



## Preparation of nanodispersed titania using stabilized ammonium nitrate melts

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### ABSTRACT

An expedite one-step approach using simple precursors has been proposed to obtain metallic oxide compounds and exemplified by preparation of highly dispersed  $\text{TiO}_2$ . The technique consists in heating to 400–500 °C of molten ammonium nitrate stabilized with an organic nitrogen-containing compound (urea, melamine, ammonium oxalate) and containing dissolved metal salt precursor ( $\text{TiOCl}_2$ ). The crystallites of the resulting  $\text{TiO}_2$  demonstrated variable size and shape as a function of stabilizer used. Their activity in photocatalytic oxidation of formic acid also depends on the nature of the stabilizer. The catalysts as-prepared showed high photocatalytic performance, superior to that of the Degussa P25 reference. Nitrogen containing stabilizers play a double role of increasing the process safety and modifying the properties of the solid products.

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### 1. Introduction

Titanium dioxide is the most active semiconductor photocatalyst [1–3] and a general purpose catalytic support which has been extensively studied for environmental applications [4–6].  $\text{TiO}_2$  is non-toxic, chemically stable and possesses high oxidation power [7]. Due to its importance for the environmental applications, a great effort has been directed to obtaining the titania-based catalytic materials with controllable properties. In a great majority of works, modifications of hydrothermal and solvothermal methods [8,9] or sol–gel techniques [10–12] are applied for preparation of titania-based materials. However, alternative techniques are considered to achieve additional control over the properties such as use of supercritical fluids [13]; applying block copolymers as surfactants [14], templating with colloidal crystals [15] and many others.

Improved control of morphological properties of inorganic materials can be achieved due to using as reaction media of ionic liquids [16], including low-melting salts such as alkali metal nitrates [17]. Molten salt (MS) technique affords various inorganic materials with advantageous morphological properties, such as niobates [18], molybdates [19] and tungstates [20], layered titanates [21–23], ferrites [24] and other mixed oxides. Earlier we applied molten salt technique to prepare pure titania and zirconia or Mn-containing VOC oxidation catalysts supported on these oxides [25].

As any preparation technique MS method has not only advantages but some drawbacks as well. First, if the reaction is carried out in the alkali metal nitrates, to obtain the target product, after the reaction the solidified melt should be extracted by large amounts of water. Furthermore, the solids obtained in alkali metal nitrates may retain significant amounts of alkali metals coming from the melt in adsorbed or even chemically bound state. This is sometimes desirable, particularly if the target solid is an alkali metal containing compound such as  $\text{LiCoO}_2$  [26] or mixed Li–Ni–Mn oxide [27]. However, for most catalytic applications the presence of alkali metal impurities in the solid catalysts should be avoided.

Recently, Morozov et al. [28,29] used ammonium nitrate (AN) to prepare mixed oxides such as Mn-containing spinels demonstrating high catalytic activity in oxidation reactions. Later this approach was applied to elaborate superconductor ceramics and yttrium iron garnet with advantageous morphological properties [30,31]. Using AN as a reaction medium has a major advantage over alkali metal nitrates, of being an extremely simple one-step method. Indeed, after heating of the reaction mixture above 200 °C, pure solid product is immediately obtained with no need of additional steps of washing, filtration, etc. Moreover, no alkali metal impurities are to be feared in the solid products. However, the drawback of this technique is a relatively low temperature limit, imposed by AN decomposition temperature. Another obvious issue is the possibility of AN explosion. Being low for moderate amounts of pure compound, the AN explosivity strongly increases in the presence of catalysts or combustible organics and may lead to disastrous accidents [32,33]. Because of the accidents involving AN or its mixtures, considerable research effort was directed to achieve thermal stabilization of AN [34,35].

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It was demonstrated that certain inorganic and organic substances behave as explosivity modifiers (or AN stabilizers), decreasing the decomposition rate and increasing the temperature limits of AN stability [36]. The knowledge developed in the safety studies can be applied to preparative chemistry. In the present work we studied preparation of titanium oxide using stabilized AN as a reaction medium. Among the substances which demonstrated stabilizing properties we have chosen nitrogen-containing organic compounds (urea, melamine, ammonium oxalate) which at high temperatures would decompose together with AN, without leaving a solid residue. Thus, we expected to improve the technique keeping its advantages of being one-step process and yielding pure product, as exemplified in the present work by preparation of TiO<sub>2</sub>.

