

Production of hydrogen peroxide from carbon monoxide, water and oxygen over alumina-supported Ni catalysts

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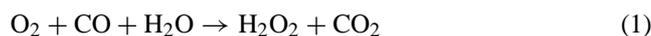
Abstract

Novel amorphous Ni–B catalysts supported on alumina have been developed for the production of hydrogen peroxide from carbon monoxide, water and oxygen. The experimental investigation confirmed that the promoter/Ni ratio and the preparation conditions have a significant effect on the activity and lifetime of the catalyst. Among all the catalysts tested, the Ni–La–B/ γ -Al₂O₃ catalyst with a 1:15 atomic ratio of La/Ni, dried at 120 °C, shows the best activity and lifetime for the production of hydrogen peroxide. The deactivation of the alumina-supported Ni–B amorphous catalyst was also studied. According to the characterizations of the fresh and used catalysts by SEM, XRD and XPS, no sintering of the active component and crystallization of the amorphous species were observed. However, it is water poisoning that leads to the deactivation of the catalyst. The catalyst characterization demonstrated that the active component had changed (i.e., amorphous NiO to amorphous Ni(OH)₂) and then salt was formed in the reaction conditions. Water promoted the deactivation because the surface transformation of the active Ni species was accelerated by forming Ni(OH)₂ in the presence of water. The formed Ni(OH)₂ would partially change to Ni₃(PO₄)₂. © 2003 Elsevier B.V. All rights reserved.

Keywords: Hydrogen peroxide; Amorphous alloy; Ni–B catalyst; Carbon monoxide; Deactivation

1. Introduction

Hydrogen peroxide is a chemical that is becoming more and more popular as an environmentally friendly oxidant, due to its unique feature of producing water as the only by-product of the oxidation [1]. The utilization of hydrogen peroxide for the novel green chemical synthesis has also made great progress [2–5]. The traditional production of hydrogen peroxide is not an economic and simple process. Commercially, hydrogen peroxide is primarily produced by the alternative oxidation and reduction of alkylanthraquinone derivatives [6]. Since this method is quite complex (a stoichiometric amount of quinone must be used and recycled), a great effort has been made worldwide towards a development of a simple but efficient production of hydrogen peroxide. Ermakov and co-workers [7] reported a synthesis of H₂O₂ from carbon monoxide, oxygen and water in 1979:



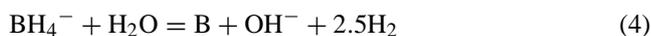
The reported TON (TON, moles of hydrogen peroxide per mole of palladium) of the applied catalyst (palladium triphenylphosphine complex) was only 5. A further improvement of the catalyst lifetime with a TON up to 87 was achieved by using the more stable triphenylarsine as the palladium ligand [8], but the process is still not suitable for a practical application. Recently, Bianchi et al. [9] have found that the palladium complexes containing bidentate nitrogen ligands efficiently catalyzed the reaction (1) with a productivity comparable to that of the current commercial process.

The production of hydrogen peroxide from carbon monoxide, water and oxygen is very promising owing to its high safety, since it can be operated in a wider range of non-ignitable gas phase composition. However, a drawback in the investigation of H₂O₂ synthesis from CO, water and O₂ is that palladium or other noble metal catalysts are required [7–11]. In addition, most of these processes employed a complex homogeneous catalytic system that requires extra separation processes or acid additives for the reaction. Only one reported work was related to the use of heterogeneous catalytic synthesis over Pd/CaCO₃ and Ru/graphite catalysts [10].

