Catalysis Communications 43 (2014) 116–120

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Search for a Raney-Ni type catalyst efficient in the transformation of excess glycerol into more valuable products

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ARTICLE INFO

Article history:
Received 31 July 2013
Received in revised form 16 September 2013
Accepted 18 September 2013
Available online 2 October 2013

Keywords:
Non-pyrophoric Raney-type Ni catalysts
Characterisation by XRD, thermal and BET measurements
Transformations of glycerol
Reuse and recycling possibilities

ABSTRACT

Al- and Si-containing Raney-Ni catalysts have been prepared with a method, which uses significantly less NaOH than the one described in the original recipe, *i.e.*, with method benign to the environment. The catalysts were characterised by a variety of techniques (X-ray diffractometry, thermal methods, and BET surface area measurements). The samples were used in transforming glycerol into more useful products. They were found to be highly active and selective in producing acetol, a compound of current interest. Nevertheless, only the silicon-containing sample behaved as a real catalyst, *i.e.* it could be regenerated and recycled. The Al-containing samples were decomposed to intermetallic- and Al-(oxy)hydroxide phases during the reaction.

1. Introduction

The traditional Raney-Ni belongs to the group of skeletal catalysts providing comparable activity to noble metal catalysts under significantly milder conditions (low temperature and pressure), thus avoiding unwanted side reactions [1]. The Raney-type catalysts are widely used for hydrogenation of various unsaturated compounds (for a review, see [2]) like olefins [3], nitriles [4], oxo [5] and nitro compounds [6], the C–S bond to C–H [7], to mention just a few, both in the laboratory as well as in the fine chemical industry [8–10]. Raney-Ni obtained *via* the original recipe [11] is highly pyrophoric due the absorbed hydrogen in the pores of the catalyst. It is advantageous on one hand, since it is the source of its high activity; however, it is a disadvantage on the other hand, because of the high risk of setting the reacting system ablaze. To avoid it the catalyst is kept under water and it is used in the form of aqueous slurry making its use in the catalysis of organic reactants tedious. The catalyst is still widely used, since the advantageous properties override the disadvantageous ones. Besides those already mentioned, among the advantages the relatively high density resulting in favourable sedimentation ability, high heat conductivity, good thermal and structural stabilities and low solubility in most organic solvents may be listed. However, mineral acids destroy the skeletal system and high Al content also decreases its stability.

The source of the skeletal catalysts is an alloy of a catalytically active and an inactive metal. The latter component is dissolved fully or at least partially, usually in a base. The primary particle diameter usually falls in the 40–80 Å range. It is larger by one order of magnitude for catalysts that were prepared from metal salts by thermal decomposition [1].

The precursor of the Raney-Ni catalyst is a 1:1 alloy of Ni and Al. The Al content is dissolved in a solution containing 20–25 wt.% NaOH. This is an exothermic reaction and is performed slowly under carefully controlled conditions. In the final step, the product is washed until neutral. The Ni content of the resulting material is 90–95%, and it is a sponge-like fine powder with high specific surface area and pyrophoric property. As it has already been mentioned the pyrophoric nature is disadvantageous, and its elimination without losing catalytic activity is really challenging. Although thermal desorption or chemical/electrochemical oxidation of the hydrogen or the combination of the two methods resulted in non-pyrophoric catalysts, the catalytic activities were found to significantly decrease as well [12,13].

Not too long ago Petró et al. were successful in the synthesis of a novel non-pyrophoric, ferromagnetic Raney-Ni catalyst with activity similar or higher in liquid-phase reactions than the traditional Raney-Ni [14]. The starting material is a 50–50 wt.% Al–Ni alloy and the resulting one is an aluminium-supported catalyst with well-dispersed Ni of 25–30 wt.%. The innovation is the use of more dilute base than usual, therefore the inactive component is just partially

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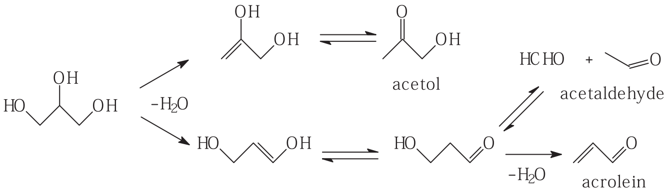
http://dx.doi.org/10.1016/j.catcom.2013.09.023



Scheme 1. Dehydration pathways and subsequent reactions of glycerol [17].

dissolved, resulting in the increase in the distance between the catalytically active Ni particles, and, thus the disappearance of the pyrophoric property.

