt-quenching method was used to manufacture amorphous alloys in this facility and specially designed equipment was required, since the liquid Ni-Al alloy is very viscous, has a high melting point and is susceptible to oxidation. This commercial demonstration unit was primarily used to optimize the design of the graphite crucible, graphite nozzles and copper roller used in the melt cooling process. A scaled-up 100 t per year production facility for the manufacture of SRNA catalysts was constructed in 1995. A unique thermal treatment procedure was developed at that time which resulted in SRNA catalysts with improved amorphism and enhanced hydrogenation activity. The process flow associated with the manufacture of SRNA catalysts in this facility incorporated the regeneration and utilization of sodium meta-aluminate by collecting the spent mother liquor and wash water to provide raw materials for the production of alumina or zeolite. This measure not only avoids environmental pollution, but also allows for the maximized utilization of aluminum feedstocks as well as reduction in the production costs of the SRNA catalysts.

5.1. The commercial application of SRNA-4 in the purification of caprolactam [41]

The post-refining of caprolactam aims to saturate any unsaturated impurities via hydrogenation, to differentiate their physical properties from those of caprolactam. The existing technology generally utilizes the Raney Ni catalyst in a hydrogenation process consisting of a series of two 10 m³ kettle-type reactors operating at 0.7 MPa and 363 K. Impurities are saturated through hydrogenation prior to being separated via distillation, which ensures high quality in nylon-6 made from the resulting caprolactam. The product's PM value is widely used as an indicator of the quality (that is, the impurity content) of the caprolactam such that the higher the PM value is, the lower the impurity content. The PM value of premium-quality caprolactam should be above 30000 s, although the value of caprolactam manufactured by existing technology is generally 20000

s, a level at which it cannot be used to fabricate commercial products by high-speed spinning. Based on the distinct advantages of the SRNA-4 catalyst over the Raney Ni catalyst in bench and pilot tests, the catalyst was successfully substituted for Raney Ni catalyst in a commercial caprolactam production process in 1998. Upon the employment of the SRNA-4 catalyst, the consumption of the catalyst was reduced from 0.21 to 0.18 kg/t, resulting in a total catalyst consumption decrease of 14%. The demand for SRNA-4 catalyst for the purification of caprolactam is currently around 150 t annually, and its market share is above 80%.

5.2. CO methanation in the hydrogenation of benzoic acid to cyclohexanecarboxylic acid [42]

The synthetic process used commercially for the production of caprolactam from toluene, the SNIA Viscosa process, consists primarily of the oxidation of toluene to benzoic acid, the hydrogenation of benzoic acid to cyclohexanecarboxylic acid (CCA) and the amidation of CCA to caprolactam. In this process, the hydrogenation of benzoic acid is carried out in a series of continuously stirred reactor tanks over a 5% Pd/C catalyst. This method, however, suffers from a number of shortcomings that lead to inefficient operation of the equipment and excessive consumption of the expensive Pd/C catalyst. In addition, recycled Pd/C catalyst exhibits catalytic activity only 1/6 to 1/5 that of fresh catalyst. Among the factors contributing to the deactivation of the catalyst, CO released from the decarboxylation of CCA is regarded as the most important, because even a trace amount of CO is sufficient to deactivate Pd. Because the SRNA-5 catalyst is effective in eliminating CO by methanation, and the presence of chromium in this catalyst can improve its acid resistance, we introduced its use into the industrial process for the hydrogenation of benzoic acid. Simultaneously, the design of the production equipment and flow process were also improved, because the use of SRNA-5 introduced problems associated with recycling and separating the catalyst.

5.2.1. The promoting effect of SRNA-5 catalyst in a conventional industrial unit

Following the incorporation of SRNA-5 into a conventional industrial process unit, the concentration of CO in the reaction system was reduced from approximately 300 $\mu\text{g/g}$ to about 100 $\mu\text{g/g}$. Increasing the amount of SRNA-5 also resulted in steady increases in the activity of the recycled Pd/C catalyst. As a result, the amount of CCA produced per kg Pd increased from 35 t using the recycled Pd/C catalyst alone to 50 t using a combination of 0.8 wt% SRNA-5 in conjunction with the recycled Pd/C. In addition, consumption of the fresh 5% Pd/C catalyst during sustained hydrogenation activity was reduced by 46%.

5.2.2. Modification of the conventional industrial process

Because the centrifuge separator employed in the traditional process was originally designed for the separation of the Pd/C catalyst, and because the SRNA-5 catalyst has a much higher density, we found that the existing unit was not sufficient to recycle SRNA-5. As a result, there were several hundred $\mu\text{g/g}$ of Ni left in the spent Pd/C catalyst, which lengthened the incineration time required to treat the spent Pd/C catalyst to two weeks, greatly increasing the cost associated with keeping spare stock of fresh Pd/C catalyst on hand. Process improvements were therefore necessary to solve the recycling and separation problems caused by the introduction of the SRNA-5 catalyst.