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Since the first report of the study on the amorphous alloys as catalysts in 1980 [12], the amorphous alloys have received much attentions over the past years. Their unique isotropic structure and high concentration of coordinatively unsaturated sites [13] lead to a better catalytic activity and selectivity compared to their crystalline counterparts. Various amorphous alloys have been prepared and employed in catalysis including electrolysis [14], hydrogenation [15,16], oxidation [17], isomerization [18], and methanation of carbon dioxide [19]. The amorphous alloy catalysts prepared by chemical reduction seem to be suitable for catalysis too. All the proposed reactions concerning the preparation of the amorphous catalyst can be described as follows [20]:



Supported amorphous alloy catalysts have been proved to be promising in industrial applications owing to the remarkable improvement in the active surface area and thermal stability of catalysts caused by the high dispersion of the amorphous alloy particles on the support and the strong metal-support interaction [21]. Among various amorphous alloy catalysts, the Ni-based amorphous alloys have been studied thoroughly [22]. These amorphous alloy catalysts exhibit higher catalytic activity, better selectivity and stronger sulfur resistance in many hydrogenation reactions.

In this work, we report an amorphous Ni oxide-supported catalyst, which shows the capability in the synthesis of H_2O_2 from CO, water and O_2 . However, the deactivation of the catalyst was observed after reaction for several hours. The aim of this paper is also to examine the possible factors responsible for the deactivation.

2. Experimental

2.1. Catalyst preparation

Table 1 presents the catalysts applied in this work. Each catalyst precursor was prepared by the chemical reduction method. The supported Ni-B/ γ - Al_2O_3 (or Ni-La-B/ γ - Al_2O_3) catalysts were prepared with the following procedures. The dried γ - Al_2O_3 carriers (40–60 mesh, 197 m^2/g) were first impregnated with a desired amount of an aqueous solution of nickel nitrate (Wenda Chemical, Tianjin, China; >99%) (or with a common solution of lanthanum nitrate (Wenda Chemical, Tianjin, China; >99%) and nickel nitrate) over night. The total amount of metal Ni loaded was 15 wt.%. The obtained samples were dried at 110 °C for 6 h, and then the dried supported catalyst precursors were reduced by the addition of an aqueous solution of 0.5 M potassium borohydride (Wenda Chemical, Tianjin, China; >99%). The initial atomic ratio of B/Ni was adjusted to 3/1 to ensure that all the Ni^{2+} ions on the

Table 1
Amorphous catalysts used in this study

Number	Composition	Atomic ratio of La/Ni	Preparation conditions
			Temperature (°C)/ drying time (h)
1	Ni-B/ γ - Al_2O_3	– ^a	– ^b
2	Ni-La-B/ γ - Al_2O_3	1:15	– ^b
3	Ni-B/ γ - Al_2O_3	– ^a	120/10
4	Ni-La-B/ γ - Al_2O_3	1:20	120/10
5	Ni-La-B/ γ - Al_2O_3	1:15	120/10
6	Ni-La-B/ γ - Al_2O_3	1:10	120/10
7	Ni-La-B/ γ - Al_2O_3	1:15	60/10
8	Ni-La-B/ γ - Al_2O_3	1:15	300/10

^a No La in the catalyst.

^b No further thermal treatment with the fresh catalyst.

support were completely reduced. During the reduction, the temperature was kept at 0 °C in an ice-bath and the mixture was stirred slowly. The resulted Ni-B/ γ - Al_2O_3 (or Ni-La-B/ γ - Al_2O_3) catalysts were then washed several times with the oxygen-free pure water. The samples were further washed with alcohol, and then heated at different temperatures (60, 120, and 300 °C) in air for 10 h.

2.2. Catalyst characterization

The amorphous structures of catalysts were determined by X-ray diffraction (XRD) using a Rigaku C/max-2500 diffractometer with a Cu $\text{K}\alpha$ radiation. The surface morphology of the catalyst was studied by a scanning electron microscopy (SEM) using a Philips XL-30 ESEM system. The surface composition and the surface electronic states of the catalysts were determined by X-ray photoelectron spectrometry (XPS) using a Perkin-Elmer PHI1600 ESCA system with a Al $\text{K}\alpha$ radiation (1486.6 eV).