This novel synthetic method is not only simpler, cheaper and faster than the traditional one, but it is more benign to the environment as well. If the amount of the precursor alloy is the same, the novel method provides 2000 cm^3 (2.2 kg) of the wet catalyst from 7 dm^3 water and 0.195 kg NaOH in 70 min, while the traditional one gives 0.5 kg (350 cm^3) catalyst using 8 dm^3 water and 2.1 kg NaOH in 270 min. The physical properties (*e.g.*, density) of the novel catalyst are also advantageous, *e.g.*, it can be easily dispersed in the reaction medium and can be readily filtered off when the reaction is complete. The precursor $NiAl_3$ and Ni_2Al_3 can be transformed into NiAl by NaOH and the majority of the Al becomes Al-(oxy)hydroxides of various kinds (gibbsite, boehmite, nordstrandite, bayerite, *etc.*). They can be regarded as the support. The catalyst does not contain either promoter or metallic Ni or NiO and can be kept in air without losing activity for years [14,15].

In this work, a number of Raney-Ni catalysts prepared with this novel method are examined and their catalytic activities in the transformation of glycerol without added hydrogen are discussed. During biodiesel production, copious amounts of glycerol are formed, significantly more than needed. If glycerol cannot be transformed into valuable products, it causes considerable burden to the environment. Obviously, methods and catalysts to transform it are always welcome. Many catalytic systems were identified for the transformation of glycerol (for a recent review, see ref. [16]). In the presence of hydrogen, supported or unsupported metals (Rh, Ru, Pt, Pd, Cu, Ni, Co, Cr) catalyse hydrogenolysis giving mainly 1,2- and 1,3-propanediols, while acidic materials (supported phosphoric acid, acidic zeolites and clays, acidic oxides) are active in its dehydration reactions. Dehydration reactions also provide a range of valuable products and they proceed over calcined layered double hydroxides of basic character as well (Scheme 1).

The market value of the products may change with time; nevertheless, acetol, acrolein, as well as acetaldehyde (formed through retro aldol dimerization on the pathway leading to acrolein) are useful products. Active and selective catalyst to any of these products is of value.

2. Experimental

2.1. Materials

For the synthesis of the catalysts the following chemicals were used: Ni–Al and Ni–Si alloys (particle sizes: 45 μm, and 50 μm, respectively, and the [mass] ratio of components was 1:1), and NaOH, all chemicals were the products of Sigma-Aldrich Chemical Co.

In the catalytic test reactions and for the identification of the compounds participating: glycerol, acetol, acrolein, acetaldehyde were used — all chemicals were from Sigma-Aldrich Chemical Co. The purities of these chemicals were over 90% and they were used as received.

2.2. Synthesis of the novel Raney-Ni catalysts

For the synthesis, 1:1 NiAl or Ni–Si alloy powder and 1.25 wt.% NaOH solution were used. The mixture was heated to 100 °C and kept at this temperature for 5–6 min. After ~30 min additional amount of NaOH (making up the concentration to 12 wt.%) has been added at 70 °C. After 20 min, the mixture was cooled to 50 °C and washed until neutral [14].

In this study, four varieties of the classical (*i.e.* Al-containing) catalyst have been used. The as-prepared catalyst is denoted as RNi; RNi120 and RNi320 are catalysts calcined at 120 °C and 320 °C for 1 h, respectively. Their Ni content was 45 to 59% depending on the method of heat treatment. The Ni content of the Si-containing was 40%. Since it turned out (see later) that heat treatment did not influence the structure of the catalyst, to make comparison easier it was calcined the same way as RNi320.

