Surface Chemical Structures of CoO$_x$/TiO$_2$ Catalysts for Continuous Wet Trichloroethylene Oxidation

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Abstract–An earlier sample of 5% CoO$_x$/TiO$_2$ used for the wet oxidation of TCE at 310 K for *ca.* 6 h has been characterized with a fresh catalyst *via* XRD and XPS measurements. The binding energy for Co 2p$_{3/2}$ of the fresh sample appeared at 781.3 eV, which was very similar to the chemical states of CoTiO$_x$ such as Co$_2$TiO$_4$ and CoTiO$_3$, whereas the spent catalyst indicated a 780.3-eV main peak for Co 2p$_{3/2}$ with a satellite structure at a higher energy region. This binding energy was almost equal to that of Co$_3$O$_4$ among reference Co compounds used. The phase structure of Co$_3$O$_4$ was revealed upon XRD measurements for all the catalyst samples. Based on these XPS and XRD results, a surface chemical structure of CoO$_x$ species existing with the fresh catalyst can be proposed to be predominantly Co$_3$O$_4$ encapsulated completely by very thin filmlike CoTiO$_x$ consisting of Co$_2$TiO$_4$ and/or CoTiO$_3$, with a tiny amount of Co$_3$O$_4$ particles covered partially by such cobalt titanates which may be responsible to the initial catalytic activity. Those CoTiO$_x$ overlayers on Co$_3$O$_4$ particles may be readily removed into the wet media within 1 h at 310 K based on our earlier study, thereby giving rapid increase in the catalytic activity for that period.

Key words: Catalytic Wet Oxidation, Cobalt Oxides, Trichloroethylene, Surface Chemical States, XPS

INTRODUCTION

Wastewaters containing chlorinated hydrocarbons such as trichloroethylene (TCE) and perchloroethylene (PCE) from many industrial processes for degreasing, resins and plastics production, dry cleaning, metal fabrication, insecticides and herbicides production and so forth are very toxic for aquatic system even at concentrations of ppm levels. Therefore, appropriate, efficient treatment technologies are required for processing them to non-toxic or biodegradable substances [Lee et al., 2004; Pintar, 2003; Sidebottom and Franklin, 1996]. Not only could chemical and physical treatments be difficult to process effluent streams including very dilute chlorinated compounds, but biological processes are also unavailable for highly concentrated chlorinated compounds. In these cases, catalytic wet oxidation can offer a suitable approach to remove such toxic organic materials from wet streams, although photocatalytic oxidation may be an alternative technique [Kim and Lee, 2004; Kim et al., 2004].

Catalytic wet oxidation technologies to process wastewaters containing organic compounds can be usually differentiated as the following two systems: homogeneous and heterogeneous wet catalyses. These catalytic processes can effectively decompose aqueous organic hydrocarbons under milder typical operating conditions (T= 353-473 K, P=101.3-2,000 kPa) than noncatalytic systems [Pintar and Levec, 1992]. Homogeneous catalytic systems generally give a better efficiency in catalytic destruction of toxic organic substances in wet waste streams compared to heterogeneous-catalyzed processes; however, the dissolved metal ions must be eliminated from the processing stream, thereby requiring complicated chemical and physical treatment steps. A very simple separation process such as

filtration needs wet oxidation of wastewaters containing chlorinated organics over heterogeneous catalysts in batch reactors; furthermore, such subsequent process is not essential if the heterogeneous wet catalysis is conducted in continuous flow type fixed-bed reactors.

