



In situ X-ray absorption spectroscopic study on the reducibility of cobalt-containing aluminophosphate molecular sieves

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Abstract

Real-time X-ray absorption spectra (XAS) during the course of temperature-programmed reduction (TPR) were recorded to investigate the reducibility of cobalt on aluminophosphate molecular sieve AlPO-5. When incorporated into the AlPO-5 framework via hydrothermal synthesis, cobalt exhibited high resistance to reduction by hydrogen. In contrast, cobalt could be fully reduced in the temperature range between 400 and 500 °C when supported on the surface of AlPO-5. The coordination number ($N_{\text{Co}-\text{Co}}$) for the first shell was 8.5 on the reduced catalyst with a cobalt loading of ~5 wt.%, corresponding to an average particle size of 35 Å.

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1. Introduction

Cobalt catalysts were widely utilized in hydrotreating processes for a long time. Recently, it has been found that cobalt-containing aluminophosphate molecular sieves exhibit remarkable catalytic activity in partial oxidation of hydrocarbons under mild conditions [1–4]. The reaction mechanism for either hydrotreating or partial oxidation usually involves the redox cycle of the catalytic center. Thus, an understanding of the redox property should be of great importance to the application of cobalt-containing catalysts.

In general, modification of acidity and creation of isolated redox centers are two main motivations

to synthesize metal incorporated zeolite-type catalysts. Compared to silicate and aluminosilicate, aluminophosphate framework was flexible enough to accommodate certain levels of other ions [5]. In the case of aluminophosphates, charges of the framework AlO_4 and PO_4 units were balanced by each other, leading to electro-neutrality of the surface. Brønsted acidity was thought to be generated by isomorphous substitution of Co^{2+} for Al^{3+} . On the other hand, if aluminophosphate was employed as the supporting material for metal catalysts, it is expected to exhibit bi-functional catalytic performance in which the supported metal acts as a redox center and the aluminophosphate framework offers the shape selectivity to reactant and/or product molecules.

In this work, two cobalt-containing aluminophosphate catalysts were prepared, namely CoAlPO-5 and Co/AlPO-5 . On the CoAlPO-5 sample, cobalt was incorporated into the aluminophosphate framework

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via hydrothermal synthesis. In contrast, cobalt exists as extraframework species on the Co/AlPO-5 sample prepared by using post-impregnation method. In situ X-ray absorption spectroscopy (XAS) was employed to characterize the active cobalt centers [6]. Particularly, X-ray absorption near-edge structure (XANES) spectra were recorded during the course of temperature-programmed reduction (TPR), which allows real-time monitoring the change of oxidation state and coordination symmetry of the cobalt species. Besides, extended X-ray absorption fine structure (EXAFS) of a full spectrum serves to reveal local atomic structure of the active sites as supplementary information in some cases.

2. Experimental

2.1. Catalyst preparation

The CoAlPO-5 molecular sieve was synthesized under hydrothermal conditions using orthophosphoric acid (Merck), pseudoboehmite (Kaiser), and cobalt sulfate (Merck) as the starting materials at a molar ratio of 0.2:0.9:2.0. Triethylamine (Wako) was used as the organic template molecule for crystallization. This template material on synthesized CoAlPO-5 sample was removed by calcination in air at 550 °C for 20 h. Detailed synthesis procedure was described elsewhere [7]. Temperature-programmed desorption (TPD) of