2.3. Methods of characterisation

The transformations of the various catalysts on heat treatment were followed by thermogravimetry (25 mg sample, 10 °C/min

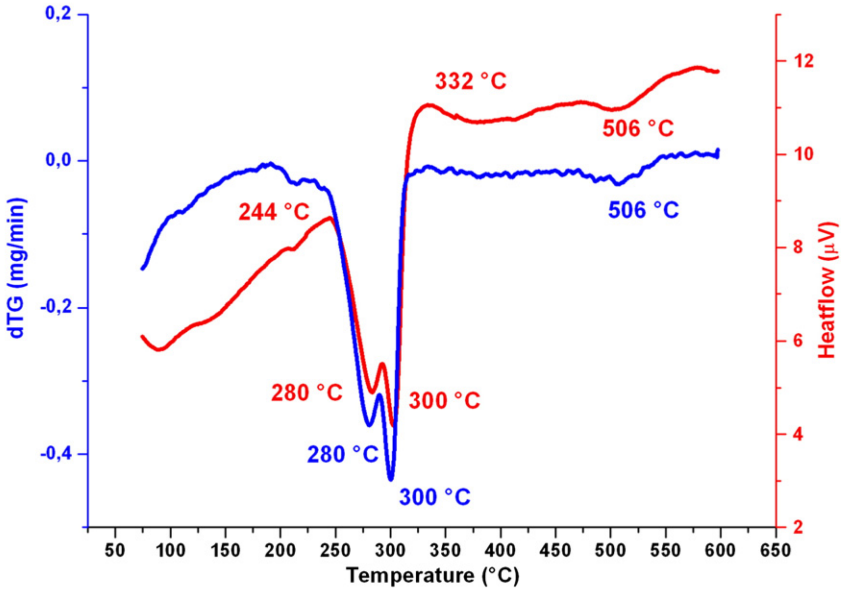


Fig. 1. DTA/DTG and DTA curves for RNi registered with 10 °C temperature ramp.

temperature ramp up to 600 °C in air — Setaram Labsys instrument, SeftSoft program).

The crystal structures and their changes after the reaction have been studied by X-ray diffractometry (Rigaku Miniflex II X-ray diffractometer, $2\theta = 3–80°$ region with 0.02° steps, CuK_α radiation — $\lambda = 1.54056$ Å). For the identification of the crystal phases and the Miller indices, the JCPDS-ICDD (Joint Committee on Powder Diffraction International Centre for Diffraction Data) database was used. For the quantitative phase analysis in the calcined as well as the spent samples the full profile fitting of the X-ray diffractograms were applied. Diffraction profile based on the assumed composition was produced, and then compared to the measured one. After some refining steps, reasonable agreement (variation is <5%) could be achieved between the simulated and the observed diffractograms, and thus the phase composition of the sample could be extracted.

The specific surface areas were determined by the BET method (adsorption of N_2 at 77 K, quantitative data were obtained with the NovaWin program).

2.4. Catalytic tests

The method of catalytic evaluation was the reactive distillation. The volatile components (like, *e.g.*, acetol) are to be found in the vapour phase and in the condensate of the vapour phase, while the heavier components are accumulated in the liquid residue.

In a reaction 50 cm^3 of glycerol was heated under continuous stirring (the amount of the catalysts was 1.2 g and the rate of stirring was 100 rpm) in the reactor. In 120 min, the temperature reached 240 °C and remained constant. Thus, the reaction time has been set to 120 min. At the end of the reaction, both the overhead products — condensed in a trap cooled by liquid nitrogen — and the liquid residue have been analysed by gas chromatography (Shimadzu 2010 GC equipped with flame ionisation detector, SPB624 [Supelco] column, temperature programme: 50 °C 4 min, heating to 150 °C with 10 °C/min rate and keeping this temperature for 10 min).

3. Results and discussion

3.1. Characteristic features of the Raney-Ni catalysts

On the basis of TG measurements, the freshly prepared RNi sample underwent several changes upon heat treatment (Fig. 1).

