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# Deactivation of $CeO_2$ catalyst in the hydrogenation of benzoic acid to benzaldehyde

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The $CeO_2$ catalyst has been investigated for hydrogenation of benzoic acid to benzaldehyde and shows little deactivation in stability test. BET results indicate that no significant sinter was observed on the used catalyst. SEM images show few changes taking place in surface feature of the used catalyst. Element analysis confirms that some coke is formed which leads to catalyst deactivation. XRD analysis reveals that crystalline size of catalyst is not relevant to the catalytic behavior in the range from 14.3 nm to 18.4 nm.

**KEY WORDS:** hydrogenation; benzaldehyde; benzoic acid; $CeO_2$; deactivation.

## 1. Introduction

Benzaldehyde is an important intermediate for synthesis of pharmaceuticals, agrochemicals, perfumes, and flavors [1]. Traditional methods to manufacture benzaldehyde are based on either oxidation or selective oxidation of toluene [2], benzene [3], styrene [4], or benzyl alcohol [5]. Since it is difficult to effectively prevent deep oxidation of benzaldehyde into benzoic acid during the reaction, these processes usually achieve a low yield of benzaldehyde. Additionally, some of them are not environmental friendly [3,5]. From green chemistry consideration, researchers have paid much attention to catalytic hydrogenation of some chemicals, e.g., benzoic acid, to produce benzaldehyde over past decades [6,7]. For example, a commercial process for the production of benzaldehyde from benzoic acid has been developed using zirconia-based catalysts by Mitsubishi Chemicals, Japan, in 1988 [7].

Recently, other metal oxide catalysts, such as ZnO [8–11], Mo oxides [12,13], and $CeO_2$ [9,14], were also studied. Based on these studies, a type of Mars and van Krevelen mechanism is proposed in the hydrogenation of benzoic acid to benzaldehyde on metal oxides catalysts [10,15], which consists of two steps: 1) hydrogen activates the oxide by the reduction to form oxygen vacancies; and 2) benzoic acid re-oxidizes these vacancy sites and yields benzaldehyde subsequently. At present, there are still many controversial issues regarding the application of metal oxides in hydrogenation of benzoic acid. One of previous studies has shown that hydrogenation of benzoic acid in presence of molecular hydrogen on Mo oxides and suboxides leads to the deep reduction of the catalysts [12]. This phenomenon results in a low catalytic performance of Mo oxides. For the weak Zn–O bond strength, ZnO catalysts in the hydrogenation of benzoic acid are not stable and produce significant amounts of by-products [11].

It's well known that $CeO_2$ has good redox ability for the capacity of active oxygen vacancies formation and steady-state concentration maintenance of them in some reactions [16]. $CeO_2$ has preferable activity to that of $ZrO_2$ for its proper bond strength and excellent redox capability in hydrogenation process [17,18]. And it turns out that $CeO_2$ is an effective catalyst for hydrogenation benzoic acid into benzaldehyde as shown in previous studies by Sakada *et al.* [14]. The effect of reaction temperature on catalytic behaviour has been investigated, as well as the effects of some metal oxides addition agents, in their work. However, catalytic stability of $CeO_2$ was not included.

This work aims to investigate the catalytic activity of $CeO_2$ in hydrogenation of benzoic acid, and, in particular, to explore the stability of $CeO_2$ and possible deactivation mechanisms.

## 2. Experimental

### 2.1. Catalyst preparation and catalytic measurements

$CeO_2$ catalyst was prepared by calcinating the ammonium cerium nitrate (Sinopharm Chemical Reagent Co.) first at 300 °C for 2 h and then at 650 °C for 4 h. Catalytic measurements were carried out at atmospheric pressure in a continuous flow fixed-bed reactor embedded with ca. 5 ml catalyst, which corresponds to a GHSV of 680 $h^{-1}$. Ratio of $H_2$ to benzoic

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acid is 92:1 and the reaction temperature is 380 °C. Prior to reaction, the catalyst was reduced at 400 °C for 1 h followed by flowing hydrogen that was introduced into the reactor through a saturator containing liquid benzoic acid. The connections between the operation units were wrapped in heating tape and held at a temperature of at least 250 °C to avoid condensation of benzoic acid. The products were collected in an ice–cold trap and analyzed by a gas chromatography (Shimadzu GC–14B) equipped with a capillary column OV–1(30 m × 0.25 mm × 0.25 $\mu$m).

### 2.2. Catalyst characterization

$N_2$ adsorption was measured with a Quantachrome Autosorb–1–C Sorption system to determine the specific surface area of catalysts by the BET method. An XL30–environment scanning electron microscope (ESEM, Philips) was employed to analyze fresh and used catalysts. Element analysis (EA) was carried out on a Flash EA1112 (ThermoFinnigan) to determine H and C composition over the used catalysts. X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku D/max–$\gamma$ diffractometer using a Cu K$a$ radiation (40 kV, 80 mA) with a 4 °/min scanning rate from 10° to 80°.

