

Poisoning effect of some nitrogen compounds on nano-sized nickel catalysts in *p*-nitrophenol hydrogenation

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Abstract

The poisoning effect of some nitrogen compounds on the hydrogenation of *p*-nitrophenol to *p*-aminophenol over the nano-sized nickel catalysts prepared by the improved chemical reduction method was studied. Experimental results show that some nitrogen compounds are obvious poisons for *p*-nitrophenol hydrogenation on the nano-sized nickel. Traces of ammonia could cause the deactivation of the nano-sized nickel catalysts. The formation of complex compounds and the dissolution of nickel are two main reasons of poisoning. The as-synthesized nickel catalysts are also poisoned in the presence of some organic amines. The primary cause could be the strong adsorption of the organic amines on the hydrogenation sites. The poisoning effect of organic amines is correlated with their solution basicities. The poisoning of organic amines (such as dimethylamine) is reversible, while the poisoning of ammonia is irreversible. In addition, the deactivation degree of the nano-sized nickel was higher than that of Raney nickel in the presence of ammonia, may be due to the higher-density surface defect sites on the nano-sized nickel.

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1. Introduction

Many fundamental investigations have revealed that some molecules containing elements of the periodic table Groups VA (N, P, As, Sb) and VIA (O, S, Se, Te) are toxic toward nickel catalysts, even if they are present in traces only [1,2]. And also, some deactivation mechanisms have been brought forward. Maxted [1] discovered that these molecules were bonded strongly to the catalysts and formed the chemisorptive bond via the unshared electron pairs, which implied that poisons at low concentrations could obviously deactivate the catalysts. The adsorption of nitrogen compounds on the metal surface has been the subject of considerable investigation [3–6]. The results showed that the chemisorption of NH₃ on the most metal surface (such as Ni, Fe) was at the on-top site by the interaction of the lone-pair electron orbit of N with 4s, 4p_z and 3d_{z²} orbitals of Ni. Baiker et al. [3] thought that the poisoning of catalysts was mainly due to the interaction of aliphatic amines with nickel and cobalt catalysts, which caused the for-

mation of metal nitride, the formation of metal carbide and carbonaceous deposits, using the catalyzed disproportionation of methylamine and dimethylamine as test reactions. Besides, the effect of nitrogen compounds on some precious metals was also studied. Hegedűs and Máthé [7] found that the poisoning of different precious metals catalysts (Pd/C, Ru/C and Rh/C) was caused by the strongly basic nitrogen atoms of the hydrogenated products pyrrolidines in the hydrogenation of some pyrrole derivatives.

In recent years, nano-sized nickel catalysts have received increasing attention since such materials exhibit many fascinating chemical and physical characteristics and potential technological applications [8]. It is reported that nano-sized nickel catalysts show better catalytic properties in the catalytic hydrogenation or dehydrogenation reactions [9–12]. But the poisoning studies about the nano-sized nickel catalysts caused by ammonia and organic amines as common poisons to metal catalysts are little reported. It is simultaneously important to understand the effect of impurity compounds included in reaction mixtures on the activity of the nano-sized nickel catalysts, because industrial feedstock inevitably contains impurities (such as ammonia and organic amines), which in many cases lead to catalyst poisoning even at low concentrations.

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p-Aminophenol is an important intermediate in the preparations of analgesic and antipyretic drugs [13–16]. The direct catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol is becoming important, because this could be an efficient and greener route [16]. In the previous work [17], we reported that catalytic properties (activity, selectivity, and stability) of the as-synthesized nickel are superior, compared with commercial Raney Ni. Furthermore, in this paper we would study the poisoning effect of some nitrogen compounds on the hydrogenation of *p*-nitrophenol to *p*-aminophenol catalyzed with the nano-sized nickel catalysts. The poisoned catalysts were characterized by XRD. After the reaction, the concentration of nickel element in the mother solution was measured by ICP. In addition, the deactivation mechanisms for ammonia and organic amines are investigated. And the catalytic performances of the nano-sized nickel and Raney nickel in the presence of 3% ammonia were compared.

2. Experimental

2.1. Catalyst preparation and characterization

The as-synthesized nickel catalysts were prepared by the improved chemical reduction method in a continuous reactor according to the literature [17]. X-ray powder diffraction patterns (XRD) were obtained on a Bruker D8 Advance instrument with Ni-filtered Cu K α radiation ($\lambda=0.154$ nm) at 40 kV and 30 mA, employing a scanning rate of 0.05 s $^{-1}$. The morphology of the samples was observed by scanning electron microscopy (SEM, LEO-1530VP).

