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# 1. Introduction

There is currently growing interest in the chemistry of higher alcohols (carbon chain  $\geq C_4$ ), due to their high versatility as precursors for more valuable products such as aldehydes, ethers, esters, oxygenated fuel additives *i.e.* acetals or synthetic resins and also due to their use in many paint/solvent related industrial sectors. Long carbon chain alcohols have become target compounds to study, especially n-butanol, as it is considered a good alternative to gasoline (or in the least a suitable additive), to an even greater extent than ethanol. Compared to ethanol, n-butanol has many superior properties as an alternative fuel: higher energy density (e.g. ethanol: 21.2 vs. n-butanol: 32.5 MJ  $L^{-1}$ ), lower volatility (*n*-butanol is six times less volatile than ethanol, whose vapour emissions cause photochemical smog), greater hydrophobicity and *n*-butanol can be used directly in a petrol engine car as a substitute for gasoline (100% ethanol is used in Brazil as a fuel, but only after

# Hierarchically porous Nb–TiO<sub>2</sub> nanomaterials for the catalytic transformation of 2-propanol and n-butanol<sup>†</sup>

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Nb-TiO<sub>2</sub> nanomaterials with hierarchical porosity (macro, meso and micropores) have been successfully synthesized using a simple self-assembly method without the need for a surfactant. Improved textural and structural properties were obtained after incorporation of Nb within a TiO<sub>2</sub> framework. High Nb dispersion and Nb-Ti interaction were achieved at the Nb-TiO<sub>2</sub> nanomaterial surface. With Nb addition to TiO<sub>2</sub>, the balance of Lewis to Brønsted acid sites was maintained however the acidity increased in strength. The catalytic transformation of 2-propanol and *n*-butanol was favoured at very low temperatures with a change in selectivity; the dehydration reaction of alcohols into alkenes was promoted by the increase in acidity of the Nb-TiO<sub>2</sub> nanomaterials.

significant engine modifications).<sup>1,2</sup> These characteristics become even more attractive in terms of economics and sustainability if we consider the fact that *n*-butanol can be obtained from biomass.

Higher alcohols such as *n*-butanol are also interesting raw materials since they can be used to produce commercially important intermediates and fine chemicals like butanal. Aldehydes are also used as accelerators in rubber vulcanisation, and in solvents and plasticisers.<sup>3,4</sup> In order to employ higher alcohols in the aforementioned applications a better understanding of the reactivity of these oxygenated compounds is required to optimise the yield of the sought after derivatives whilst considering the environmental consequences of each process. For example catalytic partial oxidation offers a mild route to convert *n*-butanol into these valuable chemical intermediates.

A diverse range of acid–base catalysts, typically based on zeolites, clays, heteropoly acids, single/mixed metal oxides and transitions metal oxides, has been extensively studied because of their wide applications in catalytic oxidation processes. It is well known that by tuning the acid–base/redox properties of such materials it is possible to impart changes in product selectivity. For many reactions the reaction pathway is complex, making it difficult to understand the structure–acid strength–activity relationship in terms of catalytic partial oxidation, as the reaction mechanisms are not fully understood yet depending certainly upon the reactant nature and much more significantly on the surface properties of the catalyst. Using Nb as a doping agent, it is possible to confer upon the catalyst structural promotion<sup>5</sup> and acid properties<sup>6</sup> with the purpose of



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improving catalytic activity and selectivity towards the desired products. In previous studies the beneficial effects of Nb doping were made evident in the catalytic elimination of volatile organic compounds (VOC) such as butanol and toluene molecules.<sup>7,8</sup> These studies have shown that Nb is able to enhance catalytic performance by decreasing the reaction temperature of a typical oxidation catalyst (Pt–TiO<sub>2</sub>) in the very low temperature range (50–100 °C). Furthermore these favourable catalytic effects are attributed to the formation of mixed noble metal species (Pt<sup>0</sup> and Pt<sup>2+</sup>) on the surface owing to the presence of Nb in the solid. However more characterization is needed to get more information about the effect/interaction of Nb over the titania support.

This work is focused on determining the role of niobium species in a hierarchically porous  $TiO_2$  material for the catalytic transformation of 2-propanol and *n*-butanol. Hierarchical structures can exhibit several advantages such as high specific surface areas, favouring active phase dispersion, and also improved mass transfer of the reactants and products *via* the presence of macrochannels. A thorough investigation of the structural, surface and acid properties of  $NbO_x$ -TiO<sub>2</sub> hierarchical materials has been done and their influence on the 2-propanol decomposition and *n*-butanol partial oxidation has been studied in detail.

