XPS study of cobalt-ceria catalysts for ammonia synthesis – The reduction process☆

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ABSTRACT

The activation process of a cobalt catalyst promoted with cerium compounds was examined. The reduction of precursor was performed in a High Pressure Cell (HPC), being a part of an ultra-high vacuum (UHV) system, at 500 °C under hydrogen atmosphere. X-ray photoelectron spectroscopy (XPS) was subsequently used to investigate the evolution of surface composition. High resolution X-ray photoelectron analysis confirms total reduction of cobalt oxide into Co metallic form. After exposure to hydrogen, Ce^{4+} ions prevail in the structure of cerium oxides identified on the surface.

1. Introduction

Surface analysis is an important tool to recognize the evolution of different materials, what is essential in case of the catalysts. These materials are often prepared in one chemical form while their active form is completely different. The understanding of the catalytic process requires a knowledge of the chemical state of an active form which in addition can be susceptible to the environmental conditions. Therefore an implementation of the experimental methods which enable the investigation of the catalysts in the state as close to the one existing in the reaction space as possible is vital.

Studies regarding ammonia synthesis is an important problem for chemistry. The first generation of ammonia synthesis catalysts were iron-based catalyst [1]. Ruthenium-based catalysts proved to be more active than conventional iron-based catalysts [2], however, high cost of ruthenium resulted in a very limited number of their industrial applications. Cobalt-based systems are promising candidates for very active ammonia synthesis catalysts with a relatively low price. Raróg-Pilecka et al. [3] have shown potential benefits of cobalt catalysts promoted with cerium and/or barium. Ceria is considered as a structural promoter for Co-based catalysts by hindering the sintering of cobalt oxide or enhancing the cobalt dispersion [3].

Cerium oxides observed in catalytic systems occur in two general chemical forms: CeO_2 or Ce_2O_3. The transformation between these two compounds, especially observed on the surface of the catalysts, may greatly influence the properties of the catalyst as a whole. The chemical

state of ceria in different chemical processes was already studied. A partial reduction of CeO_2 was often reported [4,5]. The most considerable reduction of cerium oxides proceeds at an elevated temperature above 673 K or is induced by Ar^+ ions sputtering [6–8]. A presence of ceria in the Co-Ce systems greatly affects the redox properties of this system [9,10]. Cerium addition to Co-containing systems significantly influences the reduction/oxidation parameters. It depends on dispersion, composition, spatial form and reaction conditions. The most common feature of ceria is its ability to store and release oxygen. Ernst et al. [11] have investigated highly dispersed ceria addition effect on the reducibility of Co/SiO_2 Fischer-Tropsch catalyst. They found that the surface compounds of cobalt are further reduced when ceria is present. A dispersion state of ceria was pointed out as the most likely reason, rather than the oxidation state of ceria. After reduction, there was a very little change in the chemical state of ceria. According to Liotta et al. [12], the presence of ceria induces dispersion of Co_3O_4 phase and promotes the efficiency of $Co^{3+} \rightarrow Co^{2+}$ reduction. The authors claim that high relative amount of Ce^{3+} enhances oxygen mobility. The increase of Co_3O_4 surface area facilitates the desorption of adsorbed oxygen species and reaction $Co^{3+} \rightarrow Co^{2+}$ [13]. Luo et al. [14] have shown that in Co_3O_4 crystallites encapsulated by nanosized CeO_2, cerium stabilizes cobalt oxides and reduction to metallic Co is remarkably delayed. On the other hand, because oxygen supply from CeO_2 could happen, the oxidation of Co to Co_3O_4 is promoted.

Herein the chemical evolution of cobalt-based ceria-promoted precursor into the active catalyst was studied. X-ray photoelectron

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spectroscopy (XPS) analysis of the surface coupled with High-Pressure Cell (HPC) was utilized to observe the chemical states of the precursor and the catalyst after reduction under hydrogen atmosphere at elevated temperature.

2. Materials and methods

The precursor was obtained by co-precipitation procedure described in detail elsewhere [10]. Briefly, appropriate amounts of Co$(NO_3)_2 \cdot 6H_2O$ and Ce$(NO_3)_3 \cdot 6H_2O$ were dissolved in water and potassium carbonate was added as precipitating agent. Obtained precipitate was filtered under reduced pressure (0.04 MPa) and washed several times with cold distilled water to neutral pH, in order to remove residual K^+, CO_3^{2-} and NO_3^- ions. Precipitate was dried at 120 °C and calcined at 500 °C in air. After crushing and sieving, the precursor was in a form of black powder, a grain of 0.20–0.63 mm in size.

The reduction of precursor was carried out in a High Pressure Cell (HPC), being a part of an ultra-high vacuum (UHV) system. The sample in form of a small tablet approx. 10 mm in diameter was mounted on a sample holder. It was put into HPC and sealed from UHV chamber. The HPC was flushed with pure nitrogen at atmospheric pressure and then hydrogen (99.999 vol%) was passed through the volume with a sample. The inlet gas was preheated up to 350 °C before introduction to HPC. The flow was kept constant at 20 cm^3/min. The sample temperature during the reduction process was 500 °C. The process was carried out for 5 h. After reduction, the HPC was evacuated to the pressure of 10^{-6} mbar and the sample was transferred under UHV to the analysis chamber of an electron spectrometer.