2.2. Poisoning studies

Poisoning studies were carried out on the catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol in a 300 mL stainless steel autoclave. Ammonia, tetradecyldimethylamine, laurylamine, diethylamine, dimethylamine, isopropylamine, triethanolamine and *p*-aminophenol were selected as model nitrogen compounds directly added to the fresh reaction solution. The reactor was charged with definite catalysts, *p*-nitrophenol and poisons in ethanol solution. At room temperature, air was flushed out of the reactor with nitrogen and then the reactor was completely purged with hydrogen. Next, the inlet valve was closed and heating commenced with stirring to avoid settling of catalysts. Catalysts were suspended in solution. When the designated temperature was reached, hydrogen was fed to the predetermined pressure (time zero). The time at which hydrogen pressure had a given fall of pressure was recorded. After the reaction, the poisoned catalysts were filtered and the concentration of nickel element in the mother solution was analyzed by inductively coupled plasma emission spectroscopy (ICP, Optima 2000DV). The poisoned catalyst was analyzed by energy dispersive X-ray spectroscopy microanalyzer (EDS, GENESIS).

In this report, hydrogenation rate is defined as the amount of hydrogen consumed per minute and per gram of catalyst.

Reaction conditions (except special explanations): *p*-nitrophenol 14 g, ethanol 143 mL, distilled water 20 mL, the

nano-sized nickel catalysts 0.3 g, the concentration of nitrogen compounds 0.82 mol L $^{-1}$, reaction temperature 102 °C, reaction pressure 1.65 MPa, stirring speed 350 rpm. (The kinetics study of *p*-nitrophenol hydrogenation has proved that the chemical reaction at stirring speed above 330 rpm is not influenced by external diffusion.)

3. Results and discussion

3.1. Catalyst characterization

The morphology of the nano-sized nickel catalysts was observed in the SEM micrograph, shown in Fig. 1. The average particle size is about 60 nm. The individual nickel particles are spheroidal. At the same time, there are some agglomerates due to the comparatively small grain size and the high surface energy.

The XRD pattern of the nano-sized nickel catalysts is shown in Fig. 2. Only three characteristic peaks of face-centered cubic (fcc) nickel ($2\theta=44.5^\circ$, 51.8° , and 76.4°) marked by Miller indices (1 1 1), (2 0 0), (2 2 0) are observed in the 2θ range from 35° to 80° , which reveals that the as-synthesized sample is pure fcc nickel. Some possible oxides or hydroxide such as NiO, Ni₂O₃, and Ni(OH)₂ are not observed in XRD.

3.2. Effect of ammonia concentrations

The effect of ammonia concentrations on the activity of the nano-sized nickel catalyst is demonstrated in Fig. 3 (the catalytic activity is expressed as the reaction rate at 20 min). The results show that the addition of ammonia in traces might cause the deactivation of nano-sized nickel catalysts. At lower ammonia concentrations, the catalytic activity of the nano-sized nickel catalysts is on the linear decrease with increasing ammonia concentrations. When the concentration of ammonia is at 3%, the hydrogenation rate is only 1.5 mmol min $^{-1}$ g $^{-1}$. Here, we thought that the catalysts have been deactivated absolutely. In addition, from Fig. 3(b), it is seen that degressive trends of catalytic activity caused by different concentrations of ammonia are

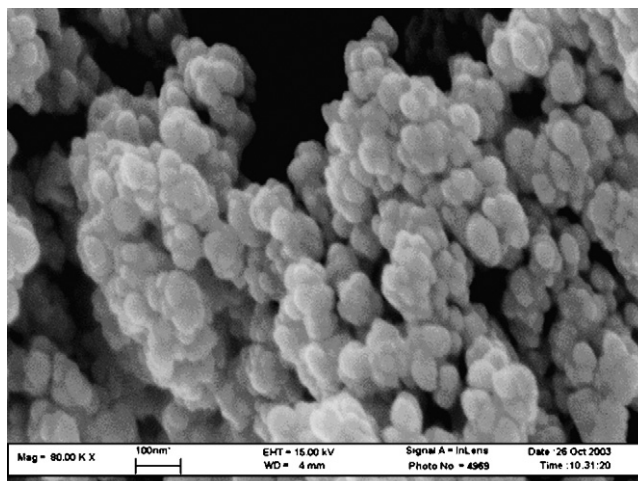


Fig. 1. SEM image of the nano-sized nickel catalysts.

