



## Local structures of cobalt in Co-doped TiO<sub>2</sub> by synchrotron x-ray absorption near edge structures

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### ABSTRACT

The local structures of cobalt in Co-doped TiO<sub>2</sub> were studied by combining K-edge x-ray absorption near edge structures (XANES) measurements with first-principles calculations. The Co/TiO<sub>2</sub> samples were prepared by (1) sol-gel and (2) co-precipitation methods. To identify the local structure around Co, the measured spectra are compared against the spectra measured from Co<sub>3</sub>O<sub>4</sub>, CoO and Co foil standard samples as well as first principles XANES based on several atomic models. For the sample prepared by the co-precipitation method, Co atoms clearly form a separated Co<sub>3</sub>O<sub>4</sub> phase because the XANES spectrum is almost identical to that of Co<sub>3</sub>O<sub>4</sub>. For the sample prepared by the sol-gel method, the spectrum does not look like a spectrum of any of the standards. The possible local structures of Co in the sol-gel prepared sample are discussed. Our work illustrated that XANES is a powerful technique that can be used to probe the local structures of minority atoms even if the standard x-ray diffraction techniques failed.

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### 1. Introduction

The Fischer-Tropsch synthesis (FTS) is a process composed of a set of chemical reactions used to produce liquid hydrocarbons from carbon monoxide (CO) and hydrogen. Because CO is toxic and the obtained hydrocarbon can be used as petroleum substitute, the process gained world wide attentions. The most effective catalysts for FTS are cobalt (Co), iron (Fe), and ruthenium (Ru) [1,2]. It is known that Co is the most active catalyst for FTS based on natural gas, has high selectivity to linear long-chain hydrocarbons, and has low activity for the water-gas shift (WGS) reaction [1,3]. The most common catalyst supports for FTS are alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), and titanium dioxide (TiO<sub>2</sub>) [3–6]. In this work, TiO<sub>2</sub> will be used as a catalyst support because of its ability to increase the reduction [6].

TiO<sub>2</sub> supported Co catalysts were prepared by sol-gel and co-precipitation methods. To characterize the samples, the x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) techniques were used. The XRD technique is a powerful technique to identify the crystal structures, especially to gain information on the

polymorph of TiO<sub>2</sub>. XRD is also a standard technique to probe a phase separated structures. In our case here, we can try to look for other phases of Co, such as CoO and Co<sub>3</sub>O<sub>4</sub>. We will show that XRD misses the phase separated cobalt oxides in our case here where they are expected to form small-size clusters. While XRD requires a long-range ordering and is not element specific, the XAS is highly element selective and does not require a long-range ordering to probe the local structure [7]. By choosing the x-ray energy, one can probe only the interested element (in our case, Co) that has excitation energy matching with the x-ray energy. XAS can be divided into two regions: x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption spectroscopy (EXAFS). Both XANES and EXAFS have been widely used to identify the local structures of the interested atoms. The spectra contain information of the local structure around the interested atom as well as the oxidation state of the atom. However, in many cases, especially for the XANES interpretations, it is quite complicated to extract the structural information without some prior knowledge of similar systems. For such cases, first principles calculations can be used in conjunction with the measurements to interpret the results. For the EXAFS analysis, some information on the bond distances and coordination number can be obtained readily by simple Fourier transform of the spectra and simple scattering models.

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In this work, a combination of Co *K*-edge synchrotron XANES measurements and first-principles calculations was used for identifying the local structures of Co atoms in Co-doped TiO<sub>2</sub> samples grown by two different methods: the sol-gel method and the co-precipitation method. We have successfully utilized the combined XANES measurements and first-principles calculations to identify the local structures of other systems [8–11].

## 2. Experiment

### 2.1. Sample preparation

In the sol-gel method, titanium isopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, Fluka, analytical grade) in an amount of 0.01 mol was slowly dropwise into 0.33 mol isopropanol (C<sub>3</sub>H<sub>8</sub>O, QR&C, analytical grade) with stirring. Ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH, Fluka, 98%) in an amount of 0.07 mol was added into the solution. After that, 0.04 mol deionized water was added and stirred until the solution was homogeneous. The sol was allowed to rest in an oven at 348 K until the gel was formed. Then, the gel was dried at 383 K for 24 h. The dried sample was further calcined at 823 K for 4 h with a ramp rate of 1.7 K/min under the flowing of N<sub>2</sub>/O<sub>2</sub> (70/30) gas with the flow rate of 100 cm<sup>3</sup>/min. The obtained sample will be referred to as TiO<sub>2</sub>-SG. For a Co-doped TiO<sub>2</sub>-SG catalyst (Co/TiO<sub>2</sub>-SG), the sample was prepared using the method described above with the addition of cobalt nitrate hexahydrate (Co(NH<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, Univar, analytical grade). The Co precursor in an amount of 10% w/w (dissolved in 0.04 mol deionized water) was added into the sol solution.

For the co-precipitation method, the sample was prepared from suspension of 0.038 mol titanium oxide (Aldrich, anatase ≥99%) in 10% w/w cobalt nitrate solution (cobalt nitrate hexahydrate in 20 cm<sup>3</sup> deionized water). Co(OH)<sub>2</sub> was precipitated from NH<sub>3</sub> solution at pH 7.5 ± 0.2 at 368 K under vigorous stirring. After that, the suspension was heated for a short period, and filtered off at the boiling temperature. The filtered solid was washed and dried at 383 K in an oven. The prepared catalyst was calcined at 823 K for 2 h with a ramp rate of 2.0 K/min under the flowing of argon gas with the flow rate of 40 cm<sup>3</sup>/min. The obtained sample will be referred to as Co/TiO<sub>2</sub>-CP.