Supported metal oxides, representatively CuO$_x$, PdO, PtO, CeO$_x$ and mixed metal oxides consisting of Cu, Zn, Mn and La, and unsupported metal oxides, such as CuCeO$_x$, MnCeO$_x$, FeO$_x$ and CuCr$_2$O$_4$, have been widely employed for heterogeneous wet catalysis of aqueous wastes containing phenol, acrylic acid, etc. in the temperature range of 353-523 K [Haumodi et al., 1998; Hocevar et al., 1999; Hosokawa et al., 1998; Larachi et al., 2001; Pintar and Levec, 1992; Sadana and Katzer, 1974; Silva et al., 2004]. The suitability of these catalysts could be associated primarily with the chemical composition of the waste streams to be processed. Cobalt oxides and their related catalysts have been widely used for gas-phase CO and (chlorinated) hydrocarbon oxidations and Fischer-Tropsch synthesis [Drago et al., 1995; Krishnamoorthy et al., 2000; Thormahlen et al., 1999]. High activity for CO oxidation even at ambient temperature was achieved with pure Co$_3$O$_4$ and supported CoO$_x$ catalysts [Thormahlen et al., 1999; Yao, 1974]. However, there are few, if any, previous studies of such cobalt oxide catalysts for heterogeneous catalytic wet oxidation of aqueous organic materials in a continuous flow fixed-bed reactor.

We have recently studied catalytic wet oxidation of TCE over a 5% CoO$_x$/TiO$_2$ at conditions under which a stable removal efficiency, by 46%, from 1 up to about 6 h is established with only an initial TCE conversion of 6% at 5 min as shown in Fig. 1 [Kim and Choo, 2004], *i.e.*, 310 K and 130 kPa. No limitation on the internal mass transport in the heterogeneous wet catalysis could occur with TiO$_2$ ranging from 20 to 80 mesh sizes, and the bare TiO$_2$ revealed zero activity in the wet TCE decomposition reaction for all on-stream hours covered. Although the 5% CoO$_x$/TiO$_2$ catalyst has been promising for continuous wet TCE oxidation at such low temperatures

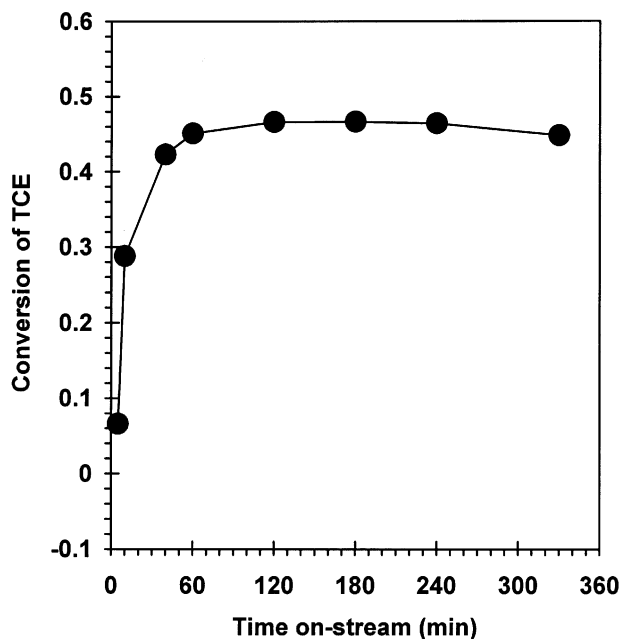[†]To whom correspondence should be addressed.
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Fig. 1. Catalytic activity profile of 5% CoO$_x$/TiO$_2$ with a 30/40-mesh size for wet TCE oxidation at 310 K [Kim and Choo, 2004].

and operating pressures, this catalyst possessed transient period in the catalytic activity during the initial reaction period. Therefore, this study was conducted to explain such earlier unsteady-state behavior *via* XRD and XPS characterizations of an earlier spent 5% CoO$_x$/TiO$_2$ with a fresh sample.

EXPERIMENTAL

1. Catalyst Preparation

A shaped DT51D TiO$_2$ (Millennium Chemicals) was crushed and sieved to a 30/40-mesh size following calcination at 843 K for 4 h in flowing air (Prexair, 99.999%) at 1 L/min. CoO$_x$/TiO$_2$ catalyst containing 5% CoO$_x$ based on the Co element was obtained by an incipient wetness technique in which an aqueous solution of Co(NO$_3$)$_2$·6H$_2$O (Aldrich, 99.999%) was impregnated dropwise. Details of such a catalyst preparation have been described previously [Kim and Choo, 2004; Kim et al., 2002]. An earlier 5% CoO$_x$/TiO$_2$ catalyst, which had undergone continuous wet TCE oxidation at 310 K for almost 6 h [Kim and Choo, 2004], was used after sufficient drying at ambient conditions.

