



Short communication

Iron modified titanium–hafnium binary oxides as catalysts in total oxidation of ethyl acetate



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ABSTRACT

Multicomponent iron–titanium–hafnium oxide materials with different compositions were prepared by combination of homogeneous precipitation with urea and incipient wetness impregnation techniques and tested as catalysts for ethyl acetate oxidation as representative VOCs. Nitrogen physisorption, XRD, Raman, UV–Vis, XPS, Mössbauer spectroscopy and TPR analyses reveal co-existence of substituted $\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ oxide, finely dispersed iron oxide species with superparamagnetic behavior and well crystallized $\alpha\text{-Fe}_2\text{O}_3$ particles, which relative part depends on hafnium content in titania lattice. The effect of phase composition on the catalytic behavior of these materials in ethyl acetate oxidation was discussed.

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1. Introduction

The knowledge of the specific effects within the multi-component nanostructured metal oxides is prerequisite for the optimization of their properties. Recently, titanium oxide has received much attention due to its superior optical, electrical, mechanical and catalytic properties combined with non-toxicity and cost effectiveness [1]. The introduction of dopant into TiO_2 lattice may significantly affect the electronic band edges or introduce impurity states in the band gap [2]. Formation of $\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ [3,4], mixture of $\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ and superparamagnetic hematite particles [5] or mixture of $\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ and pseudo brookite Fe_2TiO_5 phases [6] were registered after TiO_2 doping with iron. Segregation of $\alpha\text{-Fe}_2\text{O}_3$ phase was reported with the increasing of iron content up to 10% in [7], while Bonamali et al. [8] did not observed its formation even at 50 wt% Fe. However, to the best of our knowledge, there are only few reports on hafnium-doped TiO_2 . Using density functional theory, Lezhong et al. [9] reported that Hf incorporation in TiO_2 leads to narrower band gap, but no experimental evidence has been still reported. No data for the multi-component Ti–Hf–Fe oxide system are still available.

The aim of current investigation is to demonstrate the possibility to control the state of supported on titania–hafnia binary oxides iron species by simple variation of the support composition. Pioneer investigations on the catalytic behavior of these materials in total oxidation of ethyl acetate as representative VOCs are carried out.

2. Experimental

2.1. Materials

Hafnium-doped titania samples were prepared by homogeneous hydrolysis of aqueous solution of TiOSO_4 and HfOSO_4 with urea as a precipitation agent according to the procedure described in [10–12]. Typically, 100 g of TiOSO_4 were dissolved in 1 L hot water acidified with 10 ml 98% H_2SO_4 . After dilution in 4 L distilled water, HfOSO_4 was added for the preparation of binary materials. The pH of the initial solution of TiOSO_4 and HfOSO_4 was 2–4. Then, the solution was mixed with 400 g urea and the mixture was heated at 373 K for 6 h. During the heating, the urea started to decompose and the pH of the solution increased gradually. At the end of the precipitation procedure the pH of the solution became neutral or slightly alkaline pH (7–8). Iron modifications (12 wt%Fe) were obtained by incipient wetness impregnation of thus obtained composites using 0.2 M aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The impregnated samples were dried at room temperature for 24 h and then, treated in air at 773 K for 2 h for precursor

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Table 1Samples composition, specific surface area (S_{BET}), total pore volume (V_t) and specific activity (SA) for TiO_2 , binary TiO_2 - HfO_2 oxides and their iron modifications.