### 2. Experimental section

#### 2.1. Material preparation

Hierarchically porous Nb–TiO<sub>2</sub> nano-materials were synthesised using an auto-formation process, without the need for an external templating agent.<sup>9</sup> In total three different niobium doping amounts were realized, 1, 3 and 5 At% Nb with respect to Ti. A basic solution (pH = 12) was prepared from ammonium hydroxide and placed into a shallow dish with a large surface area. Stoichiometric amounts of Ti(iOPr)<sub>4</sub> (Aldrich,  $\geq$  97.0%) and Nb(OEt)<sub>5</sub> (Aldrich, 99.95%) were thoroughly premixed prior to being added dropwise to the basic solution. Finally the solution and the precipitate were transferred to a polypropylene autoclave and heated hydrothermally to 80 °C for 24 h. The autoclave was then cooled down to ambient temperature and the product filtered and washed. The Nb–TiO<sub>2</sub> materials were then dried at 60 °C in air overnight and calcined at 400 °C (4 h and 1 °C min<sup>-1</sup>).

#### 2.2. Characterization techniques

Textural properties were analyzed by N<sub>2</sub> adsorption–desorption at -196 °C using a Micromeritics Tristar II porosimeter apparatus with prior outgassing pretreatment at reduced pressure  $\sim 10^{-4}$  bar and heating at 150 °C. BET and BJH theories were used to determine the total specific surface, pore volume and pore size distribution of the samples. X-ray diffraction patterns were collected at room temperature using a Bruker AXS D8 Advance diffractometer equipped with a SolX energy dispersive detector in the 5–80° range (step 0.02°, 0.4 s per step), using Cu K $\alpha$  radiation ( $\lambda$  = 1.54056 Å). The Rietveld method was employed to refine the cell parameters using FullProf computer software with an LaB6 standard sample used to correct the halfwidth (HWMH) of the experimental reflection. Morphological and microstructural features were analyzed using a Scanning Electron Microscope (SEM) Hitachi S4700 SEM. Transmission electron microscopy (TEM) was performed using a Philips Tecnai 10 with an accelerating voltage of 80 kV to observe support material bound in resin and cross-sectioned using an ultramicrotome. X-ray photoelectron spectroscopy (XPS) of calcined samples was performed using a Kratos Analytical AXIS spectrometer equipped with a monochromatized aluminum source (Al K $\alpha$  = 1486.6 eV). The binding energy (BE) was calibrated based on the line position of adventitious C1s at 285 eV. CasaXPS processing software was used to estimate the relative abundance of the different species and to deconvolute the photopeaks. The evaluation of the acid properties of the hierarchically porous Nb-TiO2 nano-materials was performed using 3 different approaches:

1. NH<sub>3</sub> adsorption-desorption measurements to compare the acid site strengths. NH<sub>3</sub>-Temperature Programmed Desorption (NH<sub>3</sub>-TPD) was conducted using a Micromeritics AutoChem II coupled with an Omnistar mass quadruple detector. 100 mg of the sample were thermally treated under a He atmosphere at 300 °C for 2 h, after cooling down to 80 °C, adsorption of NH<sub>3</sub> was carried out at 80 °C until total saturation of the solid was reached which was monitored by Mass Spectrometry (about 2 h). The excess and physically adsorbed ammonia were flushed out by a He flow at 80 °C for 1 h. NH<sub>3</sub> desorption was accomplished by raising the temperature by 5 °C min<sup>-1</sup> up to 700 °C.

2. Phenylethylamine (PEA) adsorption followed by XPS analysis to evaluate the Lewis–Brønsted acid site distribution<sup>10</sup>. The activated powder (treated at 350 °C for 16 h under a residual pressure of  $10^{-3}$  mbar) was transferred to a glass cell equipped with connections for vacuum/gas line and liquid PEA (purity >99% from Fluka) was introduced into the cell until the powder was completely covered. The slurry remained at room temperature under a flow of N<sub>2</sub> for 3 h. The excess unadsorbed PEA was then removed by filtration, also carried out under N<sub>2</sub>. Deconvolution analysis of the N1s XPS photopeak allowed us to differentiate between Lewis or Brønsted site character.