2. Characterization *via* XRD and XPS

Prior to obtain X-ray diffractograms of a fresh 5% CoO$_x$/TiO$_2$, this catalyst was calcined *in situ* in the reaction system in a fashion identical to that used upon the wet TCE oxidation. Reference Co samples such as CoO, Co$_3$O$_4$ and Co(OH)$_2$ were used as-received for XRD measurements. XRD spectra of these samples were collected *ex situ* by using a Rigaku D/MAX2500 PC diffractometer equipped with a Cu Kα (λ=1.54056 Å) radiation source and a graphite monochromator. Each sample was loaded onto a thin quartz holder in the diffractometer and scanned from a 2θ value of 10 to 80° at a normal scanning rate of 2.0°/min. Subsequently, a high resolution scanning rate of 0.1°/min was allowed to obtain more accurate peaks of Co$_3$O$_4$ in the 5% CoO$_x$/TiO$_2$ catalysts and average crystallite sizes

of the Co$_3$O$_4$ were estimated based on line width at half height of the XRD peak by the crystallographic (220) plane using the Scherrer equation with Warren's correction.

Co 2p XPS spectra of 5% CoO$_x$/TiO$_2$ catalysts were obtained with a VG Scientific ESCALAB 220iXL X-ray photoelectron spectrometer, giving a dynamic vacuum below 10^{-10} Torr (1 Torr=133.3 Pa), with an unmonochromatized Mg Kα photon source having a radiation energy of 1253.6 eV. An appropriate amount (*ca.* 20 mg) of a sample of 5% CoO$_x$/TiO$_2$ after either calcination at 843 K in flowing air for 1 h or subsequent TCE removal reaction at 310 K for on-stream hours near 6 was loaded into a pelletizer with a 10-cm diameter to press it to a thin self-supporting wafer [Kim et al., 1998], but the reference Co compounds were pelletized as-received without such a pretreatment. All XPS spectra of the samples were corrected by using the C 1s peak at 284.8 eV by internal carbonaceous species.

RESULTS

The powder XRD pattern of the spent catalyst was taken to identify crystalline phase structure of the CoO$_x$ present on the TiO$_2$ surfaces and compared to those of the reference Co compounds employed and a sample of 5% CoO$_x$/TiO$_2$ following the high temperature calcination, as shown in Fig. 2. An original intensity of the XRD patterns for all the samples was reduced, by 60%, to give an easier comparison; however, all reflection peaks were clearly visible even after such reduction. The pure anatase-type TiO$_2$ showed
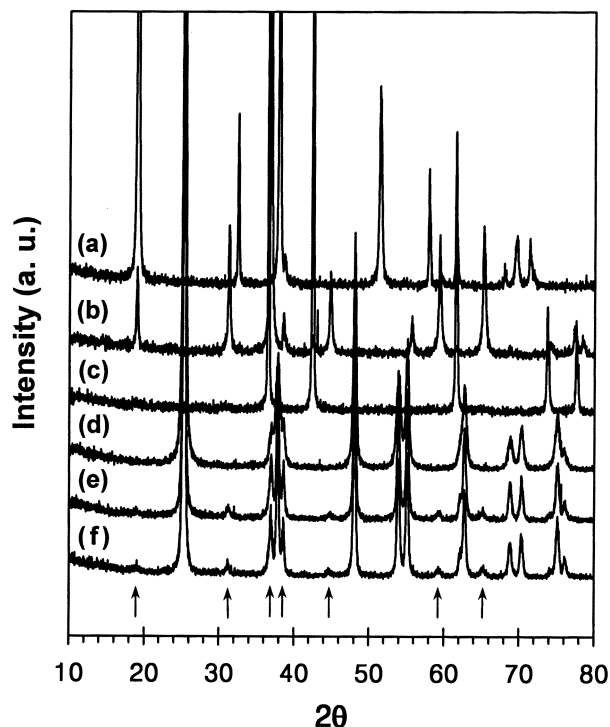