Table 1
Phase composition of the RNi materials (%) prepared from the Ni–Al alloys.

	RNi	RNi120	RNi320
Bayerite	8	8	5
Norstrandite	25	25	5
Gibbsite	45	45	9
Boehmite	10	10	22
Intermetallic phase	45	45	59

Up to 244 °C the sample lost only 2.5% of its mass, probably due to the desorption of water physisorbed on the outer surface of the sample. Raising the temperature to 304 °C resulted in further 6.7% mass loss because of the transformation of trihydrate into monohydrate occurring in two separate steps (at 280 °C and 300 °C). Further increase in the temperature yielded another 1.6% mass loss, and nothing happened by the finishing temperature (600 °C) of the measurement.

In complete accordance with stability ranges for the various forms Al-(oxy)hydroxides published previously, these results indicate that bayerit to boehmite transformation occurred around 250 °C [18] and gibbsite to boehmite conversion took place from 277 °C to 295–320 °C [19–21]. Further water loss in the 450–520 °C temperature range results in Al_2O_3 formation either from boehmite or from gibbsite [20,22].

The powder X-ray diffractograms of the various Raney-Ni samples (Fig. 2) before the chemical reaction were evaluated by the full profile fitting method.

The diffractograms of the RNi and RNi120 samples are practically identical and different from that of the RNi320 sample.

The relative quantities of the various phases are shown in Table 1. At 320 °C boehmite became the major non-metallic component mainly at the expense of gibbsite. At the same time, the relative proportion of NiAl increased.

During the chemical reaction, the catalysts underwent chemical transformations. After washing and drying, they could be separated into two parts with a simple magnet. Comparing the diffractograms of the two parts (Fig. 3b and c) to that of the freshly prepared (Fig. 3a) catalyst (RNi), it is to be seen that the intermetallic phases (AlNi and Al_3Ni_2) were completely separated from the Al-(oxy)hydroxides (Fig. 3).

From this it follows, that the catalyst is sacrificed in the reaction; accordingly, there is no chance for regeneration, at least not with the hope of returning to a Raney-type structure.

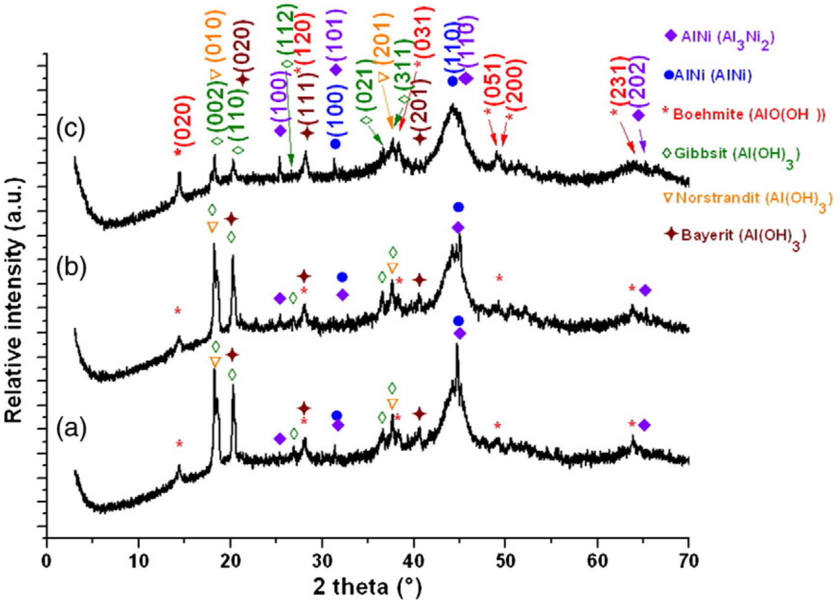


Fig. 2. The powder X-ray diffractograms of the (a) RNi, (b) RNi120 and (c) RNi320 samples.

