

Production of Hydrogen Peroxide from Carbon Monoxide, Water, and Oxygen over Alumina Supported Amorphous Ni Catalysts

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A novel amorphous Ni catalyst supported on alumina has been developed for the production of hydrogen peroxide from carbon monoxide, water, and oxygen. The experimental investigation confirmed that the promoter/Ni loading ratio and the preparation conditions show a significant effect on the activity and catalytic lifetime. Among all the catalysts tested, the Ni-La-B/Al₂O₃ catalyst with 1 : 15 molar ratio of La/Ni, dried at 120 °C, shows the best activity and lifetime for the production of hydrogen peroxide.

Hydrogen peroxide is a very important chemical applied for chlorine-free bleaching. The utilization of hydrogen peroxide for the novel green chemical synthesis has also made a great progress.¹⁻⁴ The traditional production of hydrogen peroxide is not an economic and simple process. A great effort has been made worldwide towards a development of a simple but efficient production of hydrogen peroxide.⁵⁻⁸ Among the techniques developed, the production of hydrogen peroxide from carbon monoxide, water, and oxygen is very promising owing to its high safety. However a drawback in the investigation of H₂O₂ synthesis from CO, water, and O₂ is that the palladium or other noble metal catalysts are required.⁸⁻¹³ In addition, most of these processes employed a complex homogeneous catalytic system that requires extra separation process or acid additives for the reaction. Only one work was related to the use of heterogeneous catalytic synthesis over Pd/CaCO₃ and Ru/graphite catalysts.¹³

In this work, we report an amorphous Ni oxide supported catalyst for the production of hydrogen peroxide from CO, water, and O₂. Amorphous alloys have recently attracted much attention for the use as catalysts,¹⁴⁻¹⁷ especially, for hydrogenation, dehydrogenation, hydration, dehydration, and methanation of carbon dioxide.^{16,17} Here the capability of the amorphous Ni alloys (or as the precursors) in the synthesis of H₂O₂ from CO, water, and O₂ was well demonstrated.

Table 1 presents the catalysts applied in this work. Each catalyst precursor was prepared by chemical reduction method.

Table 1. Amorphous catalysts used in this reaction

No.	Composition	Molar ratio of La/Ni	Preparation conditions
			Temperature/°C/(time/h) for drying
#1	Ni-B/Al ₂ O ₃		120/10
#2	Ni-La-B/Al ₂ O ₃	1 : 20	120/10
#3	Ni-La-B/Al ₂ O ₃	1 : 15	120/10
#4	Ni-La-B/Al ₂ O ₃	1 : 10	120/10
#5	Ni-La-B/Al ₂ O ₃	1 : 15	60/10
#6	Ni-La-B/Al ₂ O ₃	1 : 15	250/10

The supported catalysts were prepared as follows: the alumina carriers were first impregnated with an aqueous solution of nickel nitrate (or with a mixed solution of lanthanum nitrate and nickel nitrate) overnight. The total amount of metal Ni loading was 10 wt%. The catalyst was dried, and then the dried supported catalyst was reduced by dropwise addition of an aqueous solution of KBH₄ (0.5 M, $n(\text{BH}_4^-/\text{Ni}^{2+}) = 3$). The amorphous structures of catalysts were determined by XRD using a Rigaku C/max-2500 diffractometer with Cu K α radiation. The reaction was conducted in an autoclave with 350 mL distilled 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 which the partial pressure of CO was 500 kPa and that of O₂ was 2500 kPa. The reactions were carried out at 20 °C. The aqueous samples taken out were analyzed by titration using the iodometric method.

Figure 1 shows the comparative results of activities of catalysts with different La/Ni ratios. Obviously, under the same preparative conditions, the activity of Ni-La-B/Al₂O₃ (#2, #3, and #4) was increased and prolonged, compared to the catalyst #1. The results shown in Figure 1 also exhibit that the stability of catalyst was improved with increase of molar ratio of La/Ni. The lifetime of the catalyst #4 reached six hours. La has been applied here to keep the stability of the Ni supported catalyst. It has been considered that La atoms take up part of active sites (Ni) of Ni-B alloys. Upon the XPS analysis using a PHI1600 XPS system, 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 diminishing activity. The best result was obtained with the catalyst #3.

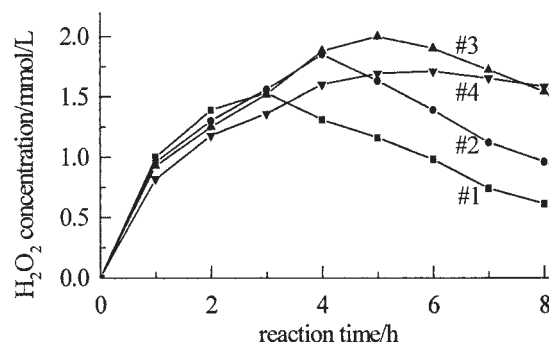


Figure 1. Comparison of catalytic activities with different La/Ni ratios.

Figure 2 presents the effect of drying temperature on catalytic activities of catalysts with the same La/Ni ratio. From Figure 2, we can see that, when drying temperature is either 60 °C (#5) or

120 °C (#3), the catalyst shows a sufficiently high activity. The activity of the catalyst #5 is just a little lower than that of the catalyst #3. However, upon the further increase in drying temperature to 250 °C (#6), the activity reduces quickly. From the XRD characterization shown in Figure 3, when the drying temperature reaches 250 °C, the amorphous Ni-La-B alloy started crystallization with induces a decrease in catalytic activity.

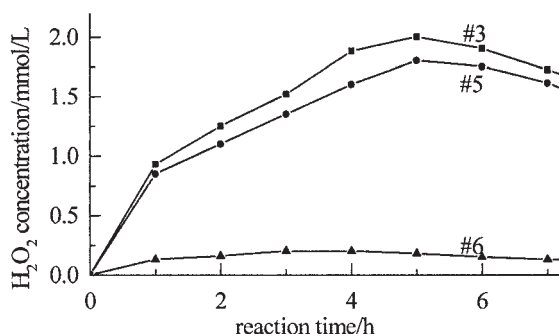


Figure 2. Effect of drying temperature on the catalytic activities.

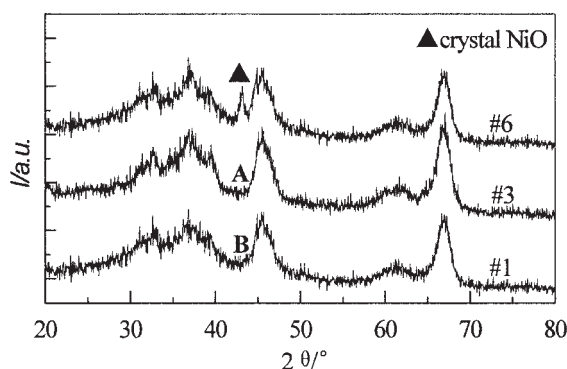


Figure 3. XRD characterization of used catalysts. (A) represents amorphous NiO; (B) represents amorphous NiO.

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).¹³ In this work, the highest activity of the catalyst #3 is 0.07 mmol/(g·h) that is comparable to the activity reported with noble metal catalysts.¹³ Further investigation is leading to a significant improvement in the production of H₂O₂ from CO, water, and O₂ using the alumina supported amorphous Ni catalysts.

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