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XPS Characterization of CeO_2 Catalyst for Hydrogenation of Benzoic Acid to Benzaldehyde

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Abstract The CeO_2 catalysts for hydrogenation of benzoic acid to benzaldehyde were characterized by X-ray photoelectron spectroscopy (XPS). The results indicate the catalyst deactivation is due to the coke formation and the valence changes of Ce over the catalyst.

Keywords XPS characterization · CeO_2 · Benzaldehyde · Benzoic acid

1 Introduction

The catalytic hydrogenation of benzoic acid to benzaldehyde is a "green" technology and an alternative to current selective oxygenation of benzene [1] or toluene [2] that are characterized by low yields or not environmental friendly [1–3]. In 1988, Mitsubishi Chemicals industrialized the direct hydrogenation of aromatic carboxylic acids over modified zirconia catalysts [4]. However, ZrO_2-based catalysts in the hydrogenation of benzoic acid are not stable and produce significant amounts of by-products. Subsequently, other metal oxide catalysts, such as ZnO [5–7], Mo oxides [8–10], were also studied. Based on these reports, a typical Mars and van Krevelen mechanism is proposed in the hydrogenation of benzoic acid to benzaldehyde on metal oxides catalysts [11], as shown in Scheme 1. Therein, hydrogen activates the metal oxide by reduction to form oxygen vacancies. Then these vacancies capture the oxygen atom of carboxyl in benzoic acid and yields benzaldehyde. Therefore, the arrangement of oxygen vacancies at the surface of the metal oxides has significant effects on catalytic behavior.

CeO_2 is one of the most interesting oxides because redox couple of Ce^{4+}/Ce^{3+} in it can transform easily, which makes oxygen vacancies formed and eliminated rapidly [12]. It also shows good activity in hydrogenation of benzoic acid into benzaldehyde [13]. Recently, we investigated the stability of CeO_2 in hydrogenation of benzoic acid [14]. The results indicate that the CeO_2 is an effective catalyst for this reaction. However, it exhibits a little deactivation due to the coke formation primarily. Therefore, the aims of this work are to further explore the possible deactivation mechanism. By employing the X-ray photoelectron spectroscopy (XPS) the valence changes of cerium and its effect on catalytic activity in hydrogenation of benzoic acid have been investigated.

2 Experimental

2.1 Catalyst Preparation and Catalytic Measurements

The catalysts preparation was reported previously [14]. Briefly, CeO_2 catalyst was prepared by calcinating ammonium cerium nitrate (Sinopharm Chemical Reagent Co.) at 300 °C for 2 h followed by 600 °C for 4 h. The obtained sample is thus referred to Ce600. Catalyst Ce800 was prepared following the same procedure as Ce600 except that it was calcinated at 800 °C for 4 h. Catalytic measurements were carried out in a continuous flow fixed-bed reactor embedded with ca. 5 mL catalyst at atmospheric pressure, which corresponds to a GHSV of 680 h^{-1}. Ratio of H_2 to benzoic acid is 92:1 and the reaction temperature is 380 °C. Prior to reaction, the catalyst was reduced at 400 °C for 1 h. Thereafter, hydrogen flowed through a saturator containing liquid benzoic acid and both

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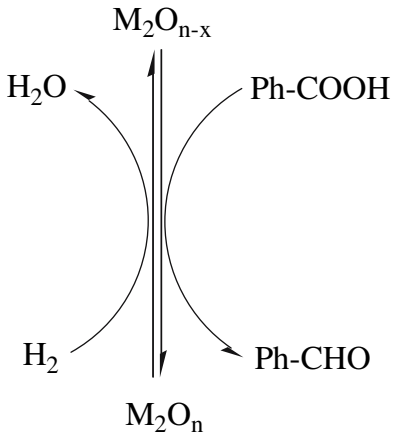

Scheme 1 The catalytic mechanism of the Ph–CHO production from Ph–COOH over metal oxide

were introduced into the reactor. To avoid condensation of benzoic acid, the connections between operation units were wrapped by heating tape and were held at a temperature of at least 250 °C. After 6-h stability test, the catalysts were regenerated in an air atmosphere at 500 °C for 4 h. Nine-regeneration and 10-stability-test cycles were conducted over the catalysts. The products were collected in an ice-cold trap at 2-h interval in each stability test and analyzed by a gas chromatography (Shimadzu GC-14B) equipped with a capillary column OV-1(30 m × 0.25 mm × 0.25 μm).