2.3. Activity test

The reaction was conducted in an autoclave with 350 ml water containing phosphorous acid (the concentration is about 0.01 M) and 5 g catalyst. Before the reaction, the pressure was increased to 3000 kPa with a partial pressure of CO (99.9%, Danpu Gas, Beijing) of 300 kPa and that of O_2 (99.9%, Huabei Gas, Tianjin, China) of 2700 kPa. The reactions were carried out at 20 °C. The aqueous samples taken at intervals were analyzed by titration using the iodometric method. The used catalyst was kept to determine if any sintering, crystallization, or surface poisoning occurred after deactivation.

3. Results and discussion

3.1. Characterization of catalysts

The amorphous structure of catalysts was identified by XRD. Typical results of amorphous Ni alloys over alumina are shown in Fig. 1. One broad peak around $2\theta = 46^\circ$ was

observed from each sample (except catalyst 8), which indicates the catalysts (1–7) are the amorphous structure [23], and the introduction of the alumina support and La does not change the amorphous structure of Ni–B alloys. The catalyst 8, which was treated at 300 °C, exhibited a sharp diffraction peak around $2\theta = 43.3^\circ$ on the XRD patterns, showing the occurrence of the slight crystallization since Ni–La–B amorphous alloys are thermodynamically metastable.

SEM determines the surface morphology of catalysts. One can see that the catalysts 3 and 5, shown in the Fig. 2, exhibit a sponge-like morphology comprised of thousands of small particles with the average size of less than 150 nm, consistent with those of other Ni-based amorphous alloy samples. It is also observed that, although with similar nickel loading, the alloy particles in Ni–La–B/ γ -Al₂O₃ were more homogeneously dispersed than those in Ni–B/ γ -Al₂O₃.

Table 2 shows the surface atomic composition of the fresh amorphous catalysts (3–6) and the corresponding

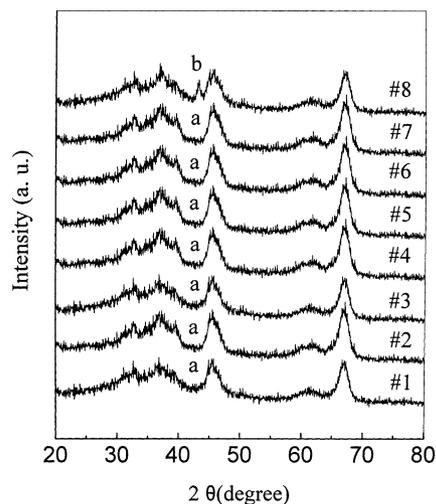


Fig. 1. XRD patterns of the catalyst samples: (a) Amorphous NiO and (b) crystal NiO.

