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Deposition of iron titanate/titania ceramic composite thin films from a single molecular precursor

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ABSTRACT

A heterobimetallic single molecular precursor, $[Fe_2Ti_4(\mu\text{-}O)_6(TFA)_8(THF)_6]$ (**1**) [TFA = trifluoroacetate, THF = tetrahydrofuran], was synthesized by the simple reaction of $[Fe_3O(OAc)_6(H_2O)_3]NO_3{\cdot}4H_2O$ [OAc = acetato] with tetrakis(2-ethoxyethanalato)titanium(IV) in the presence of trifluoroacetic acid in THF. The synthesized precursor was analyzed by melting point, CHN analysis, FTIR, single crystal X-ray diffraction and thermogravimetric analysis. Complex (**1**) crystallizes in the orthorhombic space group $Pca2_1$ with cell dimensions $a = 19.2114(14)$, $b = 20.4804(15)$ and $c = 17.2504(12)$ Å, and the complex undergoes thermal decomposition at 490 °C to give a residual mass corresponding to an Fe_2TiO_5–TiO_2 composite mixture. The synthesized precursor was utilized for deposition of Fe_2TiO_5–TiO_2 composite thin films by aerosol-assisted chemical vapor deposition (AACVD) on glass substrates at 500 °C using argon as the carrier gas. Scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and X-ray powder diffraction (XRD) analyses of the thin films suggest the formation of good quality crystalline thin films of an Fe_2TiO_5–TiO_2 composite with an average grain size of 0.105–0.120 μm.

1. Introduction

Mixed metal oxide composites and their applications have become an important research theme due to their unique magnetic, electrical, optical, and catalytic properties, which are distinctly different from those of pure bulk oxides [1]. Mixed metal oxides composites involving transition metals also have extensive applications as catalysts because of their unique textural and acid–base characteristics, which often lead to enhanced catalytic activities as compared with corresponding pure and supported oxide analogues [2].

The iron–titanium oxide composites, for example, have wide applications in the fields of magnetic semiconductors [3], magneto-optical semiconductors [4], and especially in catalysis [5,6], such as photocatalytic degradation of organic pollutants, photoelectrochemical water splitting [7,8], catalytic isomerization [9], and catalytic oxidation [10,11]. Fe_2TiO_5–TiO_2 has been found to possess unique catalytic activity in several reactions such as the oxidation of cyclohexane [2], α-pinene oxide isomerization [9], *o*-cresol photo-degradation and methanol oxidation [10]. Pure iron titanates are commonly known in three different forms, as the minerals ilmenite ($FeTiO_3$), pseudo-brookite (Fe_2TiO_5) and ulvospinel (Fe_2TiO_4), and which of the three is formed largely depends on the preparation method, composition of the precursor, and the calcination temperature [12].

Several methods have been reported for synthesizing iron titanium oxide composites such as wet impregnation [13], hydrolysis freezing [14], hydrothermal [12], co-precipitation [15], sol–gel processes, ultrasound irradiation [16], and chemical vapor deposition [17]. Fe_2TiO_5 has been typically prepared by co-precipitation or sol–gel methods [18,19]. Phani and Santucci [20] have prepared Fe_2TiO_5 from titanium isopropoxide and iron oxalate using a sol–gel technique. Camargo et al. [21] have developed the titanium iron isopropoxide $[FeCl\{Ti_2(OPri)_9\}]$ as a single source precursor to prepare an Fe_2TiO_5–TiO_2 composite by the sol–gel route. Using titanium(IV) and iron(III) acetylacetonate, a mixture of anatase and rutile was obtained at 500 °C while pseudo-brookite (Fe_2TiO_5) was formed at temperatures higher than 700 °C [22]. In a more recent study, an aerogel product obtained from titanium(IV) butoxide and iron(III) acetylacetonate also contained pseudo-brookite besides titania [10]. All synthetic procedures for Fe_2TiO_5 powders involve sol–gel acid catalyzed reactions, co-precipitation and/or thermal evaporation drying processes. The resultant powders consist of massive particles with irregular shapes and micron-sized

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dimensions, and the crystallinity of these powder particles was increased by sintering above 500 °C for several hours. Due to the large crystallite sizes the surface area was substantially reduced with a large fraction of active sites likely embedded and inactive, thus adversely affecting catalytic activity [21].