Sample	Support composition, wt%				Fe, wt%	S_{BET} $\text{m}^2 \text{g}^{-1}$	V_t , $\text{cm}^3 \text{g}^{-1}$	SA, $\% \text{m}^{-2} \text{g} * 10^2$
	Ti	Hf	O	Hf/Ti + Hf				
TiO_2	60.0	0.0	40.0		0.23		319	15
HfTi(0.8)	59.6	0.5	39.9	0.8	0.22		300	11
HfTi(1.8)	59.2	1.1	39.7	1.8	0.23		326	10
HfTi(9.9)	55.6	6.1	38.3	9.9	0.22		307	13
HfTi(14.9)	53.4	9.3	37.3	14.9	0.24		306	11
HfTi(34.8)	43.5	23.2	33.3	34.8	0.32		488	7
HfTi(41.3)	40.0	28.2	31.8	41.3	0.24		463	7
Fe/ TiO_2	60.0	0.0	40.0		0.15	12	131	45
Fe/HfTi(0.8)	59.6	0.5	39.9	0.8	0.15	12	119	34
Fe/HfTi(1.8)	59.2	1.1	39.7	1.8	0.14	12	115	54
Fe/HfTi(9.9)	55.6	6.1	38.3	9.9	0.15	12	112	48
Fe/HfTi(14.9)	53.4	9.3	37.3	14.9	0.16	12	114	47
Fe/HfTi(34.8)	43.5	23.2	33.3	34.8	0.18	12	118	46
Fe/HfTi(41.3)	40.0	28.2	31.8	41.3	0.17	12	145	37

decomposition. The samples were denoted as HfTi(x) and Fe/HfTi(x) for the parent oxides and their iron modifications, respectively, where x is Hf/Hf + Ti ratio (wt%) and data for their composition are listed in Table 1.

2.2. Characterization and catalytic tests

The surface area of the samples was determined from nitrogen physisorption isotherms using a Coulter SA3100 instrument. Elemental analysis was performed by a MiniPal 4.0 energy-dispersive X-ray fluorescence spectrometer. Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation. The UV-Vis spectra were recorded on a Jasco V-650 UV-Vis spectrophotometer. Raman spectra were acquired with a Thermo Fischer Scientific DXR Raman microscope. The X-ray photoelectron spectroscopy analyses were measured in high-vacuum chamber equipped with SPECS Xray XR-50 and SPECS PHOIBOS 100 Hemispheric Analyzer. The Mössbauer spectra were obtained at room and liquid nitrogen temperature with a Wissel electromechanical spectrometer. The TPR/TG (temperature-programmed reduction/thermo-gravimetric) analyses were performed on a Setaram TG92 instrument in a flow of 50 vol% H_2 in Ar ($100 \text{ cm}^3 \text{ min}^{-1}$) and heating rate of 5 K min^{-1} .

The ethyl acetate (EA) oxidation was tested under temperature programmed regime in a flow type apparatus ($1.21 \text{ mol}\%$ EA in air, $\text{WHSV} = 100 \text{ h}^{-1}$) equipped with GC for analyses. The selectivity of the obtained products was calculated as $S_i = Y_i/X * 100$, where Y_i was the yield of (i) product and X was the EA conversion.

3. Results and discussion

3.1. Characterization of TiO_2 - HfO_2 binary oxide supports

XRD pattern of pure titania (not shown) exhibits all reflections typical of anatase phase (JCPDS 21-1272). The observed increase in the lattice parameters after doping with Hf (Table 2) indicates incorporation of Hf^{4+} ions into the titania lattice. The increase of Hf content above 15% provokes the formation of amorphous phase. These structural changes are also confirmed by the observed increase in the BET surface area (Table 1) and with the decrease in the intensity of the main E_g mode at 149 cm^{-1} in the Raman spectra (Fig. 1a) [13]. The strong absorption feature in the UV-Vis spectrum of pure TiO_2 (Fig. S1) at ca. 350 nm is due to d-d electronic transition between Ti^{4+} ion and O^{2-} ligand in anatase. No significant changes in the band gap are observed after titania doping with hafnia and this is in contrast with the theoretic calculations reported in [10]. The broad absorption band in the $900\text{--}400 \text{ cm}^{-1}$ region in FTIR spectrum of titania (Fig. S2) could be assigned to Ti-O-Ti bending vibrations [14]. In accordance with [15] the increased

