Surface and interlayer base-characters in lepidocrocite titanate: The adsorption and intercalation of fatty acid

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ABSTRACT

While layered double hydroxides (LDHs) with positively-charged sheets are well known as basic materials, layered metal *oxides* having negatively-charged sheets are not generally recognized so. In this article, the surface and interlayer base-characters of O^{2-} sites in layered metal oxides have been demonstrated, taking lepidocrocite titanate $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ as an example. The low basicity (0.04 mmol CO_2/g) and low desorption temperature (50–300 °C) shown by CO_2- TPD suggests that O^{2-} sites at the external surfaces is weakly basic, while those at the interlayer space are mostly inaccessible to CO_2. The liquid-phase adsorption study, however, revealed the uptake as much as 37% by mass of the bulky palmitic acid (C_{16} acid). The accompanying expansion of the interlayer space by ∼0.1 nm was detected by PXRD and TEM. In an opposite manner to the external surfaces, the interlayer O^{2-} sites can deprotonate palmitic acid, forming the salt (i.e., potassium palmitate) occluded between the sheets. Two types of basic sites are proposed based on ultrafast ^1H MAS NMR and FTIR results. The interlayer basic sites in lepidocrocite titanate leads to an application of this material as a selective and stable two-dimensional (2D) basic catalyst, as demonstrated by the ketonization of palmitic acid into palmitone (C_{31} ketone). Tuning of the catalytic activity by varying the type of metal (Zn, Mg, and Li) substituting at Ti^{IV} sites was also illustrated.

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1. Introduction

Solid base catalysts are capable of activating acidic reactants [1,2] in several reactions of industrial importance, or in the synthesis of fine chemicals [3,4] and first-generation biodiesel [5]. The base-characters of metal oxides originate from under-coordinated O^{2-} sites on different locations (step, corner, terrace, etc.) of the crystals. These sites could behave as the Lewis base by donating an electron pair to reactants. The formation of surface carbonate (or bicarbonate) on oxides in contact to atmospheric CO_2 is an example of the Lewis base-character of oxides. Alternatively, the O^{2-} sites act as the Brønsted base if they abstract a proton from reactants. This is the case for the formation of the surface hydroxyl group on oxides upon contacting with atmospheric water.

Common oxides such as CaO, MgO, ZrO_2 are strongly basic, inexpensive, but typically have low surface area and random distribution of the atomic planes [6]. Their catalytic activity greatly depends on the exposed facets of the crystals which have to be controlled through a delicate synthetic procedure. In contrast, a family of solids known as layered metal oxides/hydroxides [7,8] naturally crystalizes into two-dimensional (2D) plate-like objects, composed of atomically-thin sheets as elementary units. Such crystals inherently expose the faces (i.e., the basal plane) and the edges to the environment, resulting in the *external* active sites. In addition, the 2D crystals possess the *internal* interlayer space sandwiched between the sheets. These sites can be utilized only if they are accessible to reactants. However, the accessibility to internal basic sites and the thermal/chemical stability do not necessarily coexist in the same catalyst. For example, well-known 2D metal *hydroxides* such as layered double hydroxides (LDHs) or

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layered hydroxy salts (LHSs) are considered basic largely because they exhibit high affinity toward the acidic molecule CO_2 (in the form of intercalated carbonate CO_3^{2-}), which can have the electrostatic attraction with the positively-charged sheets. However, these materials transform into (mixed) metal oxides upon contact with reactants at elevated reaction temperature [8–10], thereby losing the two-dimensionality and the associated benefits. Therefore, there is still a need to develop a new type of active and stable 2D solid base catalysts whose the external and the internal surfaces could be effectively utilized.

Lepidocrocite titanates ($A_xM_yTi_{1-y}O_4$, where A=K, M=Zn, Mg, Ni, Cu, Fe^{III}, Mn^{III}; [11,12] A=Cs, M=Zn, [13] Ni, [14] Mg, [15,16] Nb; [17] A=K, Rb, and Cs, M=Li; [18,19] A=Cs, M=cationic vacancy [20]) show great potential as thermally stable, 2D basic catalysts. The basal plane (either external or internal) is on the *ac* plane of an orthorhombic unit cell. Two types of bridging basic oxygen atoms can be found. The first one is O_{2c} coordinating to two Ti^{IV} atoms nearby, while the second one is O_{4c} and coordinates to four Ti^{IV} atoms. It is natural to assume that the negative charges on the sheets would localize at O_{2c} and O_{4c}, contributing to the base characters. Moreover, the edges of crystals also contain under-coordinated oxygen atoms of which the exact geometry depends on the extent of hydroxylation. Therefore, the nature of basic sites (O^{2-}) in layered metal oxides is fundamentally different from that in LDHs/LHSs mentioned above. Still, with the exception of a simple ion exchange of interlayer alkali cations with aqueous mineral acids [19,21–25], reports on base characters of layered metal oxides and their behavior toward other acidic probe molecules are lacking.