The production of multi-metal oxides using single source precursors (SSPs) such as the above mentioned [FeCl{$Ti_2(OPri)_9$}] requires that the precursor contains all necessary elements required for the final oxide material already incorporated in the same molecular moiety [23–27]. Among different deposition techniques, aerosol-assisted chemical vapor deposition (AACVD) is simple and quite versatile, and it has the advantage that any soluble single source precursor can be used to fabricate multicomponent oxides. Especially, AACVD diminishes the stringent CVD requirement for the precursor to be highly volatile: it is only required to be soluble in a solvent from which an aerosol can be generated [28–30]. Following our previous work [31,32] directed towards the design of heterobimetallic complexes for mixed metal oxide systems and taking advantage of carboxylate ligands, which can coordinate to the metal atoms in several ways with the possibility to gain high nuclearity species, we investigated the possibility to develop soluble and volatile metallo-organic single source precursors for iron titanate systems. In this article, we report the synthesis and characterization of the heterobimetallic precursor [$Fe_2Ti_4(\mu\text{-}O)_6(TFA)_8(THF)_6$] (**1**) (TFA = trifluoroacetate, and THF = tetrahydrofuran) and its use for the fabrication of Fe_2TiO_5–TiO_2 composite thin films by Aerosol Assisted Chemical Vapor Deposition (AACVD). The precursor (**1**) is highly soluble in THF and toluene under the experimental conditions of AACVD and is a potential candidate to deposit homogeneous good quality Fe_2TiO_5–TiO_2 composite thin films.

2. Experimental

2.1. General considerations

All manipulations were carried out under inert atmosphere of dry argon gas using Schlenk tube and glove box techniques. Solvents were carefully dried and distilled using standard methods [33]. Tetrakis (isopropanolato)titanium(IV) $Fe(NO_3)_3{\cdot}9H_2O$, trifluoroacetic acid and $CH_3COONa{\cdot}3H_2O$ were purchased from Aldrich chemicals. Tetrakis(2-ethoxyethanalato)titanium(IV) and $[Fe_3O(OAc)_6(H_2O)_3]NO_3{\cdot}4H_2O$ [OAc = acetato] were prepared according to reported procedures [34,35] and were used without any characterization. Melting points were recorded on a Mitamura Riken Kogyo (MT-D) apparatus and are uncorrected. Elemental analysis was performed using CHN analyzer LECO model CHNS-932. FT-IR spectra were recorded with a Bio-Rad Excalibur FT-IR model FTs 300MX spectrometer from KBr discs. Controlled thermal analyses were carried out in an alumina crucible under an atmosphere of flowing nitrogen gas (25 ml/min) at a heating rate of 10 °C/min by using a Seiko SSC/S200 model with computer interface.

2.2. Synthesis

2.2.1. Synthesis of [$Fe_2Ti_4(\mu\text{-}O)_6(TFA)_8(THF)_6$] (**1**)

0.5 g (0.703 mmol) $[Fe_3O(OAc)_6(H_2O)_3]NO_3{\cdot}4H_2O$ were suspended in 10 ml of THF in a 50 ml Schlenk tube fitted with vacuum line adapter and magnetic stirrer. 0.27 ml (4.9 mmol) tetrakis(2-ethoxyethanalato)titanium(IV) was added drop by drop via syringe to the suspension. 0.2 ml (2.59 mmol) of trifluoroacetic acid (TFA) was added to the reaction mixture and the contents were stirred for 1 h. The reaction mixture was evaporated to dryness under vacuum and the solid was re-dissolved in 5 ml of THF. The solution was filtered through cannula to remove any traces of solid residue and was placed in a freezer at −10 °C for crystallization. Red colored crystals were obtained after 3 days with 85% Yield. M.p.: 148 °C. *Anal.* Calc. for $C_{44}H_{56}F_{24}Fe_2O_{29}Ti_4$: C, 29.00; H, 3.20. Found: C, 29.40; H, 3.23%. FT-IR/cm^{-1}: 1672s, 1538w, 1435w, 1198s, 1146s, 1051w, 833w, 794s, 721m, 419w. TGA: 30–100 °C (10.17% wt. loss); 100–223 °C (9.74% wt. loss); 223–378 °C (50.30% wt. loss); 378–500 °C (residue of 25.50%).