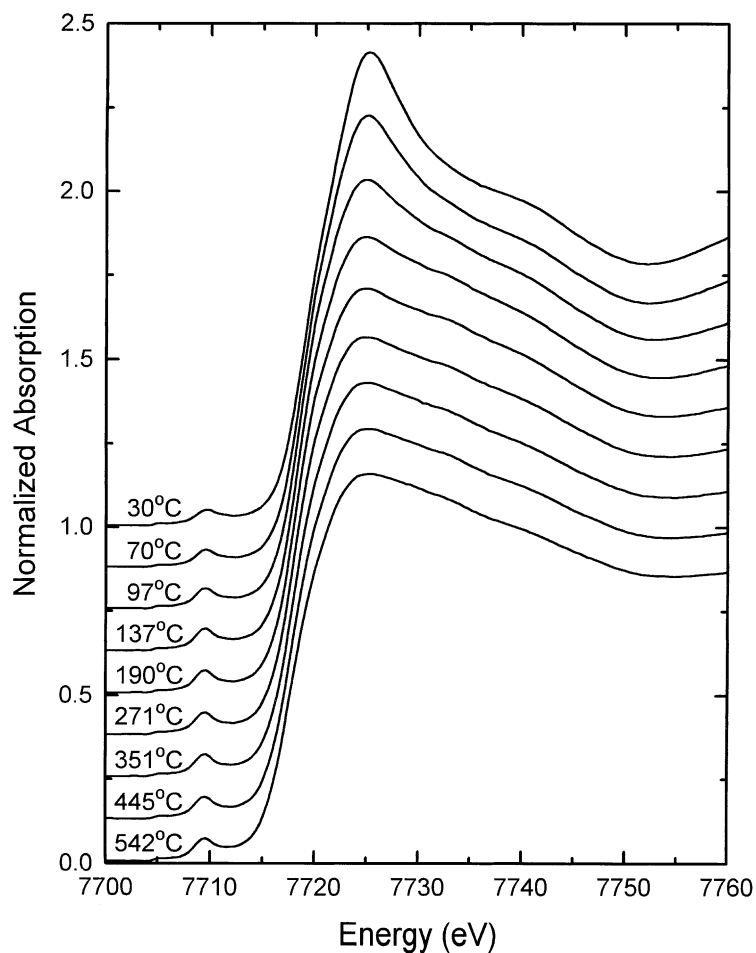


Fig. 1. Real-time XANES spectra of the CoAlPO-5 catalyst recorded during the temperature-programmed reduction. The labeled temperature for each spectrum denotes the midpoint of the recording interval.

NH_4^+ exchanged CoAlPO-5 and UV-Vis spectra of tetrahedral Co^{2+} were used to confirm the isomorphous substitution of Co^{2+} for framework Al^{3+} .

In another procedure, AlPO-5 molecular sieve was firstly synthesized without adding the cobalt salt. The resultant AlPO-5 molecular sieve was then impregnated with an aqueous solution of cobalt sulfate to incipient wetness. The Co/AlPO-5 sample was calcined in air at 550°C for 10 h. Inductively coupled plasma-atomic emission spectrometer (ICP-AES) analysis showed that cobalt contents were 2.86 and 4.87 wt.% on the CoAlPO-5 and Co/AlPO-5 samples, respectively.

2.2. X-ray absorption spectroscopy

All X-ray absorption spectra were recorded at the wiggler beam line 17C of National Synchrotron Radiation Research Center, Taiwan. The electron storage ring was operated at 1.5 GeV with a stored current of 120–200 mA. The monochromator employed two

parallel Si(1 1 1) crystals for energy selection. Spectra were recorded in a transmission mode with the intensities of incident and transmitted X-ray beams measured by gas-filled ionization chambers. Powdered samples were packed into a holder in a compact in situ cell system commercially available [8]. In order to achieve an optimal thickness of the sample, i.e. the spectral jump at the Co K-edge (7709 eV) being around unity, one side of the holder was cushioned with boron nitride spacers to adjust the packing amount. Energy was scanned from 200 eV below the edge to 1000 eV above the edge to obtain a full spectrum, in which the step size used in the near-edge region was 0.4 eV.