Fig. 2. X-ray diffraction patterns for: (a) Co(OH)$_2$; (b) Co$_3$O$_4$; (c) CoO; (d) TiO$_2$; (e) 5% CoO$_x$/TiO$_2$ calcined at 843 K in an air flow for 1 h; and (f) 5% CoO$_x$/TiO$_2$ used for wet TCE decomposition at 310 K for *ca.* 6 h. The upward arrows represent the diffraction lines by Co$_3$O$_4$.

predominant characteristic peak at a 2θ value of 25.30°, corresponding to the (101) crystalline plane, with subsequent reflections at higher 2θ values (Fig. 2d). Additional diffraction lines by CoO$_x$ species in the fresh catalyst appeared at 2θ values of 18.98, 31.19, 36.92, 38.58, 44.79, 59.37 and 65.22°, as indicated by the upward arrow in Fig. 2. Similar diffraction peaks due to CoO$_x$ crystallites were obtained for the catalyst used for the 6-h on-stream time in the aqueous solution, as shown in Fig. 2f. The Co(OH)$_2$ gave the most intense reflection at 2θ=19.04°, along with subsequent diffraction peaks at higher 2q values. Diffraction patterns, taken with the reference Co$_3$O$_4$ sample, occurred at 2θ values of 18.99, 31.26, 36.84, 38.56, 44.80, 59.38 and 65.22°, and the 36.84° peak concerning with the crystallographic (311) plane of Co$_3$O$_4$ was predominant. These reflection lines of this reference sample were quite similar to those shown in Fig. 2e and 2f. XRD measurement for the reference CoO yielded two intense peaks at 2θ=36.56 and 42.42° with three weak peaks at 2θ=61.54, 73.78 and 77.67° (Fig. 2c); however, there were no discernible CoO peaks in the 5% CoO$_x$/TiO$_2$ catalysts. The Co$_3$O$_4$ present on the TiO$_2$ support of the spent catalyst indicated a crystallite size of 29 nm, based on the 31.26° peak corresponding to the (220) plane, if it is assumed to be comprised of spherical crystallites. A very similar particle size for Co$_3$O$_4$ could be obtained with the fresh catalyst.

To determine surface chemical states of CoO$_x$ species in the spent CoO$_x$/TiO$_2$ catalyst, the Co 2p XPS spectra were obtained with this catalyst in addition to samples of a fresh 5% CoO$_x$/TiO$_2$, and reference Co compounds, as depicted in Fig. 3. The difference in XPS spectral features between the spent and fresh catalysts was of particular interest because of the need to induce the reason why the steady-state conversion was achieved *via* the transient period during the earlier wet TCE removal reaction at 310 K [Kim and Choo,

Fig. 3. Co 2p XPS spectra for reference Co compounds, and 5% CoO$_x$/TiO$_2$ (a) calcined at 843 K for 1 h in flowing air and (b) used in wet TCE oxidation at 310 K for *ca.* 6 h.

2004]. The fresh Co catalyst gave two main peaks at binding energies of 781.3 and 797.1 eV for the respective Co 2p$_{3/2}$ and Co 2p$_{1/2}$ with each corresponding satellite peak at higher energies, as shown in Fig. 3a. Co 2p$_{3/2}$ main peak for the spent catalyst appeared at a binding energy of 780.3 eV with a shake-up structure of 795.8 eV (Fig. 3b). The CoO used as a reference Co chemical was characterized by main peaks at 779.6 and 795.1 eV with discernible satellites at higher binding energies. Two predominant peaks at 781.2 and 797.2 eV for main Co 2p XPS spectra with intense satellite structures were represented for Co(OH)$_2$ and these values are very close to those obtained with the fresh CoO$_x$/TiO$_2$ catalyst. Regardless, the surface chemical states of the CoO$_x$ in the fresh catalyst would not be associated with the Co(OH)$_2$ because this had been calcined in flowing air at 843 K for 1 h prior to taking of the XPS spectrum. A main Co 2p$_{3/2}$ XPS peak at 780.3 eV with a shake-up peak at 795.5 eV was observed for the reference Co$_3$O$_4$, which is very similar to that obtained with the earlier spent catalyst.