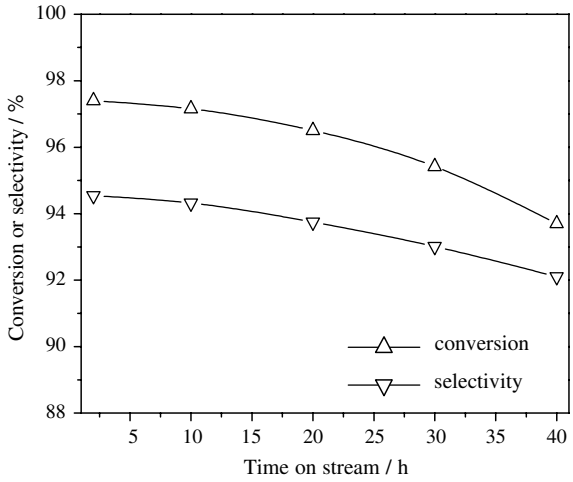


Figure 1. Stability test of $CeO_2$ catalyst.

The BET method was used to determine specific surface areas of fresh $CeO_2$ and the one used for a 40-h activity test. The results show that specific surface area is 27.7 $m^2/g$ for the fresh $CeO_2$ and 27.5 $m^2/g$ of the used one, which is approximately equal to each other. This exactly confirms that there is no significant sinter over the 40-h used catalyst. Figure 2 presents SEM images of the above two catalysts. Obviously, few changes can be

## 3. Results and discussion

### 3.1. Catalytic stability measurement

Figure 1 shows the evolution of hydrogenation performance of $CeO_2$ catalyst as a function of reaction time in a fixed-bed reactor. Initially, conversion of benzoic acid and selectivity to benzaldehyde are 97.4% and 94.6%, respectively, which are a little higher than those on Zn and Mo oxide catalysts as reported previously [8,12]. However, it is apparent that the catalytic activity declined gradually with increasing time on stream. After a 40-h test, conversion of benzoic acid decreases to 93.7%, while selectivity to benzaldehyde is 92.1%. It is very likely that the catalytic behavior would continue decline in further stability test.

### 3.2. Catalyst characterization and deactivation analysis

The deactivation of $CeO_2$ during redox process can be ascribed to the following reasons: 1) active oxygen vacancy sites decrease due to catalyst sinter; and/or 2) disintegration of the active $CeO_2$ crystal phases, which might cause the catalyst deactivation. Simultaneously, coke formation over solid catalysts from aromatic substances at high temperature can also lead to deactivation of catalyst. In order to distinguish which one is the main cause in this case regarding $CeO_2$ catalyst deactivation in hydrogenation of benzoic acid to benzaldehyde, some characterization methods have been employed to investigate fresh and used $CeO_2$ catalysts.

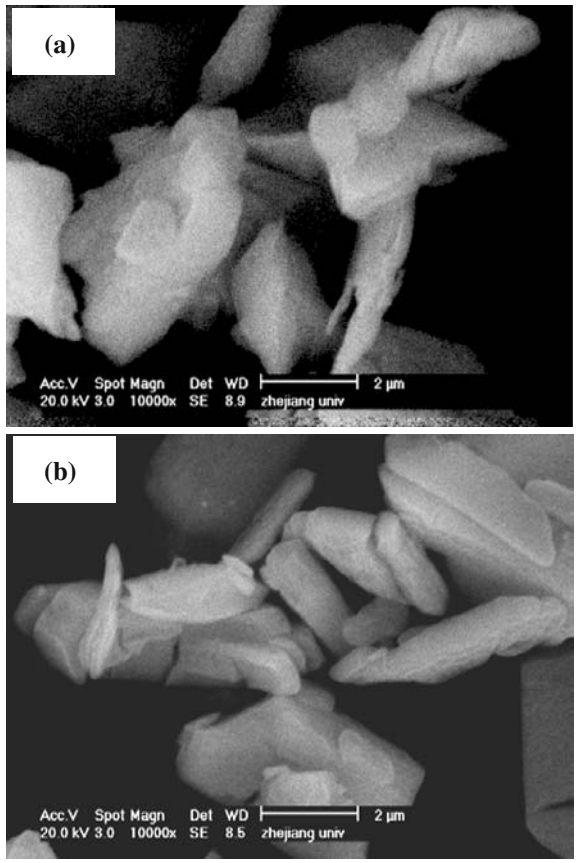


Figure 2. SEM image of (a) fresh catalyst and (b) used catalyst for 40 h.

observed in the configuration of surface of the used catalyst.

To further identify the possible reason of the catalyst deactivation, element analysis experiments were performed on the used catalyst. The results are shown in figure 3. It is can be seen that carbon composition on the $CeO_2$ is increased sharply in the range of the reaction time studied. According to the results in figure 3, the mass percentage of carbon over the used catalysts is increased from 2.1% to 2.5% with the catalyst deactivation.