With a gas mixture of 10% hydrogen and 90% nitrogen (by volume) flowing through the cell, a full spectrum was recorded at room temperature. Thereafter, the temperature was raised to 550°C at a rate of $2.5^\circ\text{C}/\text{min}$. In this period, spectra were repeatedly recorded in the near-edge region from 7690 eV to 7770 eV. It took about 5 min to collect one real-time

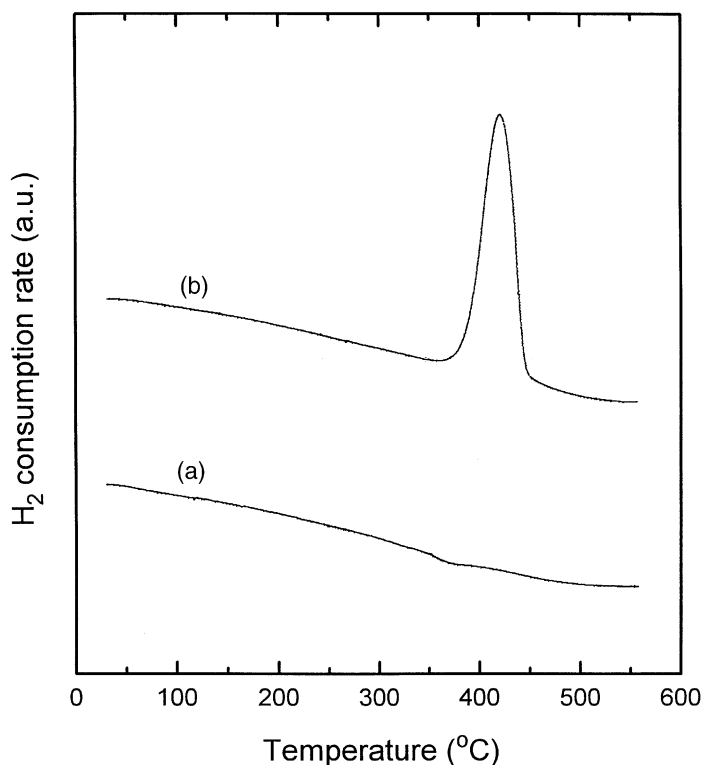


Fig. 2. TPR profiles for (a) CoAlPO-5 and (b) Co/AlPO-5 catalysts at a heating rate of $2.5^\circ\text{C}/\text{min}$.

XANES spectrum. At the end of temperature-programmed reduction, the cell was quenched to room temperature for collecting another full spectrum.

The XANES and EXAFS data were processed following standard procedures [6], including background subtraction, normalization with respect to the edge jump, Fourier transformation, and curve fitting. All the computer programs were implemented in the software package of UWXAFS 3.0 [9]. In addition, the phase shifts and backscattering amplitudes for specific atom pairs were theoretically calculated by using the FEFF6 code [10,11].

3. Results and discussion

3.1. CoAlPO-5 catalyst (via hydrothermal synthesis)

A couple of detailed structural studies based on EXAFS data analysis of various cobalt-containing aluminophosphates both in calcined and reduced forms have been reported in the literature [12,13]. Accordingly, emphasis of this work was focused on the real-time XANES spectra recorded during the TPR. As mentioned above, it takes about 5 min to record one spectrum so that the start point and the end point