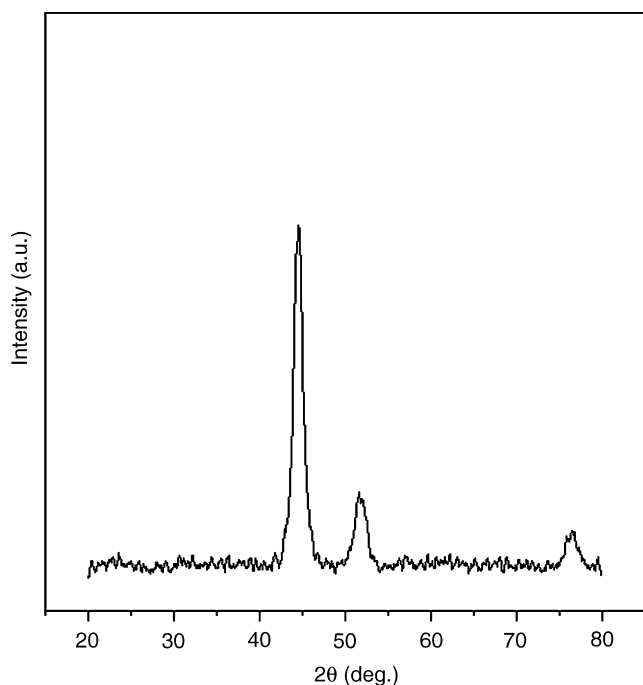


Fig. 2. XRD pattern of the nano-sized nickel catalysts.

completely different: 0.8% ammonia just lead to the decrease of catalytic activity, and the catalysts is not completely deactivated, while the addition of ammonia to feed is up to 1.9%, the reaction rate fleetly decrease close to zero along with reaction proceeding. The cause would be discussed in Section 3.4.

3.3. Effect of organic amines addition

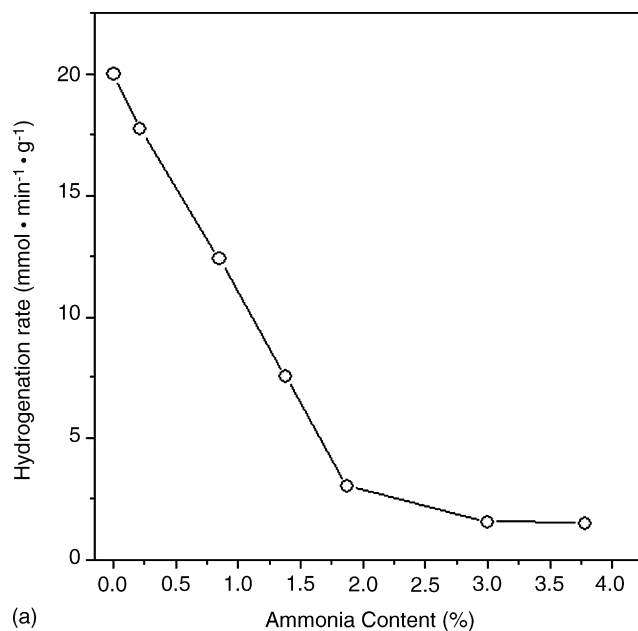
The organic amines also have nitrogen atom with the unshared electron pairs, which might have an effect on the catalytic activity of the nano-sized nickel catalysts. The catalytic activities of nano-sized nickel in the presence of the organic amines poisons were investigated. The aqueous basicity (pK_b) of organic amines used in this research are listed in Table 1. It is well-known that the smaller the value of pK_b , the stronger the aqueous basicity of the organic amines. The results show that the organic amines could also poison the nano-sized nickel catalysts. The poisoning effect of organic amines

Table 1
Effect of organic amines on catalytic activity of the nano-sized nickel catalysts and the pK_b values of the organic amines

