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Highly selective amorphous Ni–Cr–B catalyst in 2-ethylanthraquinone hydrogenation to 2-ethylanthrahydroquinone

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A nanosized amorphous Ni-Cr-B catalyst prepared by the chemical reduction method exhibited superior thermal stability and selectivity in hydrogen peroxide synthesis *via* the anthraquinone route.

The anthraquinone hydrogenation/oxidation process is by far the most popular route in the industrial production of H_2O_2,[1–3] which is an environmentally friendly reagent oxidant. In this well established process, 2-ethylanthraquinone (eAQ) is first hydrogenated to 2-ethylanthrahydroquinone ($eAQH_2$) and 2-ethyltetrahydroanthrahydroquinone (H_4eAQH_2) in the presence of a hydrogenation catalyst. Then, in an oxidation step, $eAQH_2$ and H_4eAQH_2 are completely oxidized with oxygen-containing gas to yield H_2O_2, while eAQ and H_4eAQ are recovered and enter into another cycle.

However, even on the most selective palladium catalysts, during the hydrogenation process eAQ can be degraded to 2-ethylanthracene (eAT) and 2-ethylanthrone (eAN), and H_8eAQH_2 is easily formed from H_4eAQH_2.[4] Such by-products lead to the loss of fed hydrogen and the expensive anthraquinones. On the other hand, the oxidation rate of H_4eAQH_2 is sharply slowed down relative to that of $eAQH_2$, leading to lower efficiency in H_2O_2 production.[5] Thus a catalyst exhibiting exclusive selectivity in hydrogenating the carbonyl group rather than the aromatic ring is highly desirable.

In a previous work, we have reported on a rapidly quenched skeletal Ni catalyst over which the yield of H_2O_2 as high as 97% was achieved, about 30% higher than that over Raney Ni. However, a detailed chromatographic analysis revealed that 18% of eAQ was converted to H_4eAQ, while about 3% of eAQ was deteriorated.[6] In the present work, we further developed a chemically reduced nanosized amorphous Ni–Cr–B catalyst over which the hydrogenation of the aromatic rings in eAQ was efficiently blocked, showing an attractive potential for practical application.

The amorphous Ni–Cr–B alloy catalyst was prepared as follows. 0.4 ml of a 0.48 M aqueous solution of K_2CrO_4 was uniformly mixed with 20 ml of a 0.42 M aqueous solution of $NiCl_2$. The mixture was reduced by slowly adding 15 ml of an aqueous solution of KBH_4 (2.0 M KBH_4 with 0.1 M NaOH) in an ice–water bath with gentle stirring. When no further gas was released, the resulting black precipitate was washed thoroughly with distilled water until pH ~7, then with ethanol three times. The catalyst was finally kept in ethanol for characterization and activity testing.

The activity test was carried out in a stainless steel autoclave. A mixture of trioctylphosphate and trimethylbenzene (volume ratio 3/7) was used as the solvent and the concentration of eAQ in the working solution was 50 g l^{-1}. The reaction conditions were: 0.5 g of catalyst, 70 ml of working solution, H_2 pressure of 0.3 MPa, reaction temperature of 323 K and a stirring rate of 1000 rpm. The reaction process was monitored by sampling the reaction mixture at intervals, followed by O_2 oxidation. The H_2O_2 produced was extracted by distilled water and titrated by $KMnO_4$. As previously defined,[7] the percentage yield X of H_2O_2 is expressed as the ratio of the number of mol H_2O_2 to the initial number of mol eAQ in the reactor: $X = n^t_{H_2O_2}/n^0_{eAQ} \times 100\%$, which also represented the selectivity to $eAQH_2$ and H_4eAQH_2. The two species, eAQ and H_4eAQ, were further quantified by HPLC (HP 1100) with an ultraviolet detector employing a Zorbax column (ODS, 4.6 mm × 15 cm).