2.2 XPS Characterization

X-ray photoelectron spectroscopy (XPS) spectra for fresh, reduced, and used catalysts (i.e., nine-regeneration and 10-stability-test cycles) were recorded using a PHI1600 XPS system. A Mg K_α anode was used as the X-ray source. The binding energy of C1s (284.5 eV) was taken as internal standard for binding energy calibration.

3 Results and Discussion

The surface composition of fresh, reduced, and used (nine-regeneration and 10-stability-test cycles) catalysts is summarized in Table 1. Using the values of surface atomic composition, an estimation of the O/Ce atomic ratio can be obtained. For fresh catalysts, either Ce600 or Ce800, it is observed that the surface oxygen concentration on the samples is higher than stoichiometric value, which is probably due to O_2 absorbed in the sample because of exposure to the atmosphere [15]. After the reduction of catalysts, the ratio increases further, which results from the formation of hydroxyl groups on the catalyst surface in the reduction with hydrogen [16, 17]. According to our previous work [14], the coke formation leads to the template deactivation of catalysts. The XPS results of used catalysts also confirm this conclusion. After the stability test, the content of carbon species increase significantly, especially for Ce800.

In the case of the ratio of lattic oxygen to cerium, the smaller of O/Ce ratio than stoichiometry, the more amounts of cerium in the Ce^{3+} state over catalysts. The results in Table 1 indicate that the reduction induces Ce^{4+} transformed to Ce^{3+}. After the reaction, the ratio of O/Ce of Ce800 is much higher than that of Ce600. This is induced by the deep deoxygenation of benzoic acid over Ce800 which leads an increasing amount of lattic oxygen compared to bare Ce600. Therefore the yield of benzaldehyde over Ce800 is lower than that of Ce600. Shown in Table 2 is the comparison of initial activity between reduced and used (nine-regeneration and 10-stability-test cycles) catalysts. Evidently, the Ce800 exhibits a lower activity and stability in the period investigated.

Eight peaks are shown in each XPS spectrum in Fig. 1, which is in agreement with the literature reported [18]. The four main $3d_{5/2}$ features at 882.4, 884.9, 887.9, and 898.0 eV correspond to V, V′, V″, V‴ components, respectively. And the $3d_{3/2}$ features at 900.3, 903.5, 906.9, and 916.3 eV correspond to U, U′, U″, and U‴ components, respectively. The main peaks of V‴ and U‴ represented the $3d^{10}4f^0$ initial electronic state corresponding to the Ce^{4+} ion, while a small peak of V′ represented the $3d^{10}4f^1$ initial electronic state corresponding to the Ce^{3+} ion. The XP spectrum of Ce3d exhibit peaks due to the presence of both Ce^{4+} and Ce^{3+} over the samples.

It has been widely accepted that the relative amount of Ce^{4+} in CeO_2 samples can be calculated from the percent

Table 1 Surface elemental composition of CeO_2 catalysts

Sample		Surface composition/at %			O/Ce[b]
		C	Ce	O[a]	
Ce600	Fresh	61.5	10.6	27.9 (70.07)	2.63 (1.84)
	Reduced	61.3	10.3	28.4 (61.96)	2.76 (1.71)
	Used	72.2	7.3	20.5 (68.57)	2.81 (1.93)
Ce800	Fresh	63.6	10.0	26.4 (68.30)	2.64 (1.81)
	Reduced	66.2	8.5	25.3 (59.59)	2.97 (1.77)
	Used	81.7	4.4	13.9 (62.86)	3.15 (1.98)

[a] The number in parentheses represent the atomic percentage of lattic oxygen in total oxygen content

[b] The number in parentheses represent the atomic ratio of lattic oxygen to cerium