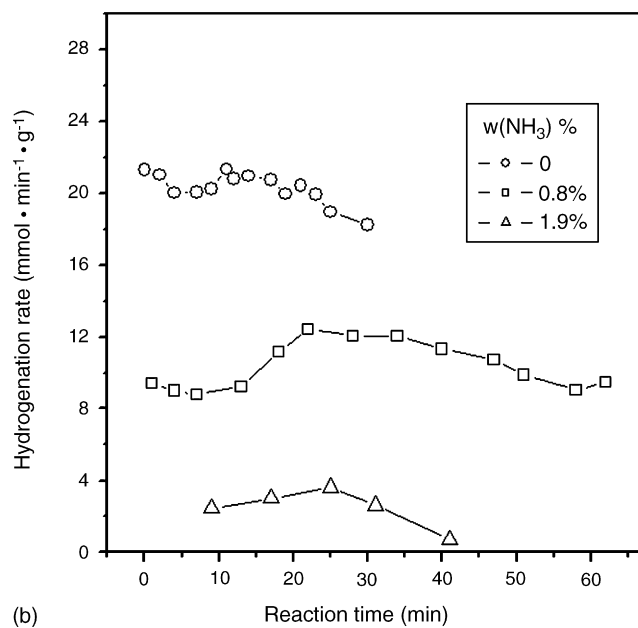
Organic amines	pK_b	Hydrogenation rate ($\text{mmol g}^{-1} \text{min}^{-1}$)
Diethylamine	2.9	– ^a
Dimethylamine	3.23	1.3
Isopropylamine	3.276	3.9
Tetradecyldimethylamine	– ^b	8.0
Triethanolamine	6.24	11.2
Laurylamine	– ^b	14.2
<i>p</i> -Aminophenol	8.5	19.2

^a At 20 min, the decrease of hydrogen pressure was not obvious.

^b pK_b values are not searched out in the past papers.



(a)



(b)

Fig. 3. Effect of ammonia addition on the catalytic activity of the nano-sized nickel catalysts. (a) Effect of ammonia concentrations on the hydrogenation rate and (b) degressive trendlines about catalytic activity of catalysts poisoned by different concentration ammonia.

is correlated with their solution basicity: the toxic degree of the nano-sized nickel catalysts decreases along with the increase of the aqueous basicity of organic amines. When the aqueous basicity are very weak, such as the product *p*-aminophenol, the organic amines would have no obvious effect on the catalytic activity of the nano-sized nickel catalysts. The aqueous basicity directly reveals the combining capacity of the catalysts and the organic amines in the reaction. The stronger combining capacity leads to the higher deactivation of the nano-sized nickel. However, Nagai et al. [18] thought that the poisoning effect of nitrogen compounds was not correlated with their solution basicity but with their gas-phase basicity in the diben-

zothiophene hydride-sulfurization on sulfided NiMo/Al₂O₃ catalysts.

3.4. Investigation of deactivation mechanisms

To investigate the deactivation mechanisms of the catalysts, the poisoned catalysts caused by different poisons were characterized by XRD, as shown in Fig. 4. The results show that the main composition of 0.2%-ammonia-poisoned catalysts is still elementary nickel, and at the same time some impurity peaks exist, while there is not elementary nickel in the 3%-ammonia-poisoned catalysts. So the 0.2%-ammonia-poisoned catalysts yet have catalytic activity and the 3%-ammonia-poisoned catalysts have been deactivated absolutely.

To further probe into the composition of the 3%-ammonia-poisoned catalysts, EDS analysis (Fig. 5) was made. The analysis results indicates that the 3%-ammonia-poisoned catalysts consist of C (25.38 wt.%), N (5.29 wt.%), O (14.8 wt.%), and Ni (54.53 wt.%). Moreover, when the reaction is carried out under the condition of no addition of *p*-nitrophenol into reaction solution, the 3%-ammonia-poisoned catalysts is chiefly composed of elementary nickel (as shown in Fig. 4(5)). Through above analysis, we think that the 3%-ammonia-poisoned catalysts might be the complex compounds of *p*-nitrophenol, ammonia, and the nickel catalysts. After calcined at 500 °C for 4 h, the organics was burned away, and the 3%-ammonia-poisoned catalysts have changed to NiO (as shown in Fig. 6).