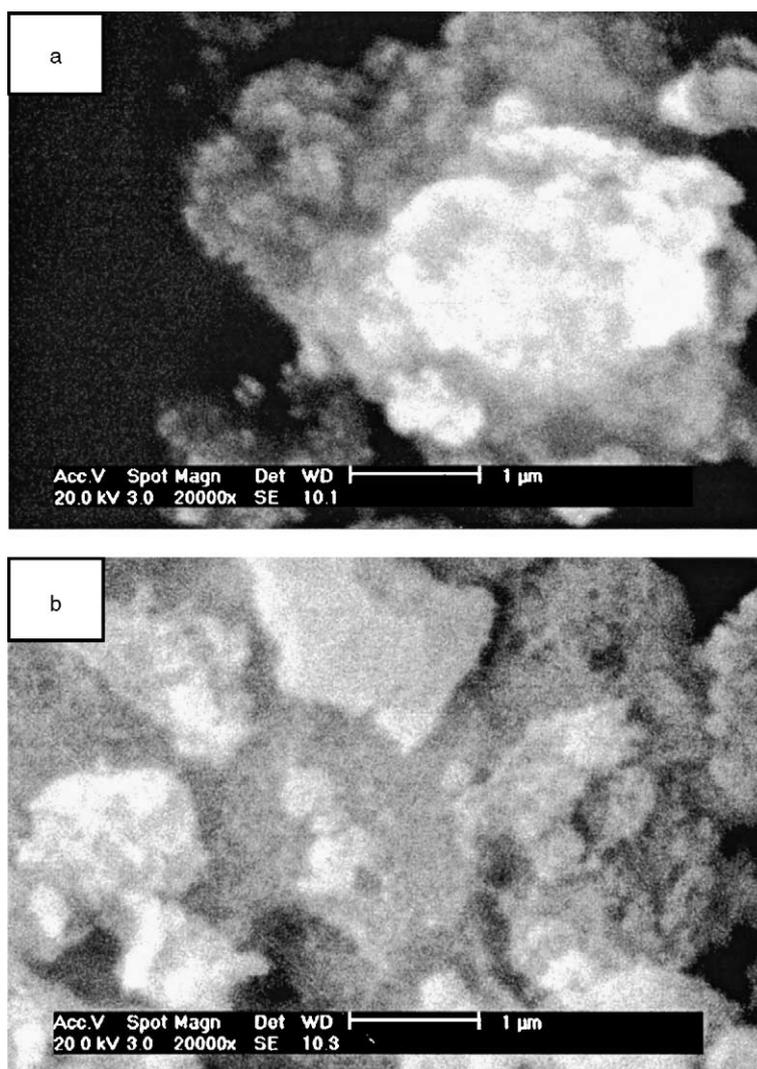


Fig. 2. SEM photos of (a) catalyst 3 and (b) catalyst 5.

Table 2
Comparison of the surface atomic composition of the catalysts

XPS level	Atomic composition (%)							
	Catalyst 3		Catalyst 4		Catalyst 5		Catalyst 6	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
Ni _{2p}	7.3	4.0	8.5	4.0	9.7	5.1	10.3	4.5
B _{1s}	3.9	3.9	3.3	3.8	3.9	4.0	6.0	6.0
La _{3d}	— ^a	— ^a	0.2	0.3	0.4	0.5	0.5	0.5

^a No La in the catalyst.

deactivated ones after reaction. From them, we can see a significant decrease in the Ni content after reaction. Because a 40–60% decrease of the surface Ni atoms was observed, the Ni of active sites of the catalyst surface must have been reduced significantly after reaction.

In order to evaluate the electronic state of the catalysts, the binding energies of Ni and B were determined by XPS under present conditions. The reference binding energies are listed in Table 3 [24]. The peaks at 853.0 eV, at 853.9 eV, and at 855.5 eV in Ni_{2p_{3/2}} spectra are ascribed to elemental nickel, nickel oxide, and Ni(OH)₂, respectively, while the peaks at 187.0 eV, at 193.9, and 193.5 eV are assigned to elemental boron, boron oxide, and H₃BO₃, respectively.

Fig. 3 shows B_{1s} spectra of the fresh and deactivated catalysts. In comparison with the binding energy of the reference substances in Table 3, the binding energy of B₂O₃ shown in Fig. 3(a) and in Fig. 3(c) is found in the XPS spectra of the catalysts 3 and 5, indicating that boron exists mainly as B₂O₃. However, the XPS spectra of the deactivated catalysts exhibit the peaks at about 193.5 eV, which point to that boron is changed from B₂O₃ to H₃BO₃ after the catalysts deactivated completely. The formation of H₃BO₃ is from the presence of phosphorous acid and H₂O.

The XPS spectra shown in Fig. 4(b) and (d) are the Ni_{2p_{3/2}} spectra of the deactivated catalyst, which is obviously different from the fresh catalysts (see Fig. 4(a) and (c)). Before reaction, most of nickel are in oxide (B.E. = 854.0 eV), while on the deactivated catalyst, Ni(OH)₂ (B.E. = 855.5 eV) are the predominant species. Little amount of Ni(OH)₂ exists on the catalyst samples, which indicates that during the preparation of catalysts, Ni(OH)₂ has been produced. When prepar-

Table 3
Binding energies (eV) of reference substances (all of these substances are commercially available)