The deactivated catalyst has been regenerated by being calcined at 500 °C for 4 h in an air environment to eliminate the coke completely in order to further clarify the relationship between coke formation and catalytic activity. The regenerated catalyst was tested again in the same condition as described previously and the results as shown in figure 4.

Compared with the original conversion of benzoic acid and selectivity to benzaldehyde obtained from fresh catalyst (figure 1), the reused catalyst almost exhibits the same reactivity performances as the fresh one. It can be concluded that it is coke formation mainly contributes to catalyst deactivation.

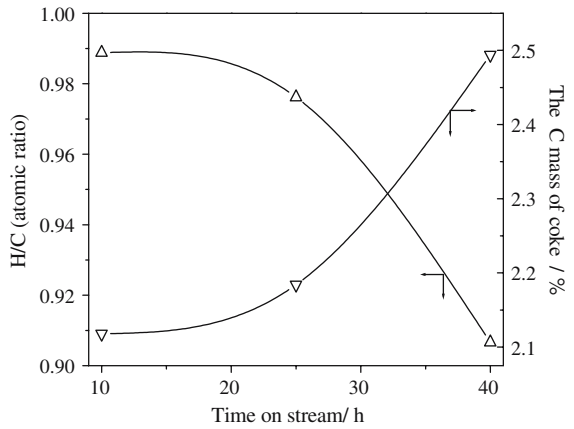


Figure 3. Element analysis of used catalysts.

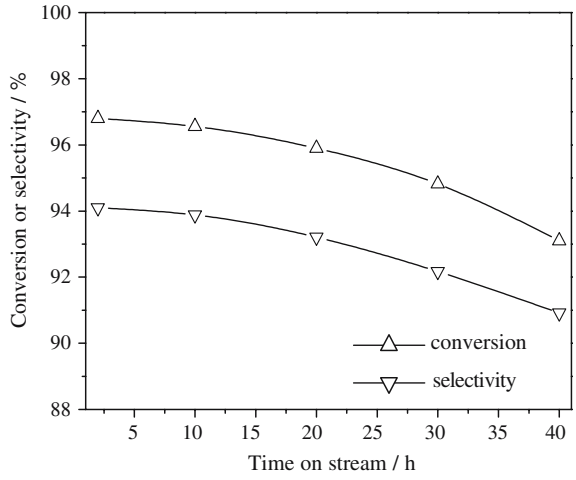


Figure 4. Stability test of regenerated $CeO_2$ catalyst.

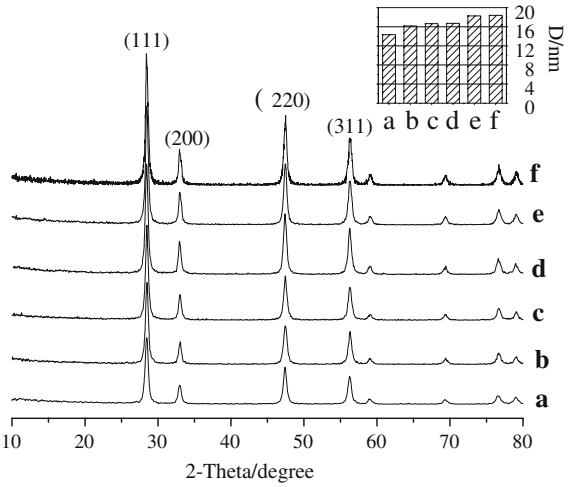


Figure 5. XRD patterns of catalysts (a: fresh $CeO_2$; b, c and d: used for10 h, 25 h and 40 h, respectively; e: regenerated $CeO_2$; f: reused for 40 h. The insert: crystallite size of the corresponding catalysts estimated by Sherrer's equation)

XRD patterns of all the catalysts mentioned above are shown in figure 5. Obviously, the $CeO_2$ is still kept the original crystal phase and not sintered after being used or reused, which is well agreed with our SEM results. The average crystallite size (D) is estimated by Sherrer equation in the (111) peak (The inset in figure 5). It can be seen that the D value of the catalysts obtained from the first test is not variational distinctly. After a wild regeneration process, the average crystallite size increases from 16.7 nm to 18.3 nm. However, there is almost nothing happened to the D value of the reused catalyst in the second test. It seems that the crystallite sizes of catalysts are not responsible for the catalysts deactivation in the range from 14.6 nm to 18.4 nm.

## 4. Conclusions

In this work, the catalytic activity of $CeO_2$ has been studied in the hydrogenation of benzoic acid to benzaldehyde. The catalyst shows a better performance compared to the reported Mo and Zn oxides. However, stability test shows that catalytic deactivation is observed. BET result suggests that the sinter of catalyst was not serious. EA results show that the mass percent of carbon is increased with the catalyst deactivation. Eliminating the coke could regenerate the deactivated catalyst. XRD patterns indicate that catalysts behavior have no relationship to the crystallite size in the range from 14.3 nm to 18.4 nm. It can be concluded that the deactivation of $CeO_2$ in the hydrogenation of benzoic acid to benzaldehyde is mainly resulted from the coke formation in this case.

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