3. PEA titration experiments to assess the total number of acid sites as well as the ratios of weak to strong acid sites<sup>11</sup>. A liquid-chromatographic line with the sample holder put in the place of the column was used for the analyses. For each experiment, a weighed amount (*ca.* 0.1 g) of fresh sample in cyclohexane was introduced into the sample holder. Pulses (20  $\mu$ l) of PEA solution in cyclohexane of known concentration (0.1 M) were sent at fixed time intervals to the catalyst sample maintained at R.T. and at a constant solvent flow rate (1 mL min<sup>-1</sup>). The amount of unadsorbed amine after each pulse was detected by UV until sample saturation, allowing the determination of the total number of acidic sites. Once the first adsorption was done, a second run was made in order to determine the fraction of strong acid sites.

Catalytic decomposition of 2-propanol was undertaken to evaluate the way these acid sites work in a typical acid-base reaction test. The tests were carried out in the temperature range 170-240 °C using a glass fix bed reactor (8 mm i.d.). The feeding is constituted by 25 mL min<sup>-1</sup> of He with 140 ppmv of 2-propanol. A gas chromatograph equipped with a flame ionization detector was used to analyze the products (essentially acetone, propylene and diisopropyl ether). The catalyst was heated prior to each run at 250 °C under pure He to purge the system and activate the catalyst. The activity in *n*-butanol catalytic oxidation was evaluated in a continuous flow fixed bed glass reactor (8 mm i.d.) at atmospheric pressure. The reaction mixture was obtained by passing 100 mL min<sup>-1</sup> of air through a stainless steel saturator chamber filled with pure *n*-butanol (assay  $\geq$  99.7%) and heated at 70 °C, allowing an *n*-butanol concentration of 800 ppmv in air. The tests were performed on 200 mg of catalyst, in a temperature range of 400  $^\circ$ C to 50  $^\circ$ C with a cooling rate of 1 °C min<sup>-1</sup> (SV = 23 000 h<sup>-1</sup>). The analysis of the outlet gas was performed on-line using a gas chromatograph, equipped with Porapak-Q and CTR I columns and FID and TCD to analyze the hydrocarbons and the permanent gases (O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>), respectively.

## 3. Results and discussion

#### 3.1. Structural characterisation

N<sub>2</sub> physisorption analysis results of both uncalcined and calcined *x*%Nb–TiO<sub>2</sub> solids are shown in Table 1. It is worth noting that the synthesis procedure led to uncalcined *x*%Nb–TiO<sub>2</sub> materials with a very high specific surface area (360–400 m<sup>2</sup> g<sup>-1</sup>) without the use of any templating agent. Usually different kinds of surfactants (*e.g.* CTAB or Brij 56) are used to synthesize solids with high specific surface values. In previous studies meso-macroporous structured pure titania<sup>9</sup> and niobia<sup>12</sup> synthesized using templating agents have shown specific surface areas of 470 m<sup>2</sup> g<sup>-1</sup> and 140 m<sup>2</sup> g<sup>-1</sup> respectively. The presence of a combination of type II and type IV N<sub>2</sub> physisorption isotherms confirms the presence of micropores and mesopores in the uncalcined *x*%Nb–TiO<sub>2</sub> materials (Fig. S1, ESI†). N<sub>2</sub> adsorption at high relative pressure (*P*/*P*<sub>0</sub> ≥ 0.8) is characteristic of macroporous solids (Fig. S1, ESI†).

SEM micrographs of uncalcined Nb-doped titania samples (Fig. 1a and b) reveal the macroporous network. These macropores



Fig. 1 SEM micrographs of (a) uncalcined 3%Nb-TiO<sub>2</sub>, (c) calcined 3%Nb-TiO<sub>2</sub>, (b) and (d) are magnified images of (a) and (c) micrographs respectively.

range from 100 nm to 250 nm in diameter and are arranged parallel to each other with a funnel-like shape. It can also be observed that the macroscopic framework is composed of titania nanoparticles, which agglomerate to form the edges and the walls of the macro-channels. Concurrently this aggregation of nanoparticles creates a mesoporous network with a wormhole-like array. The TEM images also reveal macropore walls around  $2-3 \mu m$  thick formed from the aggregation of nanoparticulate oxides and contained within these walls are interconnected wormlike channels contributing to the micro-(meso)porosity of the sample (Fig. S2, ESI†). Vantomme *et al.* have also shown by TEM of microtomed specimens that the mesoporous framework is located within the walls of the macropore structure.<sup>12</sup>