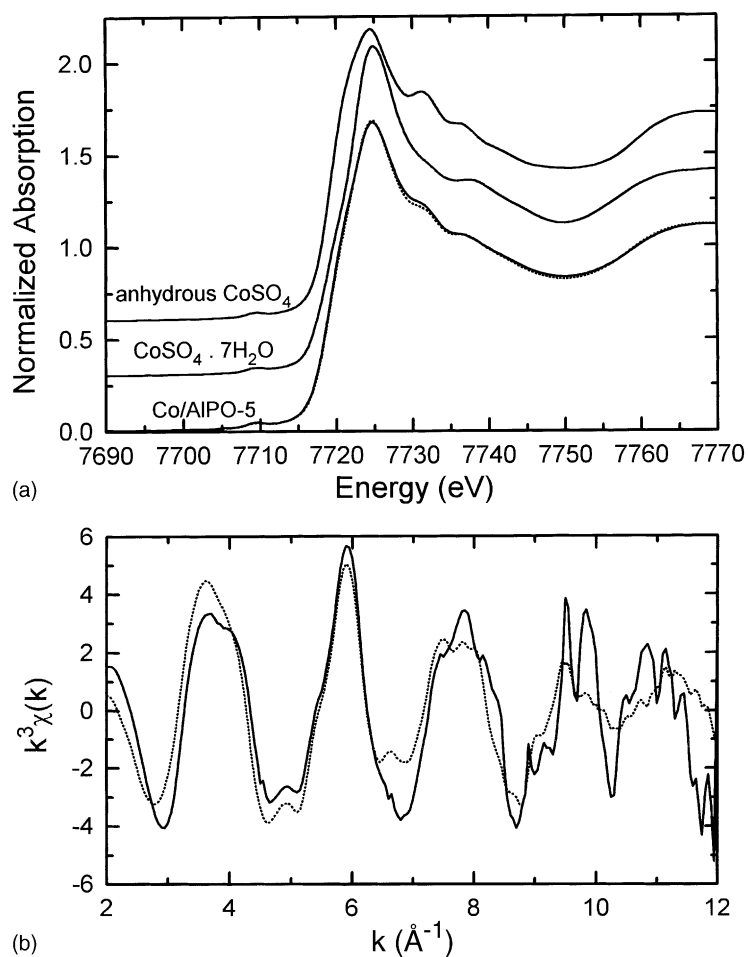


Fig. 3. (a) XANES spectra for anhydrous CoSO₄, CoSO₄·7H₂O, and the calcined Co/AlPO-5 catalyst. The dotted line shows the linear combination (50% anhydrous + 50% heptahydrate) of XANES. (b) The k³-weighted Co K-edge EXAFS of the calcined Co/AlPO-5 catalyst (solid line) compared with the linear combination of the EXAFS (dotted line) for anhydrous CoSO₄ and CoSO₄·7H₂O.

of a single spectrum represent two states with a difference of 13 °C in reduction temperature. Here, we use the average temperature to label each spectrum. Although each point in the XANES spectra corresponded to different reduction temperature (and hence different state), the transition trend of any specific feature serves to follow the progress of reduction if consecutive spectra during the TPR were over-plotted.

According to the edge position of the spectra shown in Fig. 1, the oxidation state of Co species on the CoAlPO-5 catalyst always remained divalent regardless of the reduction temperature. The most appreciable change in the spectral feature lies on the monotonic decrease in the white line intensity from

30 to 140 °C. At temperatures higher than 140 °C, the XANES undergoes negligible change. This fact indicates that no substantial reduction occurs on this catalyst. It is speculated that the initial decline of the white line on heating results from desorption of water molecules because similar spectral change also appeared on heating in helium. Prior to reduction, the calcined CoAlPO-5 sample was stored at ambient condition. Thus, water molecules from atmosphere were no doubt adsorbed on the surface, leading to the formation of some $\text{Co}\cdots\text{O}$ bonds. These extra $\text{Co}\cdots\text{O}$ bonds more or less destroy the tetrahedral symmetry around the Co center so that the original pre-edge peak (located near 7710 eV) is smaller. This pre-edge