DISCUSSION

XPS spectra of metal oxide catalysts usually consist of a main peak accompanied by an adjacent shake-up structure at higher binding energy. The measurements of the binding energy of main and satellite structures for the metal elements, the intensity ratio (S/M) of the satellite peak to the corresponding principal one and the spin-orbit coupling (ΔE) can allow us to determine their surface chemical states and composition in addition to their coordination environments [Venezia, 2003]; however, such chemical information revealed for the surface layer ranging from 20 to 50 Å can be significantly different from that in the entire sample because of typical sampling depth of the spectroscopic technique. This discrepancy can be eliminated by XRD measurements for the solid sample, although these only give us information on the bulk-phase structure.

Characterization of both fresh and spent titania-supported CoO$_x$ samples by acquiring XPS spectra of Co 2p core levels was of particular interest because this surface-sensitive technique can usually allow us to distinguish between surface structures of the CoO$_x$ species active for the wet decomposition at 310 K. CoO gives strong shake-up peaks for Co 2p$_{3/2}$ by Co^{2+} ions occupying the octahedral sites [Brik et al., 2001; Voβ et al., 2002]. Both magnetic Co^{2+} ions in the tetrahedral sites and diamagnetic Co^{3+} ions in the octahedral sites are present in Co$_3$O$_4$ but these two sites are indistinguishable by this instrumental technique [Brik et al., 2001; Ho et al., 1992; Sexton et al., 1986; Voβ et al., 2002]. The Co$_3$O$_4$ employed as a reference compound has very weak satellite structures for Co 2p$_{3/2}$ because of the coexistence of the low-spin Co^{3+} ions, compared to the CoO (Fig. 3). Thus, it is not difficult to differentiate the Co 2p, particularly 2p$_{3/2}$, spectral difference between the reference CoO and Co$_3$O$_4$ compounds. Cobalt hydroxide shows strong shoulders with the corresponding intense Co 2p core level lines at lower binding energies, which is consistent with previous study [Ho et al., 1992]. A multitude of XPS, NIR and DRS studies of Co species, such as CoO, Co(OH)$_2$, Co$_3$O$_4$, Co$_2$TiO$_4$, and CoTiO$_3$, on solid supports have been reported [Brik et al., 2001; Chuang et al., 1976; Frydman et al., 1995; Ho et al., 1992; Sexton et al., 1986; Voβ et al., 2002]. Based on those earlier results and Co 2p XPS line positions of the reference Co compounds used in this work, the Co 2p main peaks (*i.e.*,
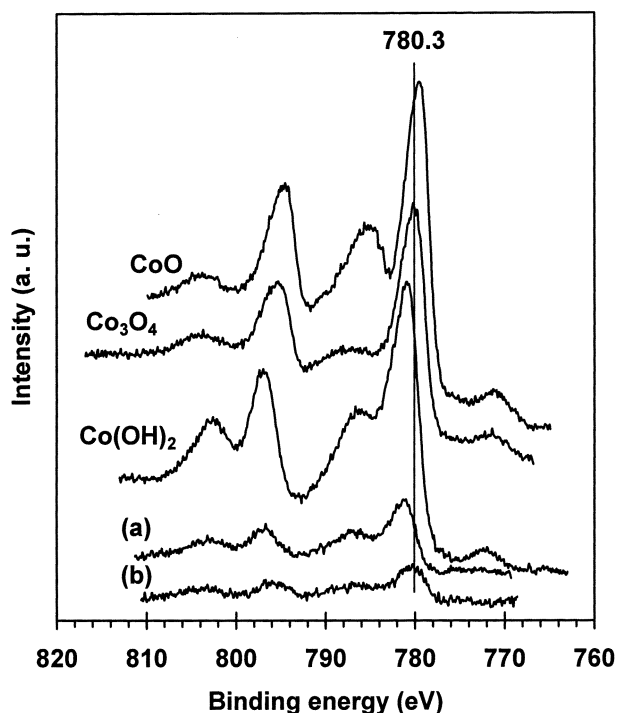
780.3, and 781.3 eV) observed for the 5% CoO_x/TiO_2 after and before reaction can be assigned. The 780.3 eV peak for the spent catalyst may indicate the presence of CoO_x very similar to the surface chemical states of Co_3O_4, while the 781.3 eV Co $2p_{3/2}$ main peak obtained with the fresh catalyst is associated probably with $CoTiO_x$ species produced on the TiO_2 support upon the calcination [Brik et al., 2001; Ho et al., 1992; Voβ et al., 2002]. As stated previously, the main peak was not due to the $Co(OH)_2$ because of the calcination of the catalyst at 843 K.