This synthesis procedure, a so-called "self-assembly" method, demonstrates how hierarchically structured materials can be spontaneously formed by the hydrolysis and condensation phenomena of metal alkoxides such as  $Ti(^{i}OPr)_{4}$  and  $Nb(OEt)_{5}$ , which were the precursors used in the present work. In the synthetic route employed the different hydrolysis and condensation reactions of the alkoxides that take place on contact with water generate alcohol and water molecules which act as porogen agents, creating the different porosity levels within the polymerized *x*%Nb–TiO<sub>2</sub> structure.<sup>12</sup> Nb addition generated Nb–TiO<sub>2</sub> hierarchically porous materials with improved textural properties. However no relationship with Nb content can be drawn at this level of doping (Table 1).

Table 1         Textural and structural properties of calcined x%Nb-TiO <sub>2</sub> hierarchically porous materials								
Sample	Specific surface area $(m^2 g^{-1})$	TiO <sub>2</sub> average	Lattice param	Unit cell				
		crystallite size <sup><math>b</math></sup> (nm)	а	С	volume (Å <sup>3</sup> )			
TiO <sub>2</sub>	140 $(399)^a$	15.2	3.7879	9.4812	136.1			
1%Nb-TiO <sub>2</sub>	$160(360)^a$	13.0	3.7888	9.4866	136.2			
3%Nb-TiO <sub>2</sub>	$(382)^a$	12.4	3.7912	9.4909	136.4			
5%Nb-TiO <sub>2</sub>	$(376)^a$	12.6	3.7922	9.4934	136.5			

<sup>*a*</sup> Before the calcination procedure. <sup>*b*</sup> Determined using the Scherrer equation:  $d = k\lambda/\beta \cos(\theta)$ , *k*: Sherrer constant,  $\lambda$ : Cu K $\alpha$  radiation,  $\beta$ : FWHM and  $\theta$ : Bragg angle.

After calcination, the materials retained significantly high surface areas since their values were about 3 times higher than that of commercial titania (Degussa  $\approx 50 \text{ m}^2 \text{ g}^{-1}$ ).<sup>13</sup> Nb addition limited the decrease in the specific surface area (Table 1). The decrease in the micropore population is responsible for the diminution of specific surface areas, since at low relative pressure in the N<sub>2</sub> adsorption isotherms a decrease in the nitrogen uptake was observed for all samples (Fig. S3, ESI†). However the meso and macro porosities were retained after calcination (Fig. 1c and d).

Powder XRD analyses were performed on the calcined x%Nb-TiO<sub>2</sub> materials. The X-ray diffraction patterns showed the presence of the anatase TiO<sub>2</sub> phase at  $2\theta = 25.3$ , 38.0, 47.9, 54.0, 55.0, 62.7, 68.9, 70.2, 75.2 and 82.6° (JCPDF 84-1286) without any Nb-based crystalline phase (Nb<sub>2</sub>O<sub>5</sub> JCPDF 30-0873,  $2\theta = 28.4, 22.6, 36.6, 46.2, 50.9$  and  $55.1^{\circ}$ ) (Fig. S4, ESI<sup>†</sup>). The low Nb loading and/or a high dispersion of Nb species within a TiO<sub>2</sub> framework could well explain these results. The structural parameters of x%Nb-TiO<sub>2</sub> solids, obtained from XRD analyses, are summarized in Table 1. TiO<sub>2</sub> average crystallite size decreased with Nb addition. This trend could be an indication of Nb incorporation which could affect the anatase structure somehow. Rietveld refinement was done to estimate the cell parameters of the anatase lattice (Fig. S5, ESI<sup>†</sup>). The unit cell volume obtained from the lattice parameters a and c are close in value and within the margin of error (Table 1). The fact that the ionic radii are close in value ( $rTi^{4+} = 64$  pm compared to  $rNb^{5+} = 70 \text{ pm}$ ) coupled with the fact that doping levels are low suggest a possible incorporation of Nb species into the anatase framework by a substitution mechanism of Ti<sup>4+</sup> ions by Nb<sup>5+</sup> ions.14,15