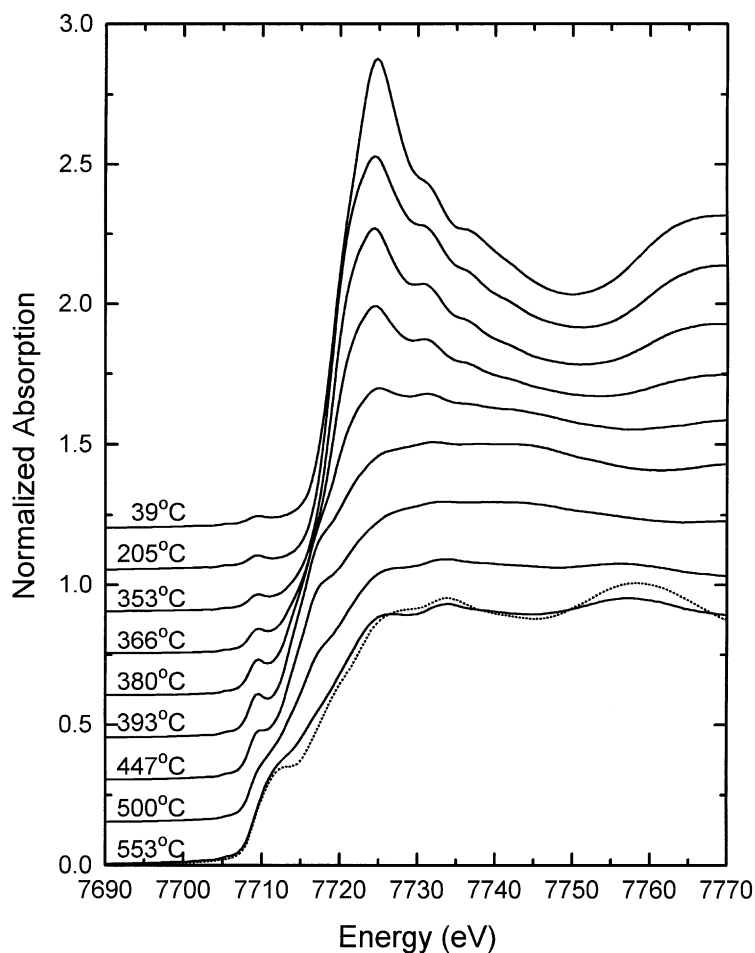


Fig. 4. Real-time XANES spectra of the Co/AlPO-5 catalyst recorded during the temperature-programmed reduction. The dotted line denotes the XANES of a reference Co foil measured at room temperature.

peak arises from the $1s \rightarrow 3d$ transition which is only quadrupole-allowed for coordination sites without centric symmetry. As the reduction temperature increased, water molecules escaped from the surface and hence a regular tetrahedral coordination was restored, accompanied by a slight growth of the pre-edge peak.

Fig. 2 shows the TPR profiles in which the hydrogen consumption rate was monitored by a thermal conductivity detector (TCD) located at the outlet from the in situ cell. A molecular sieve 5A trap immersed in an ice bath was placed between the sample cell and the TCD to remove any water vapor produced in reduction. Because the sample holder itself is not completely gas-tight (only sealed by screwing beryllium foils to both sides), a small leakage of the reducing gas out from the cell occurs during the TPR, giving an

inclined baseline of the TCD signal. Nevertheless, it can be seen from Fig. 2(a) that no hydrogen consumption was detected for the CoAlPO-5 catalyst. This evidence indicates a high resistance of Co species toward reduction by hydrogen, in agreement with the observation from real-time XANES spectra.

3.2. Co/AlPO-5 catalyst (via impregnation)

The structure of Co/AlPO-5 catalyst in a calcined form was investigated by the use of both XANES and EXAFS, as shown in Fig. 3. It is interesting to note that Co species in this state resemble a mixture of anhydrous CoSO_4 and its heptahydrate analogue with nearly equimolar ratio. A linear combination of the XANES for anhydrous CoSO_4 and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$