Standard substance	XPS level	Binding energies (eV)
Pure Ni	Ni _{2p_{3/2}}	853.0 ± 0.1
NiO	Ni _{2p_{3/2}}	853.9 ± 0.1
Ni(OH) ₂ ·H ₂ O	Ni _{2p_{3/2}}	855.5 ± 0.1
Amorphous B	B _{1s}	187.0 ± 0.1
H ₃ BO ₃	B _{1s}	193.5 ± 0.1
B ₂ O ₃	B _{1s}	193.9 ± 0.1
Na ₂ B ₄ O ₇	B _{1s}	192.0 ± 0.1
KBH ₄	B _{1s}	187.3 ± 0.1

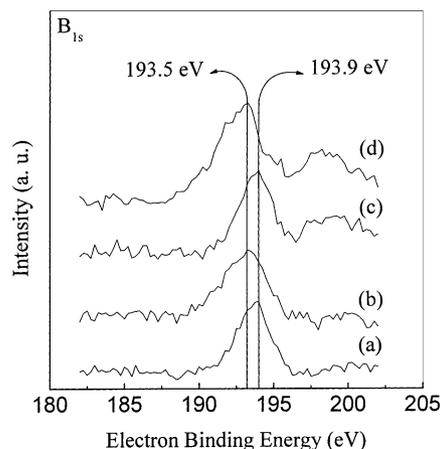


Fig. 3. B_{1s} spectra of the catalyst samples and the deactivated catalysts: (a) catalyst 3; (b) deactivated catalyst 3; (c) catalyst 5; and (d) deactivated catalyst 5.

ing the catalysts, the presence of water from the aqueous solution of potassium borohydride contributed to the formation of Ni(OH)₂.

3.2. Activity of catalysts

As shown in Fig. 5, the fresh amorphous Ni–B/γ-Al₂O₃ catalyst (1) without further thermal treatment can catalyze the synthesis of hydrogen peroxide from carbon monoxide, water and oxygen. The catalyst, however, deactivated quickly, and H₂O₂ concentration in the clave reached the maximum (0.6 mmol/l) when the reaction time was 2 h. The Ni–La–B/γ-Al₂O₃ catalyst (2), which contains a small amount of La, exhibited a longer lifetime than the catalyst 1 did. This indicates that the addition of La to Ni–B amorphous alloys can improve the stability of the catalyst and lifetime reached 3 h. But the activity of the catalyst 2 was slightly lower than that of catalyst 1 before deactivation,

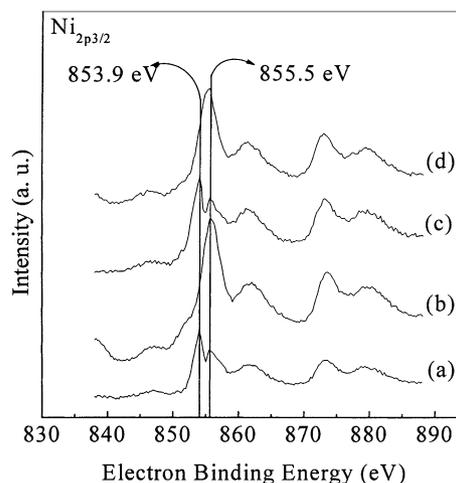


Fig. 4. Ni_{2p_{3/2}} spectra of the catalyst samples and the deactivated catalysts: (a) catalyst 3; (b) deactivated catalyst 3; (c) catalyst 5; and (d) deactivated catalyst 5.

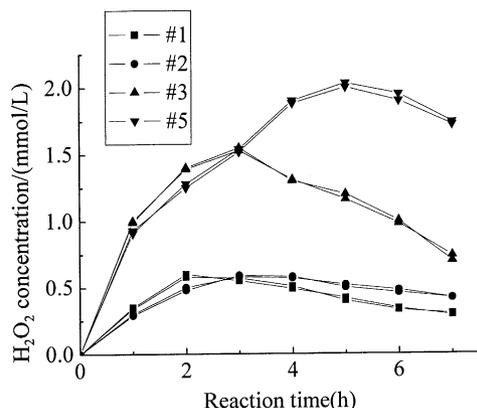


Fig. 5. Comparison of activities between the dried catalysts and the catalysts without drying treatment.

because La species cover part of the surface active area of Ni–B alloys.