#### 3.2. Surface characterisation

The results of the surface characterisation are shown in Table 2 and Fig. 2. Analysis of the O 1s core level showed the presence of two components located at 530 eV and 532 eV which correspond respectively to  $O^{2-}$  species of the oxide network (main component) and to oxygen ions with low coordination states ( $O_2^-$  and  $O^-$ ), oxygen vacancies and oxygen atoms in contaminant species (OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>). The Ti 2p<sub>3/2</sub> and Nb 3d<sub>5/2</sub> binding energies were characteristic of the presence of Ti<sup>4+</sup> and Nb<sup>5+</sup> ions respectively.<sup>16,17</sup> The Nb/Ti ratio obtained by XPS was very close to that obtained by ICP analysis and the corresponding straight line was very close to the line obtained from the Kerkhof–Moulijn model (Fig. 2).<sup>18</sup>

Table 2Binding energy values obtained from XPS analysis of calcinedx%Nb-TiO2 hierarchically porous materials

	O 1s (eV)	Nb 3d <sub>5/2</sub> (eV)	Ti 2p <sub>3/2</sub> (eV)	N $1s^a$ (eV)			
Sample				Lewis	Brønsted		
TiO <sub>2</sub> 1%Nb-TiO <sub>2</sub> 3%Nb-TiO <sub>2</sub> 5%Nb-TiO <sub>2</sub>	530.3 531.2 530.1 530.9	 207.9 207.7 207.7	458.9 458.8 458.9 458.9	399.7 (85%) 399.7 (90%) 399.8 (87%) 399.8 (83%)	401.5 (15%) 401.3 (10%) 401.6 (13%) 401.5 (17%)		

<sup>a</sup> Binding energy from N 1s of the pre-adsorbed PEA molecule.



Fig. 2 Relationship between the Nb/Ti ratio obtained from XPS analysis and the Nb/Ti ratio obtained by ICP analysis.

ToF-SIMS analyses for all hierarchically porous materials resulted first in the detection of several TiO<sub>2</sub> characteristic fragments (Fig. S6, ESI<sup>†</sup>). No polymeric niobium fragments  $([Nb_rO_v]^+)$  were detected on the solid surface as can be observed over Nb-TiO<sub>2</sub> samples prepared by an impregnation method.<sup>19</sup> This result can be explained by the high Nb dispersion in the hierarchically porous TiO<sub>2</sub> materials, and thus the statistical improbability of forming Nb-O-Nb bonding at such low loadings. The high mass resolution of ToF-SIMS analyses also showed the presence of TirNbO<sub>v</sub> fragments. The detected binary ions for 5%Nb-TiO2 in a positive polarity were  $[TiNbO_3]^+$ ,  $[Ti_2NbO_5]^+$  and  $[Ti_3NbO_7]^+$  fragments at 188.825 (188.838), ± 268.876 (268.777) ± and 348.680 (348.715) ± u, respectively (Fig. 3). The peak intensities of these fragments were much more intense for the sample prepared via the selfassembly method rather than for a mechanical mixture of TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> oxides (in a ratio to obtain a 5% At Nb loading w.r.t. Ti) (Fig. 3). This result indicated that the possible recombination of single ions to give binary ions during the ToF-SIMS analysis is very low. In the hierarchical Nb–TiO<sub>2</sub> materials, the relative ToF-SIMS intensity ratios of these binary ions were clearly proportional to the Nb loading (Fig. 4). Since Ti-Nb mixed fragments show a direct interaction between Ti and Nb species, the formation of a Nb-TiO2 solid solution on the solid surface can thus be confirmed by this ToF-SIMS analysis.

#### 3.3. Acid-base characterisation

The NH<sub>3</sub> desorption curves from the analysis of the peak intensity of m/z = 17 are shown in Fig. 5. A very broad peak of desorption was obtained, indicating that all the samples possess a wide distribution of acid site strengths. The temperature at which the ammonia began to desorb is the same (125 °C), independent of sample composition. However the desorption peaks presented a maximum which increased with Nb content (Fig. 5). It is generally accepted that desorption temperature can be related to the strength of the acid sites. An increase in

<sup>‡</sup> Theoretical ion mass value.

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Fig. 4 Relative ToF-SIMS intensity ratios of binary  $[Ti_xNbO_y]^+$  fragment ions to the sum of all detected ions obtained for calcined 5%Nb-TiO<sub>2</sub> hierarchical material.