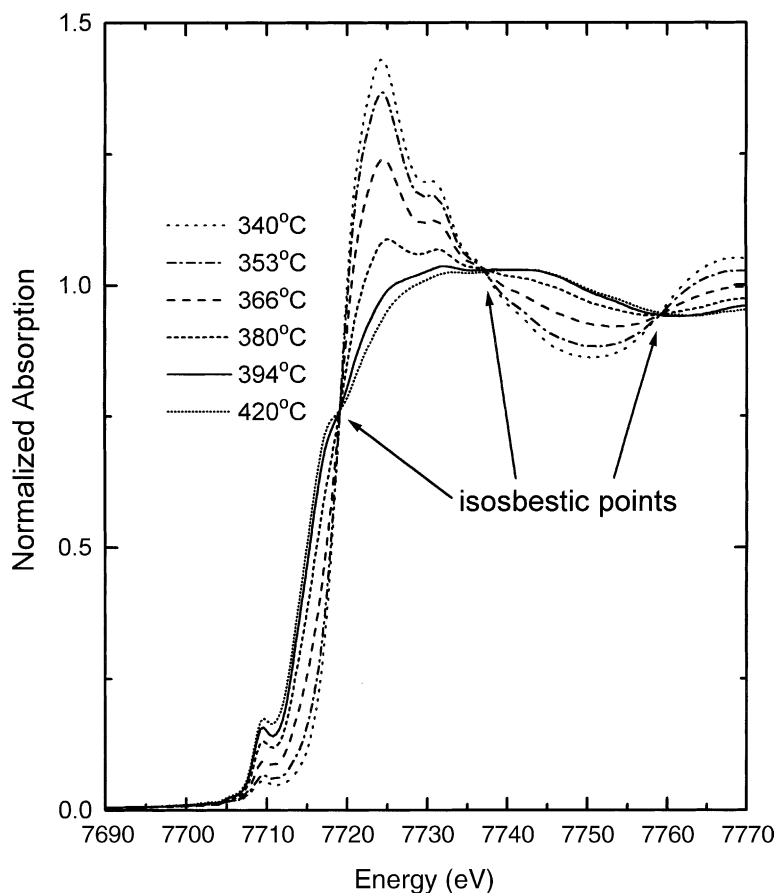


Fig. 5. Consecutive XANES spectra of the Co/AlPO-5 catalyst recorded during the reduction in the temperature range between 340 and 420 °C.

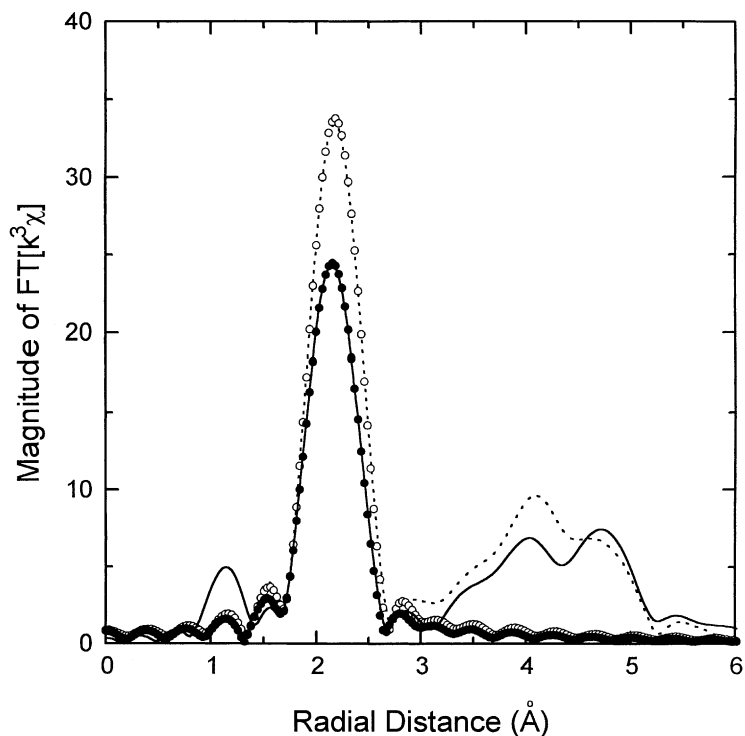


Fig. 6. Fourier transformation of k^3 -weighted EXAFS data for the reduced Co/AlPO-5 catalyst (solid line) and a reference Co foil (dotted line) measured at room temperature. Computer-fitted results to the first coordination shell were shown by circles. Data ranges for Fourier transformation (without phase correction) and fitting are $\Delta k = 3.25\text{--}11.95 \text{ \AA}^{-1}$ and $\Delta R = 1.4\text{--}2.7 \text{ \AA}$.