The dimethylamine was one of more serious organic poisons, as shown in Table 1, so it was selected as a typical example for investigating the deactivation cause of the nano-sized nickel catalysts. The results show that there are not any impurities peaks other than characteristic peaks of nickel in XRD pattern

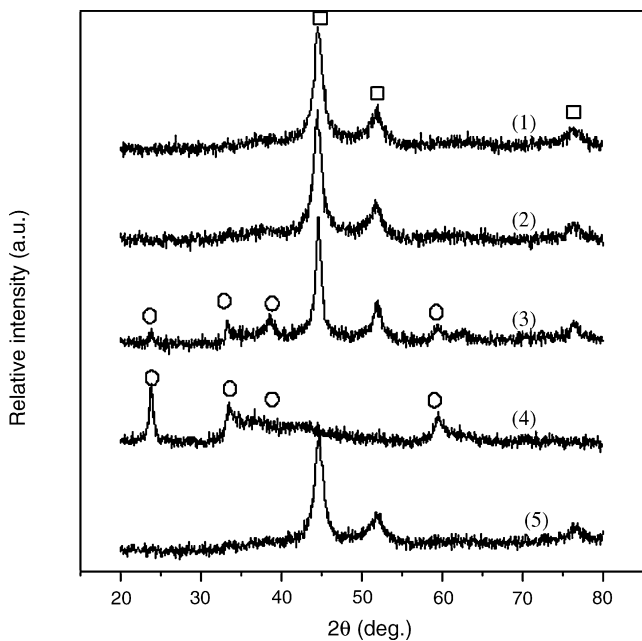


Fig. 4. XRD patterns of the fresh and poisoned catalysts (□ Ni; ○ impurities). (1) Fresh catalysts; (2) dimethylamine-poisoned catalysts; (3) 0.2%-ammonia-poisoned catalysts; (4) 3%-ammonia-poisoned catalysts; (5) 3%-ammonia-poisoned catalysts (no *p*-nitrophenol is added into reaction).

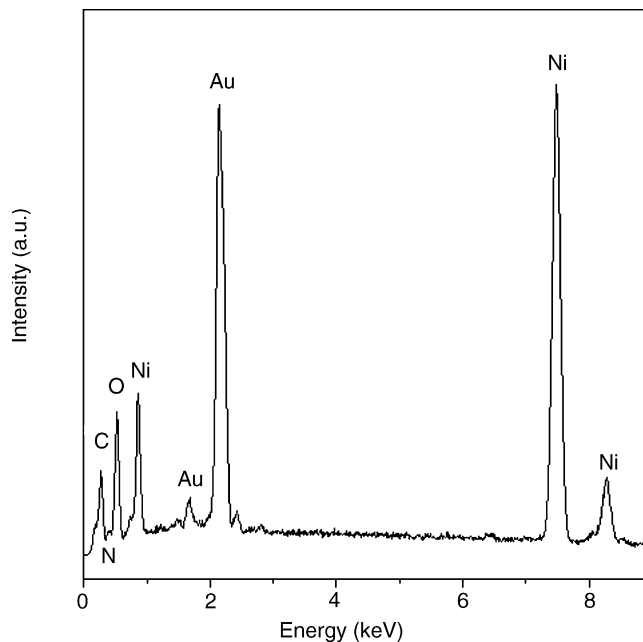


Fig. 5. EDS analysis of 3%-ammonia-poisoned Ni catalysts.

(Fig. 4(2)), which implies that the poisoning effect of organic amines on the nano-sized nickel catalysts is due to strong adsorption of the organic amines on the hydrogenation sites of the nano-sized nickel catalysts.

After the reaction, the catalysts were filtered and the concentration of the nickel element in the mother solution was analyzed by ICP, shown in Table 2. In order to investigate the effect of *p*-nitrophenol on the poisoning process, the similar process was carried out in the absence of *p*-nitrophenol. We could see that there is not nickel element in the mother solution in the absence