After being dried at low temperature, the activities of the catalyst 3 and 5 increase obviously. The activity of the catalyst 5, dried for 10 h at 120 °C, is almost three times higher than that of the catalyst 2. The treatment at 120 °C induced a significant increase in the maximal H_2O_2 concentration (from 0.6 to 2.0 mmol/l). The catalysts were treated at low temperature, which was evidently lower than the crystallization temperature [23]. As exhibited in Fig. 1, the catalysts still kept amorphous structure.

The peak of elemental nickel (B.E. = 853.0 eV) was not detected in the XPS spectra (Fig. 4) of the catalysts dried at 120 °C for 10 h. Together with the fact that the activities of the dried catalysts (3–6) were obviously higher than that of the catalysts without drying treatment (catalysts 1 and 2) (see Fig. 5), we conclude that NiO has much better activity than elemental nickel for this reaction.

Fig. 6 compares results of activities of catalysts with different La/Ni ratios. Obviously, under the same preparative

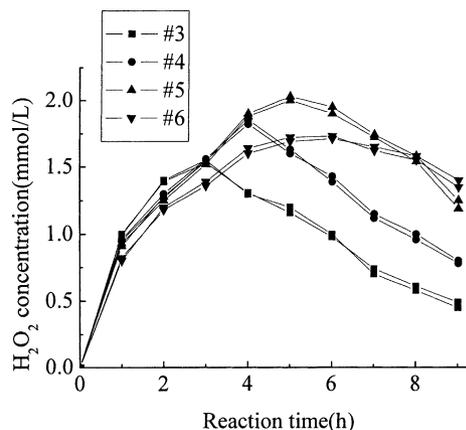


Fig. 6. Comparison of catalytic activities with different La/Ni ratios.

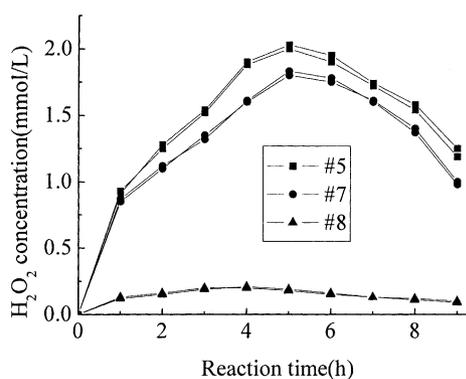


Fig. 7. Effect of drying temperature on the catalytic activities.

conditions, the activity and lifetime of Ni–La–B/ γ - Al_2O_3 (4–6) were increased and prolonged, compared to that of catalyst 3. Fig. 6 also exhibits that the stability of catalyst was improved with increase of atomic ratio of La/Ni. The lifetime of the catalyst 6 reached 6 h. La has been applied

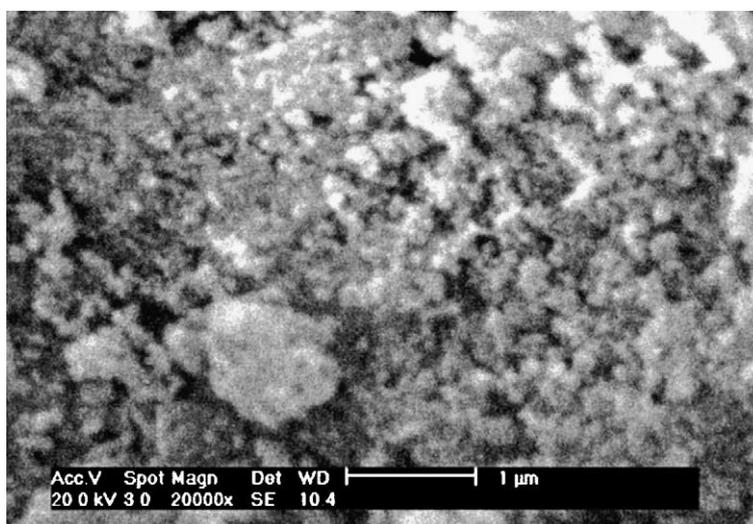


Fig. 8. SEM surface morphology of the catalyst 8.