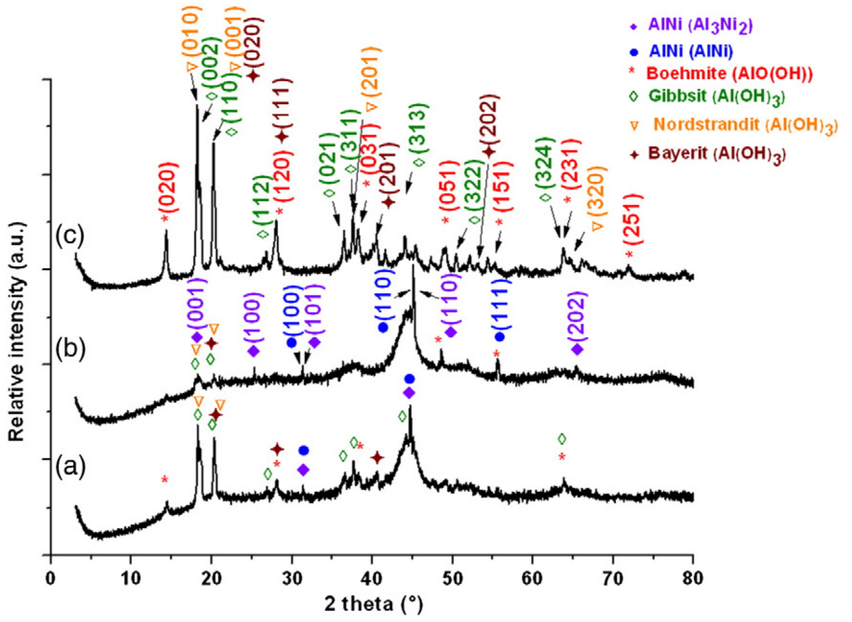


Fig. 3. The X-ray diffractograms of (a) RNi before the reactions and the magnetically separable parts of the used RNi: (b) intermetallic phase, (c) aluminium oxyhydrates.

The behaviour of the NiSi catalyst was found to be different from that of NiAl. Here, the freshly prepared and calcined (Fig. 4a) and spent catalysts (Fig. 4b) were found to be identical, and there were no magnetically separable parts either. All these mean that regeneration of this catalyst should be easy and indeed heat treatment at 600 °C resulted in a structure (Fig. 4c) identical to the previous two.

BET measurements revealed that the specific surface area of the NiSi catalyst was smaller than those of the others; it was remained unchanged even after use (Table 2, second column). The freshly prepared Raney-Ni had low specific surface area as well, just like after calcination at 120 °C (Table 2, third and fourth columns). However, heat treatment at 320 °C resulted in a significant increase in the specific surface area (Table 2, last column) due to the (at least partial) transformation of gibbsite, bayerite and nordstrandite into boehmite (Table 1); latter has smaller particle size, and consequently, higher specific surface area. Unfortunately, the separation of the intermetallic and the Al-(oxy)hydroxide phases during the reaction makes this advantageous property useless in catalytic applications.

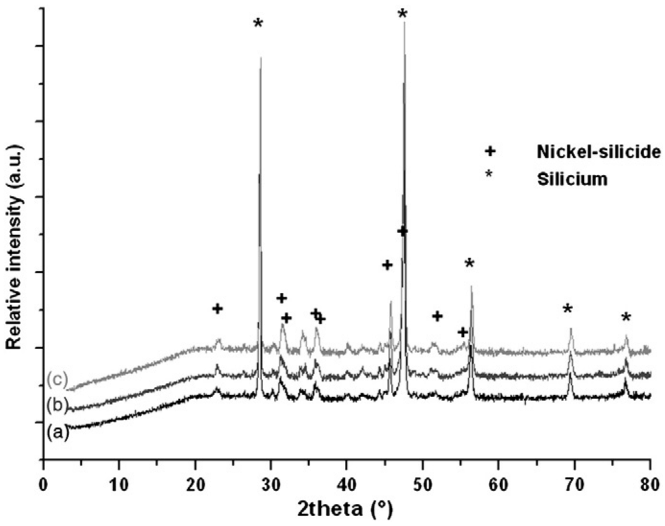


Fig. 4. XRD patterns of (a) the freshly prepared, (b) the used and (c) the regenerated NiSi sample.