2.3. X-ray crystallography

Data were collected on a Bruker AXS SMART APEX CCD diffractometer at 100 (2) K using Mo Kα radiation (0.71073 Å) in the θ rage of 2.3–30.4°. The unit cell was determined using SMART [36] and SAINT [37] and the data were corrected for absorption using SADABS in SAINT. The structure was solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL [38]. All non-hydrogen atoms were refined anisotropically. Final crystal data of precursor (**1**): $C_{44}H_{56}F_{24}Fe_20_{29}Ti_4$, FWt = 1808.19, orthorhombic, $Pca2_1$, a = 19.2114(14) Å, b = 20.4804(15) Å, c = 17.2504(12) Å, $\alpha = \beta = \gamma = 90°$, V = 6787.3(8) $Å^3$, Z = 4, D_{calc} = 1.770 mg M^{-3}. 76 783 Reflections were collected, independent reflections: 20 026 [R_{int} = 0.040]. Refinement was full matrix least square on F^2; R factors were R_1 (all) = 0.0941, R_1 ($I > 2/s(I)$) = 0.0615, wR_2 (all) = 0.1610, wR_2 ($I > 2/s(I)$) = 0.1407, Goodness-of-fit on F^2 was 1.077.

The structure exhibits whole molecule disorder by a pseudo-inversion center located in the middle of the molecule. The ratio of the two moieties refined to 0.630(1)–0.370(1). In case of a 1:1 ratio, the structure would have been centrosymmetric with the space group *Pbca* instead of the observed space group $Pca2_1$. The structure is also racemically twinned with a twin ratio of 0.69(2)–0.31(2). Refinement attempts with other unit cell orientations in the alternative $Pca2_1$ setting did result in 1:1 disorder, perfect racemic twinning and did give worse refinement results than in the chosen orientation.

Due to the excessive disorder of large sections of the structure a series of restraints and constrained were applied to achieve a meaningful and stable refinement. All carboxylate units were restrained to be flat. All C–F bonds were restrained to be of approximately the same length. The same was done with all C–O and all C–C bonds within the THF molecules. All minor TFA anions were restrained to have the same geometry as their major moiety counterparts. All ADPs of C, F and O were restrained using DELU, ISOR and SADI commands as defined in SHELXTL with standard deviations of 0.05 each. ADPs of heavily overlapping minor moiety atoms with very ill-behaved ADPs were constrained to be the same as that of their major component counterparts.

2.4. Deposition of thin films by AACVD

Thin films from precursor (**1**) were deposited on commercially available soda glass slides using a self-designed ultrasonic Aerosol Assisted Chemical Vapor Deposition assembly [39]. The glass substrate was cleaned prior to use by ultrasonically washing with distilled water, acetone and finally with ethyl alcohol. In a typical deposition, 25 ml of a 0.02 M solution of the precursor (**1**) in toluene were used. Substrate slides (2 × 2 cm) were placed inside the reactor tube and then heated up to 500 °C for 20 min. before carrying out the deposition. The aerosol of the precursor solution was formed by keeping the round bottom flask in a water bath above a piezoelectric modulator of an ultrasonic humidifier. The generated aerosol droplets were transferred into the hot wall zone of the reactor by the carrier gas. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. The deposition was conducted for a period of 45 min. Towards the end of the experiment, the aerosol line was closed and carrier