here to keep the stability of the Ni-supported catalyst. It has been considered that La species may take up part of active sites (Ni) of Ni–B alloys. Upon the XPS analysis shown in Fig. 4, the addition of La can significantly slow down the oxidation of Ni under the oxidative conditions. The lifetime of the catalyst is thereby prolonged. However, a further increase in La content leads to a reduced activity. The maximal H_2O_2 concentration was obtained with the catalyst 5.

Fig. 7 presents the effect of drying temperature on catalytic activities of catalysts with the same La/Ni ratio. From Fig. 7, we can see that, when drying temperature is either $60^\circ C$ (catalyst 7) or $120^\circ C$ (catalyst 5), the catalyst shows a sufficiently high activity. The activity of the catalyst 7 is just a little lower than that of the catalyst 5. However, upon the further increase in drying temperature to $300^\circ C$ (catalyst 8), the activity reduces quickly. From the XRD characterization shown in Fig. 1, when the drying temperature reaches $300^\circ C$, the amorphous Ni–La–B alloy started to crystallize partially that induces a decrease in the catalytic activity. In

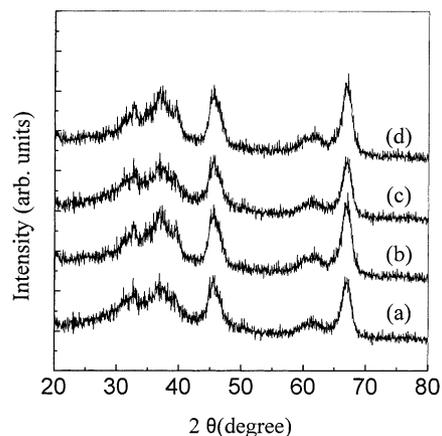


Fig. 9. XRD patterns of the deactivated catalysts: (a) catalyst 3; (b) catalyst 4; (c) catalyst 5; and (d) catalyst 6.