After PEA adsorption, the chemical environment of the nitrogen in the probe molecule changes and the binding energy of electrons stemming from the 1s orbital of the nitrogen is modified.<sup>10,21,22</sup> The N 1s signal obtained was fitted with two different components (Fig. S7, ESI $\dagger$ ). Table 2 summarises the N 1s BE and the proportion of each component obtained from the deconvolution. The major component (85%) centered around 400 eV is characteristic of the presence of Lewis acid sites while the minor component centered around 401.4 eV is attributed to



Fig. 5 NH<sub>3</sub>-TPD curves for the calcined x%Nb-TiO<sub>2</sub> hierarchically porous materials.

the presence of Brønsted acid sites. The Lewis and Brønsted acid sites distribution is relatively constant whatever the Nb content (Table 2). These results differ from those obtained by Onfroy *et al.*<sup>23</sup> who observed a change in the distribution of acid sites by impregnation of Nb on a TiO<sub>2</sub> surface. NbO<sub>x</sub> clusters (beyond 4.5 At Nb m<sup>-2</sup>) acted as Brønsted acid sites, whose proportion increased to the detriment of the Lewis sites.<sup>24</sup> In our case the high dispersion of Nb species in the TiO<sub>2</sub> network allowed to maintain the same proportion of Lewis and Brønsted acid sites.

Fig. 6 shows the evolution of the total number of acid sites of the x%Nb–TiO<sub>2</sub> samples as well as the ratios of weak to strong acid sites obtained from PEA titration experiments. The total number of acid



Fig. 6 Acid sites distribution for calcined 5%Nb-TiO<sub>2</sub> hierarchically porous materials, obtained from PEA titration experiments in cyclohexane.

sites (around 1.8  $\mu mol~m^{-2}$ ) is very similar for all the hierarchical materials. The values agreed with those mentioned in the literature data.<sup>25,26</sup> For 5%Nb–TiO<sub>2</sub>, a higher proportion of strong acid sites is obtained and corroborates well with the maximum temperature (330 °C) of the desorption peak obtained by NH<sub>3</sub>-TPD.

#### 3.4. Catalytic performances

Fig. 7 shows the evolution of the intrinsic reaction rate of isopropanol (IPA) decomposition as a function of temperature



Fig. 7 Intrinsic reaction rate of isopropanol decomposition in the presence of x%Nb-TiO<sub>2</sub> catalysts.

for the x%Nb-TiO<sub>2</sub> hierarchical catalysts. In the absence of Nb, the isopropanol started to be converted at 200 °C while for samples containing 3 and 5% Nb, the conversion of IPA started at 175 °C. The increase in activity with Nb content cannot be explained by the nature of the acid sites (Lewis-Brønsted) as their distribution was the same independent of Nb content but by the increase in acidity with increasing Nb content in the catalyst. The selectivity of the catalysts and the yields from isopropanol decomposition at 200 °C are collected in Table 3. In the absence of Nb, acetone and propene are produced in similar proportions, indicating that the basic/redox and acid sites are both used. However in the presence of Nb (within the catalyst), propene is almost the only product observed. This result could be explained by the increase in strength of the acid sites by Nb addition, which favours the isopropanol decomposition reaction into propene.

Moreover the yield reached a maximum for the 3%Nb-TiO<sub>2</sub> catalyst (Table 3). The high yield of propene observed on 3%Nb-TiO<sub>2</sub> could be due to the higher acid strength of the sites than that of the other samples in agreement with the very lower apparent activation energy of this sample (60 kJ mol<sup>-1</sup>). This result suggests also that there might be a stronger adsorption of propene on the 5%Nb-TiO2 catalyst resulting in a decrease in the detectable propene yield at 200 °C. A simple scheme is proposed to describe the role of Nb species in the isopropanol transformation. Acetone formation occurs via the isopropanol dehydrogenation reaction (Fig. 8). By incorporating niobium in the TiO<sub>2</sub> oxide by isomorphic substitution of Ti<sup>4+</sup> ions by Nb<sup>5+</sup> ions, the electronic properties of the material change and the adsorption of isopropanol could preferentially occur on the stronger Lewis acid sites. We propose that the strongest metal interaction (Nb-O) facilitates the breaking of the C-O bond, leading to the formation of a larger amount of propene by elimination of the hydrogen in the  $\beta$  position of the isopropanol molecule (Fig. 8).