In the temperature range of 25 °C–700 °C there was no significant mass change for NiSi on heat treatment (only the physisorbed water was removed); this gave the idea of using calcination as the means of regeneration, since the structure of the material heat-treated at 320 °C right after its preparation was identical to the one heat-treated at 600 °C.

3.2. Catalytic reaction

Reactions took place in the reaction mixture without catalyst, and the conversion was not negligible (~30%). The two main products were acetaldehyde (~33%) and acetol (~33%). The third main component was acrolein and a number of unidentified other products (<3%) were also found. To enhance selectivity and shift the reaction towards acetol formation, attempts were made of using the catalysts described in the previous sections.

In the presence of all the investigated RNi catalysts, the conversion of glycerol increased and the selectivity was shifted towards acetol formation (Table 3).

Unfortunately, as the previously discussed measurements proved, the Al-containing Raney-Ni catalysts lost their skeletal structure on heat treatment (either on calcination at 320 °C or during the dehydration reaction) and the (inter)metallic parts became separable from the various aluminium hydroxides and alumina by physical methods (*e.g.*, magnetically). This means that they became the physical mixture of the two component types. Thus, they cannot be regarded as catalysts in the classical sense. However, the NiSi catalyst meets all the requirements of a “good” catalyst. High conversion with favourable selectivity on first use, and very convincing performance even after using simple calcination at 600 °C as the method of regeneration. This temperature was chosen for regeneration, because it was learnt from TG measurements that there was no structural change on heat treatment up to 600 °C and at this high temperature, organic residues were possibly removed.

Table 2
BET specific surface areas of Raney-type catalysts (m^2/g).

	NiSi	RNi	RNi120	RNi320
Freshly prep.	12	28	28	73
Used/intermetallic	10	5	7	10
Used/non-metallic		17	19	26

Table 3
Conversion and selectivity of glycerol transformation in the presence of Raney-type catalysts (%).

	RNi	RNi120	RNi320	NiSi
Conversion	72	75	49	82
Acetaldehyde	2	2	0	3
Acrolein	6	2	10	8
Acetol	74	72	87	70
Others	18	24	3	19

Table 4
Conversion and selectivity of glycerol transformation in the presence of freshly calcined and recycled (four times) NiSi — regeneration was performed by recalcination after use.

	NiSi	NiSi (1)	NiSi (2)	NiSi (3)	NiSi (4)
Conversion	82	75	75	74	75
Acetaldehyde	3	6	4	3	6
Acrolein	8	10	8	8	9
Acetol	70	66	70	70	67
Others	19	18	18	19	18

3.3. Recycling studies

The NiSi material was used for recycling investigation, since it displayed high stability on heat treatment. Indeed, the substance behaved as a real catalyst. Although the overall conversion decreased somewhat in the second run (the BET surface area was also decreased after the first use), in the further three recycling runs it showed remarkable stability as far as conversion and product selectivities are concerned (Table 4).

4. Conclusions

Non-pyrophoric Raney-type Ni catalysts have been prepared and tested in the dehydration of glycerol. The Al-containing Raney-Ni samples precalcined at various temperatures were active in the reaction producing mainly acetol, however, during the reaction they were separated into an intermetallic and Al-(oxy)hydroxide phases making regeneration impossible. Although seemingly RNi320 had the best textural properties, however, the high BET surface area was mainly due to the various Al-(oxy)hydroxide phases, which were not part of the active catalyst any more. The Raney-type NiSi sample was not only active and selective towards acetol formation, but could be easily regenerated by high-temperature heat treatment producing highly active and selective catalyst again.

Acknowledgement

This work was performed with the help of the Hungarian Innovation Grant Asbóth Oszkár Nos. DAMEC09, TÁMOP-4.2.2.A-11/1/KONV-2012-0047 and OTKA 83889. The financial support are highly appreciated.

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