To fully utilize the beneficial effects of SRNA-5 in this process, we modified the existing catalyst separation unit by incorporating a hydraulic cyclone after the hydrogenation reactor and a novel magnetic separator after the evaporator. A schematic of the modified process for the hydrogenation of benzoic acid is presented in Fig. 5. In this modified process, the hydraulic cyclone recycles the majority of the SRNA-5 as well as the spent Pd/C catalyst to tank VE203, which reduces the load on the centrifuge separator. When the hydraulic cyclone was first employed in the separation unit, the level of residual Ni in the spent Pd/C catalyst was reduced substantially, to 10% of its

Fig. 5. Schematic diagram of the modified industrial process for the hydrogenation of benzoic acid. Cited from Ref. [42] with permission from American Institute of Chemical Engineers.

level before the use of the cyclone. The incineration time required to treat the spent Pd/C catalyst was accordingly shortened to 7–8 d.

Because the SRNA-5 catalyst is ferromagnetic, while the Pd/C catalyst is not magnetizable, we designed a permanent magnet-based separator operating in the magnetic condensation mode to further isolate the SRNA-5 catalyst from the Pd/C catalyst. We found that the concentration of Ni remaining in the spent Pd/C catalyst after using this three-step separation strategy was only 1/4 to 1/3 of that which remained when using a combination of the hydraulic cyclone and the centrifuge separator. The incineration time for the spent Pd/C catalyst was further shortened to 4–5 d, which is close to that required without the addition of the SRNA-5 catalyst. Moreover, because of the much more thorough recycling of the SRNA-5 catalyst, the amount of CCA produced per kg Pd was increased by approximately 20% as compared with using the centrifuge separator alone. The consumption of fresh Pd/C catalyst was reduced by about 50%, while the purity of CCA was increased by 0.5%, demonstrating the superiority of the modified process for the hydrogenation of benzoic acid. Moreover, the modified industrial unit exhibited greater temperature and pressure stability, meaning that fewer ongoing adjustments of these parameters were required. Finally, the prolonged lifetime of the Pd/C catalyst allowed less frequent recovery of the spent Pd/C catalyst, thus improving the process efficiency. This improved design concept and separation strategy may also present opportunities for the improvement of other industrial hydrogenation processes which may have issues with CO poisoning of catalysts.

6. Conclusions

This paper presents an overview of our research efforts concerning the innovation of amorphous Ni alloy catalysts prepared by the melt-quenching technique and related chemical engineering processes. The inherent disadvantages of amorphous alloy catalysts, in terms of small specific surface area and low thermal stability, have been successfully mitigated, which allows the possibility of developing these materials into practical catalysts with improved performance, as substitutes for the Raney Ni catalyst. Based on these endeavors, we have achieved the first successful commercial applications of skeletal amorphous Ni alloy catalysts in the international arena. Our work to date has been primarily limited to the study of Ni-based amorphous alloy catalysts, and there are many potential applications for these catalysts which have not yet been fully explored. Further investigations may include the development of skeletal amorphous alloy catalysts based on other metals such as Co, Fe, Cu or Ru, which may find important applications in selective hydrogenation, CO hydrogenation, ammonia synthesis, biomass conversion, and other industrial processes. Nevertheless, our work forms a preliminary basis for the understanding of the physicochemical properties and catalytic behaviors of new skeletal amorphous alloy catalysts. We believe that more comprehensive and in-depth investigations in this field will undoubtedly improve the practical appli-

cations and theoretical understanding of skeletal amorphous alloy catalysts, with significant benefits to the fine chemical and petrochemical industry.

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Graphical Abstract

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Research, development, and application of amorphous nickel alloy catalysts prepared by melt-quenching

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Transforming crystalline Raney Ni into an amorphous structure by the application of a melt-quenching technique can significantly enhance the material's catalysis of hydrogenation reactions.

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急冷非晶态镍合金催化剂的研究开发和工业应用

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摘要: Raney Ni 催化剂是石油化学工业用量最大的催化剂之一, 通过急冷技术将其晶态结构转变为非晶态结构, 能够提高加氢活性. 但非晶态合金热稳定性差、比表面积小限制了这类催化材料的工业应用. 通过加入少量稀土元素, 使非晶态 Ni 晶化温度提高 200 K 以上; 通过加入 Al 再碱抽 Al, 使非晶态 Ni 比表面积增加 100 倍以上; 通过加入功能助剂调节非晶态 Ni 的加氢选择性、增加抗酸碱腐蚀性和磁性, 从而形成了系列非晶态 Ni 加氢催化剂 (商品名为 SRNA). 其中, SRNA-1 用于药物中间体加氢; SRNA-2 用于葡萄糖加氢制山梨醇; SRNA-3 用于汽、柴油吸附脱硫; SRNA-4 用于己内酰胺加氢精制; SRNA-5 用于苯甲酸加氢中替代 Pd/C 催化剂, 使后者的用量减少了 50%.

关键词: 非晶态合金; 骨架镍; 加氢; 脱硫; 工业化

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