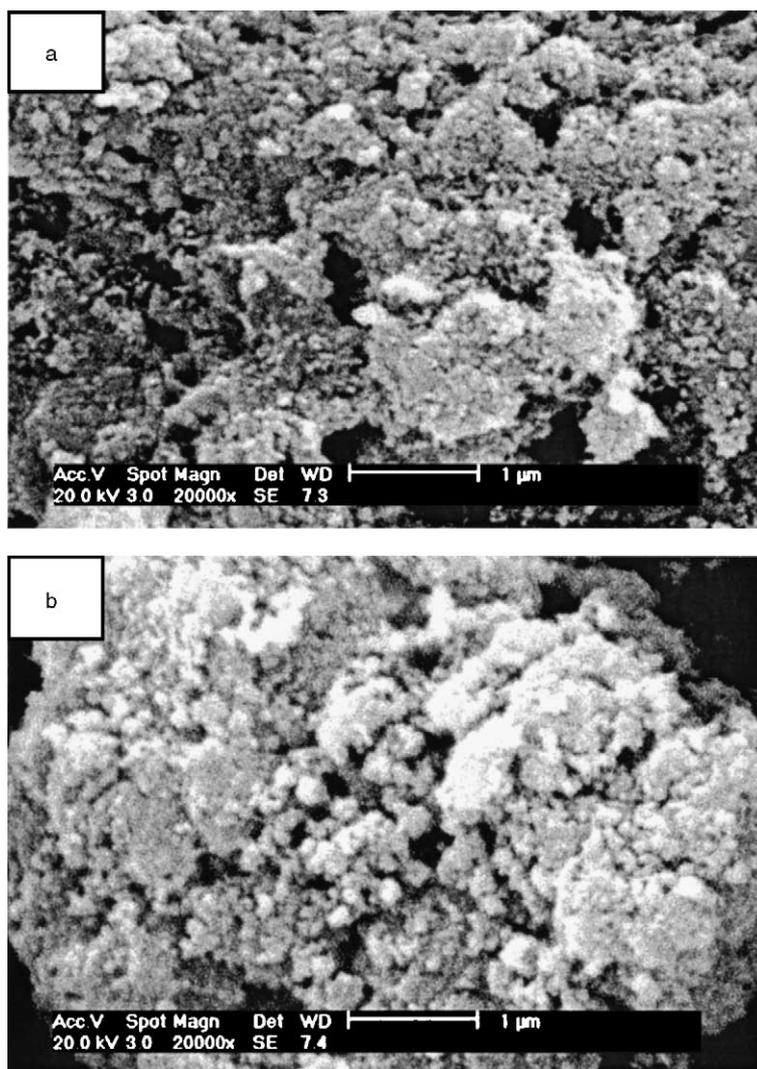


Fig. 10. SEM surface morphology of (a) deactivated catalyst 3 and (b) deactivated catalyst 5.

addition, a SEM characterization (Fig. 8) suggested that a sintering occurred after catalyst 8 was dried at 300 °C.

3.3. Analysis of deactivation

In general, the deactivation of supported nickel catalysts may result from (a) sintering, (b) poisoning, and (c) loss of active species [25]. SEM characterization exhibits that during the present preparation all the catalysts did not sinter except for catalyst 8. Since the reaction temperature was comparatively low (20 °C), sintering can be excluded. Fig. 9 shows the XRD patterns of the deactivated catalysts (3–6), which is the typical XRD pattern of the alumina support. The fact that we did not observe the crystallization of catalysts indicates that the main reason of deactivation is not crystallization, thermal deactivation can be also excluded.

On the other hand, water has a negative effect on the supported nickel catalyst [26]. During the reaction, the active Ni species (NiO) reacted with H₂O in the media to form catalytically inactive Ni(OH)₂. But Ni(OH)₂ was not a ultimate deactivated substance of active Ni. Phosphorous acid in the reaction media, which played an important role in the stability of H₂O₂, can react with Ni(OH)₂ to form Ni₃(PO₄)₂. With the progress of reaction, the formed surface Ni salt can partially dissolve in the media. So a significant decrease of the surface Ni atoms occurred. The result of XPS characterization also showed that 1.5–2.0% P existed on the surface of the deactivated catalysts.

Fig. 10 shows SEM images of the surface morphology of the deactivated catalysts. We can see that the deactivated catalysts are made of even layers, and the characteristics of the amorphous structure disappeared completely.

4. Conclusions

Brill reported that the catalytic activity of the 5% Pd/CaCO₃ and 1% Ru/graphite catalysts for H₂O₂ production reaches 0.1 mmol/(g h). In this work, the highest activity of the catalyst 5 is 0.07 mmol/g h which is comparable to the activity reported with noble metal catalysts. La incorporation has a strong effect on Ni amorphous catalyst, and the stability of the catalyst will thereby be improved. Suitable drying temperature can raise the activity of the catalyst. The Ni–La–B/γ-Al₂O₃ catalyst with a 1:15 atomic ratio of La/Ni, dried at 120 °C, shows the best result.

In the present work, we also studied the deactivation behavior of the amorphous Ni–B/γ-Al₂O₃ or Ni–La–B/γ-Al₂O₃ catalyst for the production of hydrogen peroxide from carbon monoxide, water, and oxygen. It was found that, under the reaction conditions, the cause of the deactivation is

water poisoning and the loss of the surface active Ni species. Water plays an important role in the deactivation process of the amorphous Ni–B/γ-Al₂O₃ or Ni–La–B/γ-Al₂O₃ catalyst, and the active Ni species to the inactive Ni speeds up the transformation to the salt.

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