Fig. 9 shows the evolution of the total conversion of *n*-butanol as a function of temperature. In the temperature range 50–150 °C, all the catalysts gave similar *n*-butanol conversion rates. At higher temperatures (150–250 °C), Nb containing catalysts became much more active. The  $T_{50}$  temperature (temperature to reach a *n*-butanol conversion of 50%) is 224 °C for TiO<sub>2</sub> and is between 170 and 180 °C for Nb containing catalysts. The presence of Nb thus enabled a reduction in the  $T_{50}$  of about 50 °C. *n*-Butanol is totally converted at 250 °C for Nb doped catalysts, while for pure TiO<sub>2</sub> a temperature of 350 °C

Table 3 Selectivity, yields and intrinsic reaction rates for isopropanol decomposition at 200 °C in the presence of x%Nb-TiO<sub>2</sub> catalysts

Sample	$E_{\rm app\ propene}{}^a/{\rm kJ\ mol^{-1}}$	Selecti	Selectivity/%		Yield/%	Yield/%		
		$\mathbf{A}^b$	$\mathbf{P}^{c}$	$\mathrm{DIE}^d$	$A^b$	$\mathbf{P}^{c}$	$\mathrm{DIE}^d$	$r_{\rm IPA}  (10^{-4}  \mu { m mol}  { m min}^{-1}  { m m}^{-2})$
TiO <sub>2</sub>	127	44	38	9	0.24	0.20	0.05	0.5
1%Nb-TiO <sub>2</sub>	133	2	96	1	0.05	3.00	0.01	1.2
3%Nb-TiO <sub>2</sub>	60	4	95	1	0.11	16.60	0.14	1.5
5%Nb-TiO <sub>2</sub>	110	2	97	1	0.13	8.60	0.08	2.7

<sup>*a*</sup> E<sub>app propene</sub>: apparent activation energy for propene production. <sup>*b*</sup> A: acetone. <sup>*c*</sup> P: propene. <sup>*d*</sup> DIE: di-isopropyl ether.



Fig. 8 Isopropanol decomposition scheme



**Fig. 9** Evolution of the *n*-butanol conversion as a function of temperature and catalyst composition.



**Fig. 10** Butanal and butene yields for *n*-butanol partial oxidation in the presence of x%Nb-TiO<sub>2</sub> catalysts ( $\phi$ : TiO<sub>2</sub>,  $\blacksquare$ : 1%Nb-TiO<sub>2</sub>,  $\blacktriangle$ : 3%Nb-TiO<sub>2</sub>,  $\bullet$ : 5%Nb-TiO<sub>2</sub>).

is needed to obtain total conversion (Fig. 9). These results can be partially explained by the increase in  $TiO_2$  specific surface area (post-calcination) by Nb addition (Table 1).

Besides butanal and butenes, which are the major products observed, other by-products such as ethanal, propanal and propene were also detected. The yields of the *n*-butanol oxidation towards butanal and butenes (1 and 2-butenes) are shown in Fig. 10. In the presence of TiO<sub>2</sub>, butanal production extends over a wide temperature range (100–350 °C). When Nb is incorporated into the catalyst this temperature range is greatly reduced (100–250 °C) and a decrease in the butanal yield to the benefit of the production of butenes was observed (Fig. 10). This behaviour can be attributed to the strengthening of the Nb–TiO<sub>2</sub> acidity. The dehydration reaction of *n*-butanol is favoured over stronger Lewis acid sites, as previously observed for the isopropanol decomposition reaction.

# 4. Conclusions

New materials with hierarchical porosity were synthesized by an auto-assembly method. The hierarchical TiO<sub>2</sub> oxide was doped with small amounts of Nb (until 5 At%). The calcination of these materials at 400 °C induced a crystallization of these oxides in the TiO<sub>2</sub> anatase phase and a preservation of the meso-macroporous structure independent of Nb loading. Nb incorporation within the TiO2 structure takes place by an isomorphic substitution mechanism in which a Ti<sup>4+</sup> ion was replaced by a Nb<sup>5+</sup> ion. This substitution had a promoter effect on the TiO<sub>2</sub> textural properties. The surface of these materials consisted of a mixed Ti<sup>4+</sup>-O-Nb<sup>5+</sup> oxide. Nb incorporation influenced the acid properties of these materials. Even though the Lewis-Brønsted acid site balance was preserved, a strengthening of acid sites was noticed upon Nb addition. As a result, catalytic activity of hierarchically porous TiO<sub>2</sub> in the oxidation of *n*-butanol and in isopropanol decomposition is greatly improved by Nb doping. The strengthening of acidity played a key role in the dehydration reactions of alcohols with transformation selectively leading to the formation of alkenes.