The noticeable difference in the XPS spectral features between the spent and fresh 5% CoO_x/TiO_2 is the value for the binding energies of the Co 2p main peaks. The main structure binding energy for Co $2p_{3/2}$ in the XPS spectrum (Fig. 3b) of the spent catalyst is similar to those in numerous previous Co 2p XPS spectra for titania-supported cobalt oxides, such as 5.22% CoO_x/TiO_2 and 7.6% CoO_x/TiO_2 [Brik et al., 2001; Voβ et al., 2002], and in Co_3O_4 used as a reference chemical in this work. The value of the binding energy obtained with the Co_3O_4 is in good agreement with earlier studies [Brik et al., 2001; Chuang et al., 1976; Sexton et al., 1986; Voβ et al., 2002]. The binding energy for Co $2p_{1/2}$ main peak of the spent catalyst is almost equal to those for the 5.22% CoO_x/TiO_2 and the Co_3O_4. The Co $2p_{3/2}$ main peak at 781.3 eV is shown for the fresh 5% CoO_x/TiO_2 catalyst and this value is significantly greater than the binding energy for Co $2p_{3/2}$ in the catalyst after the wet TCE removal reaction, although 0.7% CoO_x/TiO_2, Co_2TiO_4 and $CoTiO_3$ [Brik et al., 2001] and our reference $Co(OH)_2$ give binding energies very close to that for the clean Co surface unexposed to the wet reaction stream at 310 K.

The previous discussion for the supported CoO_x catalysts and reference Co compounds suggests that the outermost surface layer of the fresh 5% CoO_x/TiO_2 calcined at 843 K consists predominantly of the same chemical states as that of $CoTiO_x$ such as Co_2TiO_4 and $CoTiO_3$, more likely the latter cobalt titanate. This is consistent with an earlier XPS result [Ho et al., 1992] that such calcination of TiO_2-supported catalysts, having CoO_x weight percents greater than unity, at 673 K in an oxygen-rich flow could lead to formation of surface $CoTiO_3$ in addition to Co_3O_4 particles, thereby giving significantly higher Co 2p binding energies (781.2±0.2 eV). Those $CoTiO_x$ compounds could be also formed by such high temperature treatment of a mixture of either CoO or Co_3O_4 and TiO_2 in the presence of oxygen [Brik et al., 2001; Yankin et al., 1999]. Although the fresh 5% CoO_x/TiO_2 produces Co 2p binding energies very similar to those reported previously for 0.7% CoO_x/TiO_2 on which CoO has been predominant as characterized by XPS, XRD and TEM [Brik et al., 2001], this catalyst may not be in the form of CoO because of the CoO_x loading too high to be dispersed as only the CoO on the TiO_2 surface. Another indication that there is no presence of CoO is that the bulk phase structure associated very closely with Co_3O_4 has been revealed upon XRD measurements for the fresh catalyst. In the case of the 5% CoO_x/TiO_2 catalyst used for the earlier wet TCE decomposition at 310 K, it is shown that the surface chemical states of this spent sample are identical to that for the reference Co_3O_4, as indicated by XPS. This is consistent with earlier results for CoO_x/TiO_2 catalysts having CoO_x contents comparable to the spent catalyst [Brik et al., 2001; Voβ et al., 2002]; furthermore, reliable evidence can be supported by XRD patterns in which the spent catalyst gave only characteristic reflections corresponding to Co_3O_4. Conse-
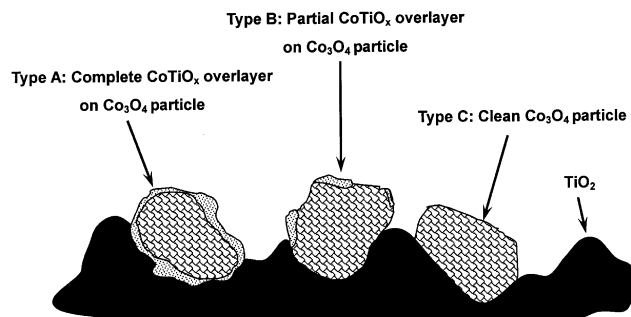
Fig. 4. A proposed model for the surface chemical structure of Co_3O_4 particles produced on the calcined TiO_2 surfaces.