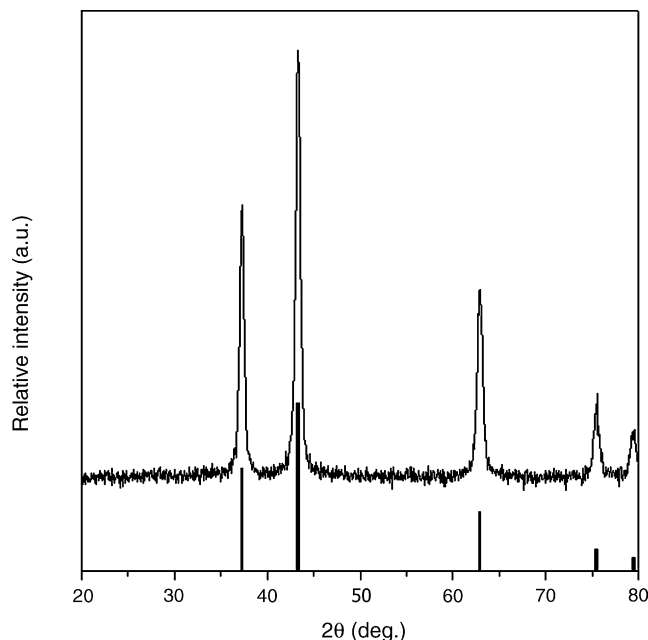


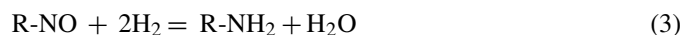
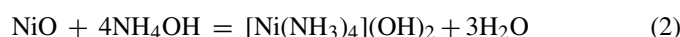
Fig. 6. XRD pattern of 3%-ammonia-poisoned Ni catalysts after calcined at 500 °C for 4 h. (The characteristic peaks of NiO are lined out by vertical lines.)

Table 2
The concentration of nickel element in mother solution

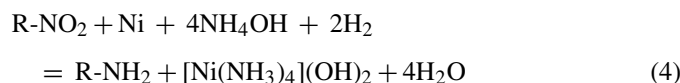
Poisons	Nickel concentrations (mg L ⁻¹)
No poisons	Close to zero ^a
3% Dimethylamine	Close to zero ^a
0.2% Ammonia	0.52
3% Ammonia	6.62
3% Ammonia (in the reaction, no <i>p</i> -nitrophenol is introduced)	Close to zero ^a

^a There is almost no nickel element.

of *p*-nitrophenol or poisons. It was verified that the nickel catalysts could be oxidized by nitro-compound to form nickel oxide in the catalytic reaction [19]. The introduction of ammonia might dissolve the new-generated nickel oxide, therefore in the reaction solutions with ammonia there is nickel element. Moreover, the concentration of nickel element in the mother solution is on the increase with the increase of ammonia amount. We suggested that these reaction steps would take place during poisoning of the catalyst caused by ammonia:



So, according to the reaction Eqs. (1)–(3), the gross reaction equation is as follows:



While organic amines could not dissolve the new-generated nickel oxide, so no nickel element exists in the reaction solution. Therefore, we suppose that both ammonia and organic amines could cause the deactivation of the nano-sized nickel catalysts, but the deactivation mechanisms are fully different. About the poisoning effect of the ammonia, there are two main reasons. First, ammonia might react with nickel catalysts and *p*-nitrophenol to form complex compounds. Second, nickel metal could be oxidized by *p*-nitrophenol to produce the nickel oxide, which would be dissolved by ammonia. While the primary cause of the poisoning effect of organic amines could be the strong adsorption of the organic amines on the hydrogenation sites. Borgna et al. [20,21] studied the interactions of nitrogen-containing compounds with a reduced Ni/SiO₂ sample using magnetic measurements and infrared spectroscopy. And they thought ammonia chemisorbed mainly onto nickel catalysts and the adsorption was, at least, partially dissociative. The cyclic nitrogen-containing compounds were bonded to the nickel surface via the nitrogen lone-pair electron without cracking of the molecule.

After the poisoned catalysts were simply washed by distilled water, the catalytic activities were investigated in the hydrogenation reaction of *p*-nitrophenol to *p*-aminophenol. The results are shown in Fig. 7. It can be seen that, after washed by distilled water, the dimethylamine-poisoned catalysts could recover the catalytic activity, but the ammonia-poisoned catalysts could