reproduces that of Co/AlPO-5 catalyst quite well. Similar situation occurs on the EXAFS data. On heating in air, the $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ precursor will dehydrate to form the anhydrous product. This anhydrous form is stable up to 700°C [14]. Therefore, it remained intact during the calcination. Once stored in ambient condition, a portion of anhydrous CoSO_4 was re-hydrated on the AlPO-5 support. The TPR profile of a supported Co catalyst starting from sulfate was found essentially the same as that of the unsupported cobalt salt, suggesting negligible interaction between the support and the salt. This was also observed by Van Steen et al. [15] with the TPR peak temperature 100°C higher than that observed in this work. The difference might be ascribed to lower heating rate and higher H_2 concentration in the gas stream employed here.

Fig. 4 presents the real-time XANES spectra of the Co/AlPO-5 catalyst at Co K-edge during the TPR. In contrast to the case of CoAlPO-5, dramatic change in XANES was observed for the Co/AlPO-5 catalyst

as the reduction temperature increased. The intensity of the white line progressively diminished with the position of absorption threshold shifting to lower energy. Both facts reflect the reduction of cobalt species. Most markedly, the spectral features show rapid transition in the temperature range between 340 and 420°C . To have a closer examination to the transition, all consecutive spectra in this temperature range are over-plotted in Fig. 5. It is worth noting that every spectrum passes through some common points, so-called isosbestic points. The appearance of such isosbestic points generally implies one-step transition [16]. Indeed, the TPR profile for the Co/AlPO-5 catalyst exhibited a single peak at 420°C (see Fig. 2b), fairly consistent with the XANES evidence in terms of the reduction mechanism.

As the reduction temperature was increased, the “take-off” point of the edge jump shifted to lower energy. Finally, the small pre-edge peak observed in the calcined state merged with the edge jump to appear

as a shoulder, which is a characteristic feature for the metallic cobalt. The XANES of 553 °C-reduced sample showed almost the same edge position and relative intensity of the shoulder as those of a reference Co foil (see Fig. 4). From this evidence, we can infer that all Co species on the Co/AlPO-5 catalyst have been fully reduced. The slight difference existing between these two spectra was attributable to the following issues: the metallic Co particles thus formed are quite small so that metal-support interactions incur a perturbation to the electronic structure and hence the spectral features in near-edge region. Moreover, the real-time spectrum was recorded at relatively high temperature in which higher thermal disorder of neighboring atoms leads to smaller EXAFS oscillation amplitude.

Due to the low signal-to-noise ratio, no attempt was made to analyze the EXAFS data collected at high temperatures. Instead, Fig. 6 shows the radial distribution function (without phase correction) around Co atom obtained by taking Fourier transform of k^3 -weighted EXAFS data collected at room temperature. As can be clearly seen in Fig. 6, both Co/AlPO-5 catalyst and Co foil have substantially the same local atomic structure. This evidence again indicates full reduction of Co species on the Co/AlPO-5 catalyst. The coordination number for the first Co–Co shell ($N_{\text{Co-Co}}$) was found to be 8.5 on the reduced Co/AlPO-5 catalyst, in comparison with the value of 12 for bulk Co foil with a hcp structure. This calculated $N_{\text{Co-Co}}$ value corresponds to an average particle size of about 35 Å on the assumption of the close-packed structure [17,18]. Because the dimension of intraframework channels of AlPO-5 is smaller than 10 Å, most Co metal particles should reside on the external surface of AlPO-5 crystals.

4. Conclusions

The reducibility of cobalt-containing aluminophosphates was studied by means of combined XAS and TPR techniques. When incorporated into the AlPO-5 framework (as for CoAlPO-5), the oxidation state of cobalt always remained divalent and no hydrogen consumption was observed during the TPR. However, the

extraframework Co species on Co/AlPO-5 were reduced to metallic state at temperatures higher than 400 °C. The information from real-time XAS and TPR provides a detailed insight into the reduction mechanism and helps to elucidate the redox property of the catalysts.

Acknowledgements

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