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Titanate nanotubes as support of solid base catalyst

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ABSTRACT

Modified titanate nanotubes with enhanced basicity were synthesized by the incipient wetness impregnation of sodium titanate nanotubes (Na-TNT) with basic cations (Mg^{2+}, K^+, Ba^{2+}, Zn^{2+}). The essential morphology and mesoporosity of the nanotubes were maintained, as well as the tri-titanate structure, although in some cases (Mg^{2+}) ion exchange and intercalation reactions brought about some contraction of the rolled titanate layers. Basic sites were probed with CO_2 adsorption microcalorimetry and infrared spectroscopy, revealing strong ($Q_{ads} > 150\,kJ\,mol^{-1}$), medium ($150 < Q_{ads} < 120\,kJ\,mol^{-1}$), and weak basic sites that were absent in Na-TNT. These sites could be identified correspondingly with IR bands for relevant carbonate and bicarbonate complexes. All modified TNT catalysts demonstrated high conversions for the COS and CS_2 hydrolysis reactions at 553 K, confirming the presence of important basic sites.

1. Introduction

Titanate materials, in which anionic TiO_6 units are countered by other metal cations in a variety of crystal structures, are commercially important and employed, for instance, as capacitors due to high di-electric properties and most phases are ferromagnetic. While possessing excellent refractory properties, they suffer from low specific surface area, due to the high processing temperatures required for traditional preparation from solid state reaction between stoichiometric mixtures of metal carbonates and TiO_2 [1–9]. In 1998 Kasuga et al. [10] demonstrated the rather simple hydrothermal method to synthesize titania nanotubes (TNT) from bulk TiO_2 phases. The structure that forms consists of ca. 10 nm diameter rolled TiO_6 sheets typically of Ti_3O_7 crystal structure, but imparting considerable mesopore area that is not available via the conventional synthesis route. Access to the charge-balancing alkali cations (Na^+) is facilitated via the interlamellar spacing; hence leads to the possibility of ion exchange with other metal cations.

The selective adsorption of Sr^{2+} and Ba^{2+} in aqueous media was investigated for NaTNF (nanofibers) by Yang et al. [11,12]. Sorption uptake rate and capacity were both faster on the TNF material than with layered clays and zeolites. It was also observed that structural deformation occurred during the adsorption, making it irreversible. In a later publication [13], using Raman and XRD data, the authors proposed that the active exchangeable sodium cations were those located at the corner of the TiO_6 octahedra slabs and on the plane (0 0 3). Lewis and Brönsted acidity had been introduced by HCl leaching of Na-TNT following the hydrothermal synthesis step. Kitano et al. [14] investigated protonated titanate nanotubes as solid acid catalyst in the Friedel–Crafts alkylation of toluene with benzyl chloride. The catalyst showed high catalytic activity at 300 K with 90% benzyl toluene yield after 3 h. Pyridine adsorption FTIR confirmed the presence of both Brönsted and Lewis acid sites, and the authors attributed the high activity to the presence of both types of sites in protonated TNT. In another study, Liu et al. [15] enhanced Lewis and Brönsted acidity on the surface of hydrogen titanate nanotubes by adding V_2O_5 and $Ti(SO_4)_2$ to give good catalytic performance for the selective oxidation of methanol to dimethoxymethane. They also used NH_3 adsorption microcalorimetry and infrared spectroscopy in order to correlate enhanced acidity with correspondingly higher heats of adsorption. Enhanced Brönsted acidity was also evident in a hydrotreating catalyst consisting of NiMo particles supported on acid-washed TNT [16]. This was confirmed by thermal desorption of n-propylamine, and manifested itself in higher yields of tetralin ring-opening than observed with alumina supported catalyst.