quently, the surface of the fresh 5% CoO_x/TiO_2 may be chemically altered during the course of the wet TCE oxidation at 310 K for about 6 h and such change in the outermost surface chemical states can offer reasonable explanation on the transitory behavior in the earlier wet oxidation.

Based on these XPS and XRD results, coupled with the earlier observation of the transient behavior in catalytic activity vs. time on-stream during the activity measurements at 310 K with 5% CoO_x/TiO_2, and the previous discussion, to a very good approximation three types of model CoO_x structures can be proposed to exist in these CoO_x/TiO_2 catalysts, as shown in Fig. 4: Type A, Co_3O_4 particles completely encapsulated by $CoTiO_x$, exhibiting inactivity in the wet catalysis but being highly active with removal of the $CoTiO_x$ in the wet stream containing TCE; and Type B, Co_3O_4 particles partially covered by $CoTiO_x$, which to a good approximation, may be associated with the initial catalytic activity although XPS and XRD measurements have no evidence of that cobalt species, perhaps because of amounts too small to be appreciably detected by those techniques. Type C, clean Co_3O_4 particles, can be eliminated based on the XPS and XRD measurements from which such Co species was not indicated either. The Co 2p XPS spectrum of the fresh catalyst consisting predominantly of the Type A Co_3O_4 particles with a very large crystallite size near 29 nm would be very similar to that for $CoTiO_x$ compounds due to such complete encapsulation but XRD measurements may give discernible peaks for the phase structure of Co_3O_4 because of very thin $CoTiO_x$ overlayer on the outermost surface of the Co_3O_4 particles and their crystallite size sufficient to be visible by XRD. Such cobalt titanates can leach out into the wet reaction media, thereby causing exposure of the Co_3O_4 to the surface along with a very small amount of CoO_x loss in weight and creating rapid increase in the catalytic activity at the initial period during the wet oxidation, as discussed earlier [Kim and Choo, 2004].

CONCLUSIONS

Different XPS spectral features were indicated for the fresh and spent 5% CoO_x/TiO_2 catalysts. The main peak with a Co $2p_{3/2}$ binding energy of 781.3 eV appeared for the former sample, which is very similar to the chemical states of $CoTiO_x$ such as Co_2TiO_4 and $CoTiO_3$. The spent catalyst gave a 780.3-eV main peak for Co $2p_{3/2}$ with a corresponding satellite structure and that binding energy was almost equal to that of Co_3O_4 among reference Co compounds used here. Regardless, XRD measurements indicated the phase struc-

ture of Co$_3$O$_4$ for all the catalysts. Based on these XPS and XRD results, a tenable model structure of CoO$_x$ species existing on the titania surfaces can be proposed to be predominantly Co$_3$O$_4$ encapsulated completely by very thin filmlike CoTiO$_x$ consisting of Co$_2$TiO$_4$ and CoTiO$_3$, i.e., Type A, with a very small amount of Co$_3$O$_4$ covered partially by such cobalt titanates (Type B). Consequently, this simple model can reasonably explain the unsteady-state behavior of 5% CoO$_x$/TiO$_2$ catalyst in the initial period during the wet catalysis at 310 K.

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