Table 2 Comparison of initial activity between reduced and used catalysts

Sample	Conversion of benzoic acid/%		Yield of benzaldehyde/%	
	Reduced	Used	Reduced	Used
Ce600	99.4	95.4	94.6	91.7
Ce800	95.1	94.3	89.9	81.0

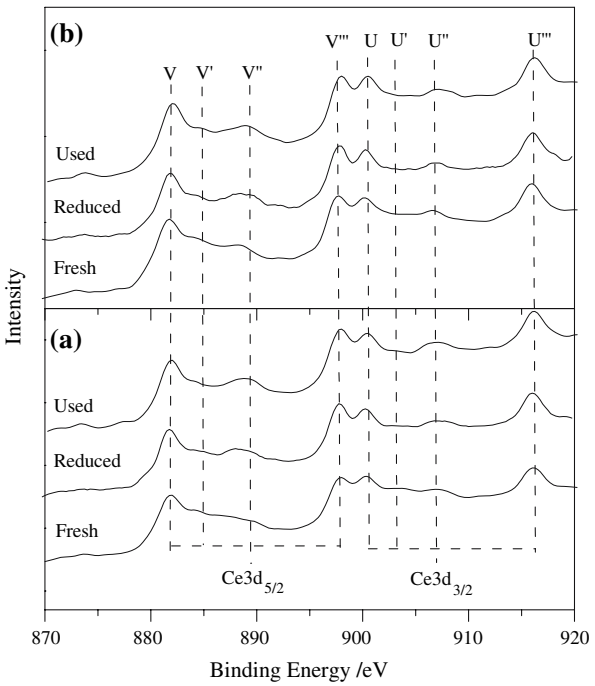

Fig. 1 XPS of Ce3d level for catalysts of (a) Ce600, and (b) Ce800

area of U‴ peak in the total Ce3d region (Ce $3d_{5/2}$ and Ce $3d_{3/2}$), assuming no preferential enrichment of Ce^{4+} over Ce^{3+} or vice versa [19]. This is due to the lack of the $4f^0$ configurations in the formal Ce^{3+} state [20]. The calculated percent area of the U‴ peak so defined is shown in Table 3 for the catalysts studied here. For comparison purposes, reference values for compounds containing cerium in only the Ce^{4+} or Ce^{3+} oxidation state are also given. The U‴ peak for $Ce(OH)_4$ amounts to 12.4% in the Ce3d region while for $CeAlO_3/Al_2O_3$, where cerium is in the Ce^{3+} state, the U‴ peak is absent [19]. Assuming a linear dependence between percent U‴ and Ce^{4+} composition using the values of Table 3, the Ce^{3+} concentration over the catalysts can be estimated. For the transformation of Ce^{4+}/Ce^{3+} couple over the catalyst in the reaction, it is reasonable that the concentration of Ce^{3+} undergoes a reverse change to that of the ratio of lattic oxygen to the cerium (Table 1). The significantly lower concentration of cerium in the Ce^{3+} state observed for used Ce800 is most probably due to the deep

Table 3 Percent area of U‴ peak in the total Ce 3d region ($Ce3d_{5/2}$ and $Ce3d_{3/2}$)

Sample		U‴ in Ce3d/%	Ref.	Ce^{3+} concentration/at %
$Ce(OH)_4$		12.4	[19]	100
7% $CeAlO_3/Al_2O_3$		0	[19]	0
Ce600	Fresh	8.46	This work	31.78
	Reduced	7.20	This work	43.94
	Used	9.16	This work	26.13
Ce800	Fresh	7.97	This work	35.73
	Reduced	7.61	This work	38.62
	Used	9.97	This work	19.57

deoxygenation of benzoic acid, which makes the oxygen vacancy filled while Ce^{4+} is dominant over the catalyst.

4 Conclusions

In present work, the valence changes of cerium over CeO_2 catalysts for hydrogenation of benzoic acid have been investigated by XPS. The results in our experiments show that, compare to Ce600, poorer property of Ce800 could be ascribed to two reasons. The one is more coke formation on the catalysts. The other one is the valence changes of Ce over the catalyst. Because of the deep deoxygenation of benzoic acid, the transformation of the Ce^{4+}/Ce^{3+} couple over the Ce800 is unfavorable.

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