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# Notes and references

- 1 S. Atsumi, T. Hanai and J. Liao, Nature, 2008, 451, 86-90.
- 2 M. Harper, K. Van Geem, S. Pyl, G. Marin and W. Green, *Combust. Flame*, 2011, **158**, 16–41.
- 3 S. Bhaduri and D. Mukesh, *Homogeneous Catalysis. Mechanisms and Industrial Applications*, Sumit Wiley Interscience, 2000, ISBN: 0-471-37221-8.

- 4 J. Requies, M. Güemez, P. Maireles, A. Iriondo, V. Barrio, J. Cambra and P. Arias, *Appl. Catal.*, *A*, 2012, **423–424**, 185–191.
- 5 F. Noronha, D. Aranda, A. Ordine and M. Schmal, *Catal. Today*, 2000, **57**, 275–282.
- 6 T. Onfroy, G. Clet, S. Bukallah, T. Visser and M. Houalla, *Appl. Catal.*, *A*, 2006, **298**, 80–87.
- 7 M. Franco Finol, J. Rooke, B.-L. Su, M. Trentesaux, J.-M. Giraudon and J.-F. Lamonier, *Catal. Today*, 2012, **192**, 154–159.
- 8 J. Rooke, T. Barakat, M. Franco Finol, P. Billemont, G. De Weireld, Y. Li, R. Cousin, J.-M. Giraudon, S. Siffert, J.-F. Lamonier and B. L. Su, *Appl. Catal.*, *B*, 2013, 142–143, 149–160.
- 9 K. Xia, D. Ferguson, Y. Djaoued, J. Robichaud, N. Tchoukanova, R. Brüning and E. McCalla, *Appl. Catal., A*, 2010, **287**, 231–241.
- 10 M. Johansson and K. Klier, Top. Catal., 1997, 4, 99-108.
- 11 P. Carniti, A. Gervasini and C. Fisica, *Adsorpt. Sci. Technol.*, 2005, **23**, 739–749.
- 12 A. Vantomme, A. Léonard, Z.-Y. Yuan and B.-L. Su, *Colloids Surf.*, A, 2007, **300**, 70–78.
- P. Panagiotopoulou, A. Christodoulakis, D. Kondarides and S. Boghosian, J. Catal., 2006, 240, 114–125.
- 14 A. Ruiz, G. Dezanneau, J. Arbiol, A. Cornet and J. Morante, *Chem. Mater.*, 2004, **17**, 862–871.

- J. Arbiol, J. Cerdà, G. Dezanneau, A. Cirera, F. Peiró, A. Cornet and J. R. Morante, *J. Appl. Phys.*, 2002, 92, 853.
- 16 D. Morris, Y. Dou, J. Rebane, C. Mitchell and R. Egdell, *Phys. Rev.*, 2000, **61**, 445–457.
- 17 B. Mei, M. Sánchez, T. Reinecke, S. Kaluza, W. Xiaa and M. Muhler, *J. Mater. Chem.*, 2011, 21, 11781–11790.
- 18 V. Leon, Surf. Sci., 1995, 339, L931-L934.
- 19 S. Bukallah, M. Houalla and D. Hercules, *Surf. Interface Anal.*, 2000, 29, 818–822.
- 20 G. Busca, E. Finocchio, G. Ramis and G. Ricchiardi, *Catal. Today*, 1996, **32**, 133–143.
- 21 L. Dussault, J. C. Dupin, E. Dumitriu, A. Auroux and C. Guimon, *Thermochim. Acta*, 2005, **434**, 93–99.
- 22 A. Gervasini, S. Bennici, A. Auroux and C. Guimon, *Appl. Catal.*, *A*, 2007, **331**, 129–137.
- 23 T. Onfroy, G. Clet, S. Bukallah, T. Visser and M. Houalla, *Appl. Catal.*, *A*, 2006, **298**, 80–87.
- 24 R. Ladera, E. Finocchio, S. Rojas, J. L. G. Fierro and M. Ojeda, *Catal. Today*, 2012, **192**, 136–143.
- 25 Q. Sun, Y. Fu, H. Yang, A. Auroux and J. Shen, J. Mol. Catal. A: Chem., 2007, 275, 183–193.
- 26 M. Manríquez, T. López, R. Gómez and J. Navarrete, J. Mol. Catal. A: Chem., 2004, 220, 229–237.