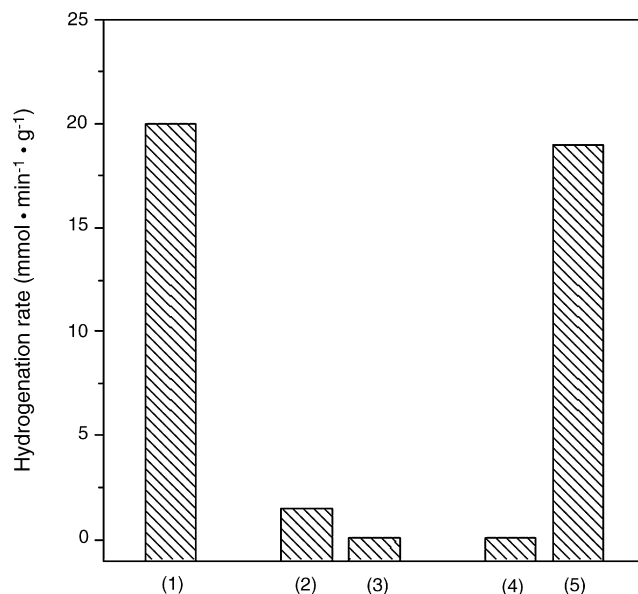


Fig. 7. The catalytic activity of poisoned catalysts before and after washed. (1) Fresh catalysts; (2) 3%-ammonia-poisoned catalysts; (3) 3%-ammonia-poisoned catalysts washed by the distilled water; (4) dimethylamine-poisoned catalysts; (5) dimethylamine-poisoned catalysts washed by the distilled water.

not. This illuminates that the poisoning of dimethylamine is reversible, while the poisoning of ammonia is irreversible. This also proves that the mechanisms of deactivation caused by ammonia and dimethylamine are different.

Besides, the catalytic performances of the nano-sized nickel and Raney nickel provided by Anhui Bayi Chemical Co., Ltd. in the presence of 3% ammonia were compared at similar reaction conditions, shown in Fig. 8. The results showed that the catalytic activity of Raney nickel had a decrease of 75% in the presence of 3% ammonia, while that of nano-sized nickel decreased about 92.5%. That is, the deactivation degree of the nano-sized nickel

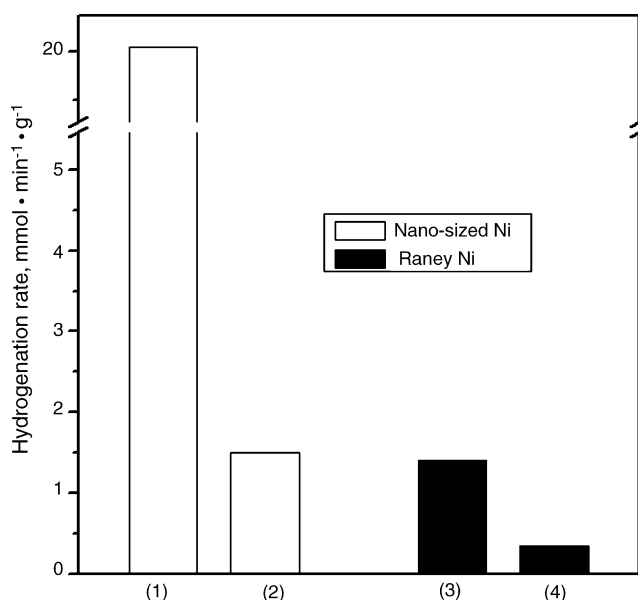


Fig. 8. The catalytic activity of the nano-sized nickel and Raney nickel: (1) and (3) in the absence of the ammonia; (2) and (4) in the presence of the ammonia.

was higher than that of Raney nickel in the presence of ammonia. This might be ascribed to the higher-density surface defect sites of the nano-sized nickel.

4. Conclusions

In this work, the effects of nitrogenous poisons on the catalytic activity of nano-sized nickel were examined, and the deactivation mechanisms were studied. Traces of ammonia could cause the deactivation of nano-sized nickel catalysts. In the presence of *p*-nitrophenol and ammonia, the formation of complex compounds and the dissolution of nickel were two main reasons of poisoning. The nano-sized nickel catalysts could also be deactivated in the presence of some organic amines. The primary cause could be the strong adsorption of the organic amine on the hydrogenation sites. The combining capacity decreased with increasing acidity (pK_b) of the organic amine, and corresponding deactivation degree of the nano-sized nickel catalyst was on the decrease. In the hydrogenation reaction of *p*-nitrophenol to *p*-aminophenol, the poisoning of dimethylamine is reversible, while the poisoning of ammonia is irreversible. In addition, the deactivation degree of the nano-sized nickel was higher than that of the Raney nickel in the presence of ammonia, may be due to the higher-density surface defect sites of the nano-sized nickel.

Acknowledgments

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