In this work, the surface basicity of lepidocrocite titanate $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ has been characterized by CO_2 temperature programmed desorption (CO_2 TPD). In combination with FTIR and ^1H ultrafast MAS NMR, surface hydroxyl can be revealed. Results were compared to TiO_2 and the well-known basic catalyst such as MgO. Bulky acidic probe molecule, palmitic acid (C_{16} acid), was employed to test the accessibility to the interlayer basic sites via liquid phase adsorption (intercalation). We further demonstrated the application of some lepidocrocite titanates ($K_{0.8}Zn_{0.4}Ti_{1.6}O_4$, $K_{0.8}Mg_{0.4}Ti_{1.6}O_4$ and $K_{0.8}Li_{0.27}Ti_{1.73}O_4$) as catalysts for the gas-phase ketonization of palmitic acid, in comparison to the mixed Mg/Al oxides from the decomposition of LDH. The ketonization of carboxylic acids to the respective ketones is of industrial importance as a processing step in biomass conversion to hydrocarbon fuels [26–29].

2. Material and methods

2.1. Synthesis

Lepidocrocite titanate $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ was synthesized [11] by the calcination of the stoichiometric mixture of K_2CO_3, ZnO, and TiO_2 at 900 °C for 20 h. Two other compositions, $K_{0.8}Mg_{0.4}Ti_{1.6}O_4$ and $K_{0.8}Li_{0.27}Ti_{1.73}O_4$, can be prepared similarly but replacing ZnO with MgO [11] and Li_2CO_3 [18,19], respectively. The layered double hydroxide with Mg/Al mole ratio of 2.5 was synthesized by a co-precipitation method [30] and was calcined at 450 °C for 6 h, giving the mixed Mg/Al oxide "MgAl2.5". Potassium palmitate was obtained as the white powder from the reaction between KOH(aq) and palmitic acid. The PXRD patterns of other materials in addition to $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ can be found in Figs. S1 and S2 in Supporting Information. All chemicals are of reagent grade and were used as received, except K_2CO_3, Li_2CO_3, KOH and palmitic acid which were dried 120 °C overnight prior to use.

2.2. CO_2 temperature programmed desorption

Approximately 200–300 mg of the sample was activated in situ at 450 °C for 2 h under air zero in a quartz tube reactor, followed by a cooling to room temperature under N_2 gas. Gaseous CO_2 was then flown through the sample at the flow rate 30 mL/min for an hour, followed by a flow of helium at the same flow rate for another hour. Next, the temperature was raised from room temperature to 600 °C at 5 °C/min using pure helium as a carrier gas. The CO_2 desorption profile was recorded by a thermal conductivity detector and was normalized by mass of the sample employed. The basicity was expressed as mmol of CO_2 per g of the sample. The peak area obtained was compared to that from a known amount of $CaCO_3$ which decomposes completely and quantitatively to CaO and CO_2. All gases are the commercial products of Praxair with the purity of 99.99% and were used as received.

2.3. Adsorption of palmitic acid

An amount of 2.0 g of $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ was heated with 150 mL of a 5% w/w palmitic acid (Fluka, 97%+) in isopropanol at 60 °C from 1 to 36 h. The liquid was withdrawn at certain intervals, and the content of adsorbed palmitic acid was determined based on Eq. (1), together with an appropriate conversion of concentration to mass. Here, A_0 is the corrected peak area of palmitic before the adsorption, and A_t is the corrected peak area of palmitic acid remaining in the mother liquor after the adsorption time t.

$$\%\text{Adsorption} = [(A_0 - A_t)/A_0] \times 100\% \tag{1}$$

The solid was filtered, washed with isopropanol, and then dried at 70 °C overnight. The experiment with decanoic acid was performed similarly. A control experiment was performed by heating $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ with isopropanol at 60 °C in the absence of any carboxylic acid. Another control experiment was also performed, where $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ was magnetically stirred with 1 M HCl (3 times, 12 h each, with the fresh HCl loaded between repetition) [24] so as to obtain the proton-containing lepidocrocite where K^+ is ion exchanged with $H^+ \cdot H_2O$.

2.4. Characterization

Powder X-ray diffraction (PXRD) measurements were conducted on a Rigaku DMAX 2200/Ultima+ diffractometer, employing a Cu-Kα radiation at 40 kV and 30 mA. The sample was scanned in the range $2\theta=5$–65° at a 0.05°/step and a detection time of 0.6 second/step. BET specific surface area of the sample was determined by a Gas Adsorption Analyzer (Autosorb-1C, Quantachrome). For TGA (Perkin-Elmer, Pyris 1), the sample was heated from room temperature to 900 °C (10 °C/min) under nitrogen gas flowing at 20 mL/min. FTIR spectra of the pelletized samples (prepared by grinding with KBr) were collected on a Spectrum GX (Perkin Elmer) spectrometer. SEM images were acquired on a Zeiss EVO/MA10 scanning electron microscope, while TEM images were acquired on a JEOL JEM 2010 transmission electron microscope. ^1H MAS NMR (spinning speed: 100 kHz) of $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ was recorded using a JEOL ECA-600 spectrometer with a 0.75 mmφ MAS sample rotor. Depth2 pulse sequence with 1.3 μs of 90° pulse length and 5.0 s of repetition time were applied to obtain a spectrum.

2.5. Catalytic activity testing

Catalytic activity testing was conducted in a continuous fixed bed down-flow reactor made of glass (length, 50 cm; outer diameter, 8 mm; inner diameter, 6 mm) under atmospheric pressure