### 2.2. Sample characterization

#### 2.2.1. X-ray diffraction (XRD)

X-ray diffraction is a powerful technique to determine the crystalline phases in the samples. For our study, we focus our attentions to the anatase or rutile phases of TiO<sub>2</sub>. We also tried to look for other phases of Co, such as CoO and Co<sub>3</sub>O<sub>4</sub>. The later is to see if Co forms clear phase separated structures. The measurement was conducted using a Philips X'Pert diffractometer with Cu *K*<sub>α</sub> (λ = 1.54 Å) source. The spectra were scanned with the step size of 0.01° in the scanning range 2θ = 10°–80°.

#### 2.2.2. X-ray absorption spectroscopy (XAS)

To study the local structures around the Co atom in the sample, we used the XAS technique with the Co *K*-edge photon energy. XAS measurements were performed in the transmission mode at the XAS beam line (BL-8) of Synchrotron Light Research Institute, Thailand. The electron energy was 1.2 GeV with the beam current of 150–80 mA. A double crystal monochromator Ge(220) was used to scan the photon energy. For the Co *K*-edge XANES measurements, the scanning step was set at 0.2 eV in the photon energy range of 7669–7819 eV. To process the XANES spectra, we performed a standard routine, i.e., a background subtraction and normalization of the raw data.

## 3. Computational method

### 3.1. Crystal structure and formation energy

To gain insight of the stability of Co atom at various sites in TiO<sub>2</sub> crystal, the first principles formation energy calculations were performed. The calculations were based on density functional theory within the local density approximations (LDA). For the electron–ion interactions, we used projector augmented wave potentials [12], as implemented in the VASP code [13,14], with an energy cutoff of 500 eV for the plane-wave basis set. The calculated lattice parameters of anatase TiO<sub>2</sub> are *a* = 3.767 Å, *c/a* = 2.513 Å, and *u* = 0.208 which are in good agreement with the experimental values of *a* = 3.785 Å, *c/a* = 2.513 Å, and *u* = 0.208 [15].

To study defects such as Co substitute for Ti (Co<sub>Ti</sub>) or interstitial Co (Co<sub>i</sub>), a supercell approach was used [16]. We used a 108-atom supercell, which is a 3 × 3 × 2 repetition of the conventional 8-atom TiO<sub>2</sub> unit cell. The Monkhorst-Pack scheme [17] with a sampling mesh of 2 × 2 × 2 special *k*-points is used for the *k*-space integrations. All atoms in the supercell were allowed to relax until the Hellmann-Feynman forces [18] on all atoms become less than 10<sup>−3</sup> eV/Å. The defect formation energy is defined as

$$\Delta H_f = E_{tot}(D, q) - E_{tot}(0) + \sum \Delta n_x \mu_x + q(E_f + E_v), \quad (1)$$

where  $E_{tot}(D, q)$  is the calculated total energy of a supercell with defect *D* in charge state *q*,  $E_{tot}(0)$  is the calculated total energy of a supercell without any defect.  $\Delta n_x$  is the number of atoms from species *X*, where *X* can be Ti, O, or Co, being added (removed) to (from) a supercell, from (to) its respective reservoir with chemical potential  $\mu_x$ , to form the defect cell.  $E_f$  is energy of the electron reservoir with which the electrons are exchanged. The energy level also referred to as Fermi level.  $E_v$  is the valence band maximum (VBM) which we used the average value overall sampling *k*-points following the scheme of Zhang [19,20]. To align the energy levels between the supercell containing a defect with that of the bulk, we aligned the core potential of atoms far away from the defect in the supercell containing a defect with that of the corresponding atoms in the defect-free supercell. The upper limits for  $\mu_{Ti}$  and  $\mu_o$  are the energies per atom of metallic Ti and gaseous O<sub>2</sub>, which are offset to zero in the present study. To grow the TiO<sub>2</sub> crystal in equilibrium, it is required that  $\mu_{TiO_2} = \mu_{Ti} + 2\mu_o$ , where  $\mu_{TiO_2}$  is the formation energy per molecular formula of anatase TiO<sub>2</sub> (calculated value:  $\mu_{TiO_2} = -9.98$ ) [20]. For the chemical potential of cobalt ( $\mu_{Co}$ ) we used the energy per Co atom of metallic Co and Co<sub>2</sub>O<sub>3</sub> for Ti-rich and O-rich growth condition, respectively.

### 3.2. X-ray absorption spectroscopy

In order to calculate the Co *K*-edge XAS spectra in the XANES region of Co-doped TiO<sub>2</sub> from the model structures, FEFF8.2 codes were used [21,22]. The codes utilize the full multiple scattering approach based on *ab initio* overlapping muffin-tin potentials. These potentials were obtained using self-consistent calculations with Hedin-Lundqvist exchange–correlation function [23]. The self-consistent calculations were performed in the sphere with a radius of 5.5 Å (containing approximately 70 atoms) around the selected absorber (in this case, Co) atom. The full multiple scattering calculations, which include all possible paths within a larger cluster radius of 8.4 Å (containing approximately 240 atoms), were used. The core-hole correction was also applied. The results presented in this work are presented *without* shifting any of the simulated spectra to align with those of the experiment.

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