absorption in the $600\text{--}500 \text{ cm}^{-1}$ range for all Hf doped materials could be carefully assigned to the presence of TiHfO_4 structures. The Ti 2p core level spectra (Fig. 2) represent highly resolved peaks at binding energy of 458.5 eV and split about 5.7 eV which is assigned to Ti-O bonds in TiO_2 [16]. The second component at BE of 456.9 eV represents titanium ions in Ti_2O_3 . Note the almost linear increase in the Ti^{3+} content with the increase of Hf amount which could be due to homogeneous incorporation of Hf in titania with the formation of defects (Table 3, Fig. S3). The Hf 4f spectra for all materials (Fig. S4) represent peaks at BE of 19 and 17 eV, which is assigned to Hf^{4+} ions. For all Hf doped titania samples the calculated Hf/Hf + Ti ratio overcomes the expected nominal one (Table 3) indicating high degree of exposure of Hf ions at the surface. On the base of this observation partial segregation of finely dispersed HfO_2 particles over the titania ones could not be excluded. The O1s core level spectra (Fig. S5) could be assumed as superposition of peaks assigned to oxygen in various states, such as H_2O molecules, surface OH- groups as well as to oxygen anions in Ti-O and Hf-O structures. The observed higher oxygen content than the theoretic one (Table 3) indicates high concentration of hydroxyl groups which are usually related to oxygen vacancies [17].

Table 2XRD data for TiO_2 , various TiO_2 - HfO_2 binary oxides and their iron modifications.

Sample	Phase	D, nm	Strain $e * 10^3$, a.u.	a, Å	c, Å
TiO_2	TiO_2 (anatase)	4.3	6.067	3.793	9.518
HfTi(0.8)	TiO_2 (anatase)	5.0	6.179	3.802	9.522
HfTi(1.8)	TiO_2 (anatase)	4.4	8.299	3.801	9.529
HfTi(9.9)	TiO_2 (anatase)	5.1	7.080	3.804	9.545
HfTi(14.9)	TiO_2 (anatase)	5.6	6.338	3.806	9.556
Fe/ TiO_2	TiO_2 (anatase)	4.4	8.273	3.794	9.509
	$\alpha\text{-Fe}_2\text{O}_3$ (hematite)	4.4	8.273	5.041	13.821
Fe/HfTi(0.8)	TiO_2 (anatase)	5.6	6.629	3.795	9.487
	$\alpha\text{-Fe}_2\text{O}_3$ (hematite)	4.5	9.042	5.016	13.813
Fe/HfTi(1.8)	TiO_2 (anatase)	5.9	6.416	3.795	9.491
	$\alpha\text{-Fe}_2\text{O}_3$ (hematite)	5.4	2.709	5.006	13.854
Fe/HfTi(9.9)	TiO_2 (anatase)	5.5	6.787	3.799	9.508
	$\alpha\text{-Fe}_2\text{O}_3$ (hematite)	5.3	8.140	5.043	13.865
Fe/HfTi(14.9)	TiO_2 (anatase)	6.1	5.932	3.804	9.505
	$\alpha\text{-Fe}_2\text{O}_3$ (hematite)	4.5	9.049	5.032	13.872
Fe/HfTi(34.8)	TiO_2 (anatase)	8.4	4.363	3.801	9.522
	$\alpha\text{-Fe}_2\text{O}_3$ (hematite)	5.8	7.586	5.043	13.872
Fe/HfTi(41.3)	TiO_2 (anatase)	9.1	3.223	3.796	9.532
	$\alpha\text{-Fe}_2\text{O}_3$ (hematite)	21.6	2.848	5.052	13.763

 TiO_2 (anatase) S.G.: $I4_1/amd$ (141) – tetragonal. $\alpha\text{-Fe}_2\text{O}_3$ (hematite) S.G.: R-3cH (167) – trigonal.

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