The chemical composition of the as-prepared Ni–Cr–B sample is $Ni_{75.3}Cr_{3.6}B_{21.1}$ with a BET surface area of 134.7 $m^2\ g^{-1}$. Its XRD pattern shows a broad peak at $2\theta \approx 45°$, indicating its amorphous character,[8] which is further confirmed by SAED as only a diffractive halo rather than distinct spots are observed. TEM reveals an average particle size of 7 nm and homogeneous size distribution. As compared to Ni–B with particle size of around 35 nm,[9] it can be concluded that the addition of Cr dramatically decreases the dimensions of the amorphous alloy. The smaller particle size does not result in lower thermal stability, however, DSC reveals that its crystallization temperature is 31 K higher than that of Ni–B. Moreover, the Cr 2p XPS pattern shows two peaks at 577.1 and 586.8 eV, corresponding to the Cr $2p_{3/2}$ and $2p_{1/2}$ peaks of Cr(III) species, respectively.[10]

The yield of H_2O_2 and the evolution of eAQ and H_4eAQ as functions of time are plotted in Fig. 1 as an average of three independent runs. In Fig. 1, the yield of H_2O_2 increases steeply up to ~100% in a reaction time of 60 min, then began to fall very slowly. HPLC analysis shows that the amount of eAQ remains constant and no H_4eAQ is detected within this period. Prolonged reaction time leads to a decrease in the amount of eAQ and simultaneously an increase of H_4eAQ. Nevertheless, even after a reaction time of 240 min the amount of eAQ only dropped by 10%, while products other than eAQ and H_4eAQ correspond to ~1%, demonstrating the excellent operability of the as-prepared amorphous Ni–Cr–B alloy catalyst.

From the characterization and the activity test shown above, the possibilities for the superior selectivity of Ni–Cr–B in carbonyl group hydrogenation can be accounted for as follows. First, due to their coordinatively unsaturated nature,[11] the amorphous alloys tend to bond tightly with hydrogen, which is disadvantageous for hydrogenation of the aromatic ring.[5] Fig. 2 unambiguous shows that the population of the strongly bound hydrogen (at ~580 K) is much larger than that of the weakly bound hydrogen (at ~450 K) on Ni–Cr–B, while on Raney Ni

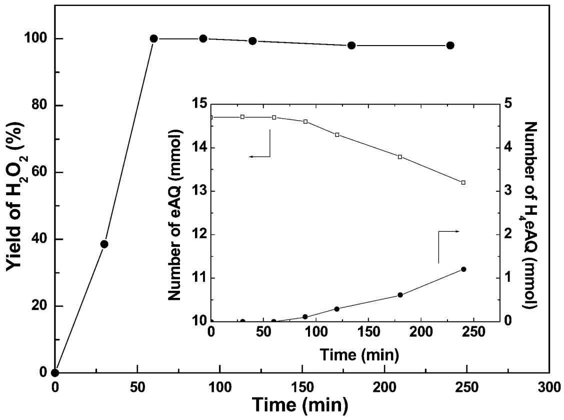

Fig. 1 The percentage yield of H_2O_2 and the amount of eAQ and H_4eAQ in the working solution after oxidation as a function of hydrogenation time.

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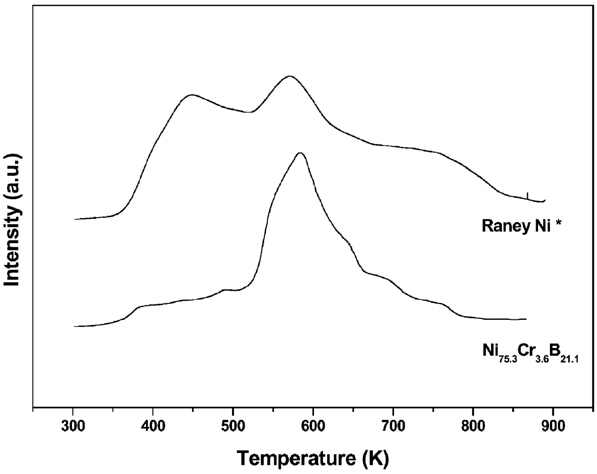

Fig. 2 The H_2 TPD feature over the as-prepared Ni–Cr–B catalyst; *quoted from ref. 6.

the populations of these two species are comparable.[6] Secondly, in the case of glucose hydrogenation to sorbitol over transition metal-modified Raney Ni, Gallezot *et al.* suggested that the Cr(III) species, functioning as a Lewis acid, could activate the carbonyl group by accepting the lone electron pair on the oxygen.[12] The activation favors the nucleophilic attack of the carbon by hydrogen dissociatively adsorbed on nickel, leading to enhanced hydrogenation activity of the carbonyl group and consequently superior selectivity in eAQ hydrogenation to $eAQH_2$.

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