FTIR studies of surface hydroxyl groups, and the adsorption of CO and CO_2 are useful for identifying the nature of Lewis acid and base sites in titanias [17–19]. Martra [19] reported that particles of the pre-dominantly anatase P25 Degussa are prismatic, with exposed (0 0 1) and (0 1 0) surface planes that on a dehydrated surface give rise to strong Lewis acid–base pair sites. Adsorbed CO bands (at 100 K) indicate the Lewis acid centers are exposed Ti^{4+} cations coordinated to five oxygen anions, the acidity varying in relation to the local geometry of neighboring O^{2-} ions. The basicity of these anions was confirmed by CO_2 adsorption, thus also confirming the acid–base pair relationship. When hydrated, these particles contained basic hydroxyl groups. In general, differences in plane

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structure and the presence of surface defects are defining factors in the density and strength of the acid–base pairs. Recently, Toledo-Antonio et al. [20,21] investigated the surface of acid-treated titania nanotubes annealed to 773 K and 873 K. In comparison with other anatase nanostructures they studied (8 nm nanoparticles; 873 K annealed nanofibers) of similar surface area, low temperature CO adsorption results on nanotubes and nanofibers showed only one CO band, associated with surface OH groups, whereas nanoparticles showed four bands, the additional bands corresponding to interactions with coordinately unsaturated Ti^{4+} (Lewis acid) and O^{2-} (Lewis base) sites. The adsorption of pyridine and lutidine provided additional evidence for the lack of Lewis acidity or basicity in the nanotube layer structure, showing only weak H-bonding interactions with the OH groups. However, the authors observe that the surface coverages of these physisorbed probe molecules were more than two-fold higher than with nanoparticles of similar surface area, indicative of the high OH accessibility due to the nanotube topography.

CO_2 adsorption microcalorimetry provides a direct measure of the surface density and strength of base sites [22–25]. Bordaweker et al. [23] report the initial heat of adsorption of CO_2 on pure titania (anatase particles) to be 180 kJ mol^{-1}, slightly higher than on γ-Al_2O_3 (155 kJ mol^{-1}), yet declining with increasing coverage. The addition of 5 wt% Sr^{2+} or Rb^{+} cations added base sites of 70–100 kJ mol^{-1} strength, and significantly suppressed surface acidity (NH_3 adsorption results). In other studies in which γ-Al_2O_3 was doped with basic cations [22,25–28], it is apparent that at low loadings where the basic cations are well dispersed on the support, Lewis acidity persists in the form of exposed dopant or Al^{3+} cations. Increased basicity is evidenced by increased CO_2 surface density as dopant concentrations increase, even while Lewis acidity persists, implying acid–base pair sites. Initial Q_{ads} values increase when separate crystalline MO phases are detected. Parallel IR studies show that the abundance of bicarbonate and carbonate species correlates with increased alkali metal loading, although the relative abundance of the species shifts toward carbonates as alkali ions displace protons on surface hydroxyl groups [25,29,30]. In K-doped alumina, the strongest base sites are identified as bidentate carbonate species [25]. Knöfel et al. [31,32] performed CO_2 calorimetry on mesoporous titania with and without a aminopropylsilane (APS) grafted surface. Their un-grafted titania showed lower Q_{ads} values ($\leq$80 kJ mol^{-1}) than reported by Bordaweker [23], perhaps due to differences in surface texture, although the APS-grafted titania showed stronger adsites for coverages up to 1 μmol m^{-2}. In combination with IR results, these sites were attributed to CO_2 interacting with the functionalized amine group, forming strong carbamate, carbamic acid, or bidentate carbonate complexes.

Most of the studies performed on titanate nanotubes have focused on acidic properties, yet comparative information on the basicity and catalytic activity of alkali metal oxide-loaded titania/titanate nanotubes is lacking in the literature. In this work, starting with the sodium titanate nanotube structure and morphology, we have prepared several alkali metal oxide-loaded titanate nanotube catalysts via incipient wetness impregnation and subsequent thermal treatment. Microcalorimetric studies of CO_2 adsorption, complemented with IR spectroscopy, allow us to evaluate catalyst basicity, as well as structural features through diffraction analysis and TEM. Catalyst reactivity was analyzed for the hydrolysis of COS and CS_2 reactions. Several publications have demonstrated that the COS and CS_2 hydrolysis might be employed as a test reaction of metal oxide hydroxyl and surface oxygen basicity [33–36]. Both COS and CS_2 form during the thermal step of the Claus process, and titania is known to be a viable catalyst for elimination of these compounds during the subsequent catalytic steps.