The X-ray photoelectron spectra were obtained using Al K_a (hν = 1486.6 eV) radiation with a Prevac system equipped with Scienta SES 2002 electron energy analyzer operating at constant transmission energy (E_p = 50 eV). The spectrometer was calibrated using the photoemission line (with reference to the Fermi level): EB Ag $3d_{5/2}$ = 368.3 eV. The instrumental resolution, evaluated by the full-width at half maximum (FWHM) of the Ag $3d_{5/2}$ peak, was 1.0 eV. The pressure in the analysis chamber during experiments was maintained under 1×10^{-9} mbar. The surface composition of the samples was calculated on the basis of the peak area intensities of the C 1s, O 1s, Co 3p and Ce 3d transitions using the sensitivity factor approach and assuming homogeneous composition of the surface region. Relative sensitivity factors were based on the work by Scofield [15]. The analysis of XPS spectra was preceded by subtraction of a background by application of a multi-region Shirley method [16] (cf [17]).

3. Results and discussion

The application of a High Pressure Cell to the analysis of chemical states of catalysts is vital since many of them contain a metallic active phase. The exposure of these metallic particles to the air leads to their partial or complete oxidation rendering the chemical state of the material to an inactive state. It is imperative to maintain activated catalysts away from the atmosphere not only during the surface analysis but during a whole process, from chemical reactor to the analytical system.

Usually the pressure in the surface analytical systems during the analysis must be kept in mbar range at the highest [18]. Therefore the chemical reactions proceed under these conditions differently than under industrial conditions (pressure gap). A different approach is the application of a HPC combined with an UHV system where a sample is transferred between HPC and analysis chamber without exposure to air. This approach was applied in the studies described herein.

The chemical composition of the sample surface was first investigated before reduction process. A survey spectrum acquired by XPS experiment is shown in Fig. 1a. The presence of cerium, cobalt and oxygen was observed. A relatively small quantity of adventitious carbon was also identified. A quantitative evaluation of surface chemical composition of the precursor is shown in Table 1. The surface is rich in
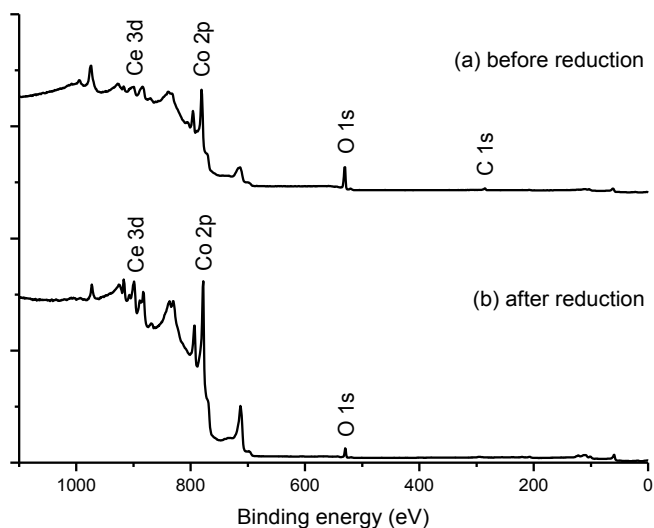
Fig. 1. The survey X-ray photoelectron spectra of ceria-promoted cobalt catalyst for ammonia synthesis. (a) Before reduction, (b) after reduction.

Table 1
Atomic concentrations of Ce, Co, O and C in precursor (before reduction) and active catalyst (after reduction), estimated from the survey spectra.

	Ce (% at.)	Co (% at.)	O (% at.)	C (% at.)
precursor (before reduction)	6	33	48	13
catalyst (after reduction)	16	69	15	–

oxygen as expected for a material composed from oxides.

The sample was next transferred to HPC and reduced under pure hydrogen at 500 °C. After termination of the reduction the sample was transferred back to the analytical chamber for the surface analysis. The transfer took less than 5 min and the sample was kept under the pressure below 1×10^{-9} mbar. A survey spectrum acquired for reduced sample is shown in Fig. 1b. Only cerium, cobalt and oxygen was observed after the reduction. Carbon was completely removed from the catalyst surface (see Fig. 1b and. Table 1). The main constituent of the surface region of the catalyst is cobalt.

High resolution spectra of cobalt and cerium were used to evaluate the chemical state of these elements before and after reduction under hydrogen. XPS Co 2p spectra are presented in Fig. 2. A characteristic
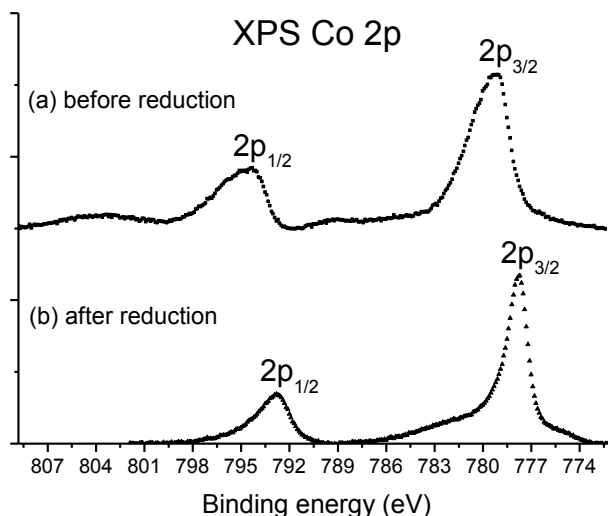
Fig. 2. X-ray photoelectron spectra of Co 2p. (a) Before reduction, (b) after reduction.