2. Experimental

2.1. Sample preparation

Sodium titanate nanotubes (NaTNT) were synthesized using a hydrothermal method. Several grams of commercial TiO_2 (Sigma–Aldrich) were added to a sufficient amount of 10 M NaOH to make a suspension that was treated in a Teflon-lined autoclave at 403 K for 60 h. Modified nanotubes, designated CTx10 (x = Mg, K, Ba, Zn), were prepared by incipient wetness impregnation of NaTNT using aqueous solutions of nitrate salts of the corresponding metal cation to achieve the additive metal loading of 10 wt% in each case. The moist solid was dried initially at 373 K for 2 h, and then calcined in a tube furnace at 773 K for 2 h in flowing oxygen.

2.2. Characterization

X-ray diffraction analyses were recorded on a powder diffractometer (Siemens D-500 and Rigaku DMAX-2200), operating with Cu Kα radiation (40 kV/40 mA or 36 kV/30 mA). Both instruments were equipped with a graphite secondary-beam monochromator. Diffraction data were collected in step mode (0.02° s^{-1}) between 4° and 80° 2θ. Samples were characterized by high resolution transmission electron microscopy on a Phillips TECNAI-F30 operated at 300 kV. Samples were prepared for analysis by dispersing the powder in alcohol with ultrasonic treatment, then depositing a drop onto a holey carbon film grid. Infrared spectroscopy analysis was obtained on a NICOLET 8700 FTIR, collecting diffuse reflectance data, using a Harrick praying mantis cell with environmental chamber equipped with CaF_2 windows. Uncompressed powder sample was initially treated in situ in the IR cell at 773 K under dry nitrogen flow for 2 h, evacuated at that temperature and cooled to ambient temperature before being exposed to 20 ml min^{-1} pure CO_2 flow. Each spectrum was obtained from 100 scans at a resolution of 2 cm^{-1} and studied in the 4000–400 cm^{-1} range. Difference absorbance spectra were obtained by subtracting from sample spectra the corresponding background spectra of the non-adsorbed CO_2 sample. Differential heats of CO_2 adsorption were measured at 473 K using a differential heat-flow microcalorimeter of the Tian–Calvet type [37] coupled to a diffusion-pumped high vacuum system capable of sustaining 10^{-6} mbar, and to a calibrated gas dosing section equipped with a precision capacitance manometer (Baratron, MKS Instruments). Identical quartz adsorption cells were used as sample and reference (empty). In each experiment, 0.1–0.5 g catalyst was heated with periodic exposures (30 min intervals) to 50 mbar O_2 and evacuations to 773 K, and then out-gassed at that temperature for 12 h, after which it was cooled down under vacuum to 473 K. Following a leak test ($\leq 10^{-4}$ mbar min^{-1}), successive doses of CO_2 were admitted to the sample, with each dose allowing sufficient time (45–60 min) for the recorded heat signals to re-establish baseline. Dosing was continued until a final equilibrium pressure $\geq$5 mbar was achieved. Subsequently, the sample was re-evacuated and the desorption thermal trace recorded to assess the reversibility of sites adsorbed.

The COS and CS_2 hydrolysis reaction test were carried out at 553 K in a differential fixed-bed tubular reactor, using a bed of 250 micron sieved granules of 0.1 g catalyst diluted with 0.4 g quartz crushed to the same size. The reactant feed consisted of a mixture of COS (0.9%), CS_2 (0.1%), H_2O (20%), in a balance of CO_2. The contact time (W/F) was held constant at 84 g h mol^{-1}. Reaction products were analyzed on-line by GC using a Varian chromatograph with three columns in a dual column configuration (CP-Porabond U; MS-5A + Hayesep Q). The column effluents were analyzed with TCD detectors. Composition data were collected in 20 min intervals over a test period of 3 h. Reaction products were essentially H_2S, S, and CO_2. Surface area measurements were conducted by obtaining