## 2. Experimental

The mixtures containing TiOCl<sub>2</sub> precursor salt, a 10-fold molar excess of AN and eventually a stabilizer in a weight amount equal to AN, (all high purity chemicals purchased from Aldrich) were placed in a glass reactor under a nitrogen flow. Dehydration at 120–180 °C and reaction at 400–500 °C were subsequently carried out. After reaction, the powders were taken and handled without other treatments. The components used in the preparations are indicated in Table 1. Four solids were obtained this way including the sample prepared in pure AN. Degussa P25 titania was applied as a reference for comparison.

Powder X-ray diffraction (XRD) patterns were obtained on a BRUKER diffractometer using CuK $\alpha$  emission. The XRD patterns were analyzed using the standard JCPDS files. The average size of catalyst crystallites was estimated by the Scherrer equation. The specific surface area and pore volume of the solids were determined by nitrogen adsorption–desorption at 77 K using Micromeritics ASAP 2010 device. Prior to measurements, the samples were evacuated for 2 h at 400 °C under high vacuum. Specific areas were computed from these isotherms using BET and BJH methods. Transmission electron micrographs were obtained on a JEOL 2010 device with accelerating voltage 200 keV. Chemical analyses were carried out by the atomic emission method. Diffuse reflectance UV–visible spectra were measured on a Perkin Elmer Lambda 35 spectrometer in the range 200–1000 nm, with MgO reference.

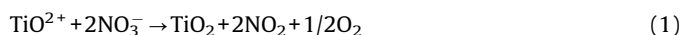
The gaseous products evolved upon heating of the samples were studied using a mass-spectrometer Gas Trace A (Fison Instruments) equipped with a quadrupole analyzer (VG analyzer) working in a Faraday mode. The ionization was done by electron impact with electron energy 65 eV. The samples (ca. 0.1 g) were heated from room temperature to 550 °C in a glass cell at the heating rate of 1.5 °C min<sup>-1</sup>. A silica capillary tube heated at 180 °C continuously bled off a proportion of the gaseous reaction products. Several signals were registered, corresponding, respectively, to ionized species of NH<sub>3</sub> (17), HCl (36), H<sub>2</sub>O (18), NO (30), N<sub>2</sub>O (44, 14), N<sub>2</sub> (28), O<sub>2</sub> (32), CO<sub>2</sub> (44, 12) and NO<sub>2</sub> (46). Scanning electron microscopy (SEM) images were obtained on a Hitachi S800 device.

Formic acid was purchased from Acros Organics with the highest purity grade (99%). Photocatalytic degradation experiments were carried out in a 100 ml photoreactor equipped with a circulating water cell to remove IR radiations thus preventing any heating of the solution. The UV source was a Philips HPK 125 W high pressure mercury lamp. The quantitative analysis of formic acid was made by liquid phase chromatography. The HPLC system comprised a Varian Prostar Model 410 pump, a Varian Prostar 330 PDA photodiode array detector adjusted at 210 nm. The formic acid analysis was performed with a cation-exchange chromatography column (Sarasep CAR-H 300 × 7.8 mm<sup>2</sup>) using a H<sub>2</sub>SO<sub>4</sub> solution (5 × 10<sup>-3</sup> M) as the mobile phase at a flow rate of 0.7 ml min<sup>-1</sup>; The volume injected is 20 ml. The 30 ml of an aqueous solution (50 ppm) was prepared with pure water. A magnetic stirrer was used to ensure a good homogenization of the solution during the photodegradation. The analyzed volume sample was 0.3 ml extracted from the reactor using a syringe and filtered with Milipore disks (0.45 mm).

## 3. Results and discussion

### 3.1. Reactivity in the melts

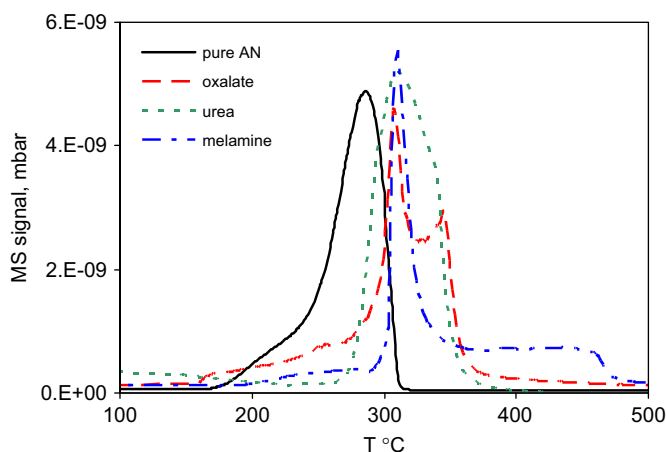
Titanium oxychloride is supposed to react with nitrate melts according to the Lux-Flood acid base mechanism, Eq.(1). Ammonium nitrate sublimation and decomposition begin simultaneously with its melting at 169 °C. At relatively low temperatures and for pure AN, nitrous oxide was detected as a main product, Eqs. ((2) and (3)) [37]:



However, other nitrogen-containing gases including N<sub>2</sub> and NO are formed in large proportions depending on the temperature and on the reaction mixture composition. Therefore, other reactions of AN decomposition might be considered, such as Eq. (4). Decomposition of AN proceeds via an ionic mechanism above 200 °C and formation of nitronium ion seems to be rate-determining [38,39]. Acidic species are known to increase the rate of AN decomposition, while bases generally retard decomposition. Chloride ion has a strong destabilizing effect [40,41]. At the same time the presence of chloride induces the increase in nitrogen rather than nitrous oxide gas formation. Since the TiOCl<sub>2</sub> precursor contains chloride and has a strong acidity, the maximum on the decomposition curve is markedly shifted to lower temperature (284 °C) as compared to the decomposition of pure AN for which the literature DSC-derived value is 326 °C

**Table 1**  
Phase composition, particle size and textural properties of the synthesised solids.

Sample name	Dopant	Phase, XRD (vol%)	D <sub>XRD</sub> (nm)	S (m <sup>2</sup> g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )
<b>a</b>	Undoped	A	28	54	0.26
<b>b</b>	Urea	A	14	91	0.20
<b>c</b>	Ammonium oxalate	A	9	63	0.25
<b>d</b>	Melamine	A 88 R 12	19	58	0.31



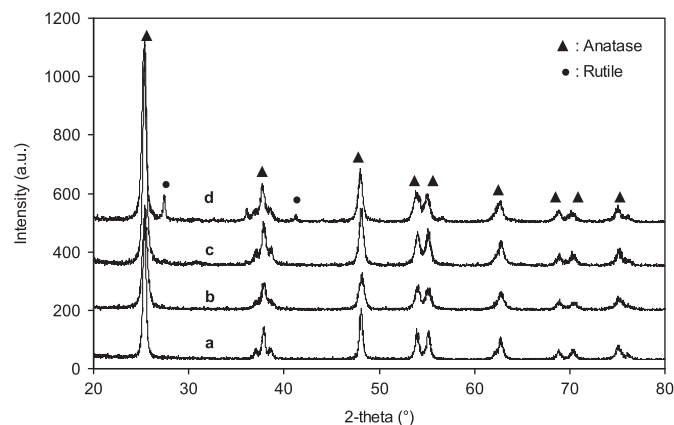
**Fig. 1.** Production of  $N_2$  gas detected by mass spectrometry ( $m/z=28$  signal) as a function of temperature, for the reaction mixtures of  $TiOCl_2$  with AN in the absence and in the presence of stabilizers.

(Fig. 1). Addition of stabilizers increases the maximum temperature of nitrogen oxide production, in agreement with the literature. However, the absolute values of this maximum are lower than reported for the AN-stabilizers mixtures (380–390 °C) in the absence of  $TiOCl_2$ . Apparently this is the result of a struggle between two opposite effects: that of AN destabilization by  $TiOCl_2$  precursor and that of its stabilization by the nitrogen-containing compounds. The resulting effect of stabilizers is an increase of decomposition maximum by ca. 50 °C. The shape of gas production curves as a function of temperature is multimodal, thus suggesting a stepwise mechanism of reaction in all cases, which should be different as a function of stabilizer. Indeed, if non-doped and urea-doped mixtures initially produced transparent melts, the oxalate-doped mixture was milk-white, suggesting probable formation of some titanium oxalate insoluble species. More detailed mechanistic study is beyond the scope of this work. Due to the intense decomposition of AN (2)–(4) simultaneous with the Lux-Flood Reaction (1) and owing to the possibility of interaction between the gaseous species, the contribution of nitrogen oxide coming from the  $TiOCl_2$  reaction is difficult to separate from the total gas production. In the high-temperature region, which is of particular interest for us, nitrogen production becomes the most important and can be considered as diagnostic for the whole decomposition reaction. The integral effect of stabilizers is therefore clearly seen from the nitrogen production curves (Fig. 1). Expectedly, carbon dioxide, ammonia and hydrochloric acid were also observed as abundant products for all stabilised reaction mixtures. The reactivity seems to be unequal and the most reluctantly decomposed is the melamine-doped mixture, probably due to high thermal stability of melamine [42,43]. While for melamine-doped mixture the main decomposition maximum is close to those of other stabilizers, there is a long high-temperature nitrogen production tail in the curve. According to visual observation after 350 °C there is no more melt at these temperatures and the solid product releases nitrogen. This probably occurs due to formation and further decomposition of the Ti(IV)–melamine complex [44]. For the non-stabilized reaction mixture a very strong volume expansion was observed at the point of maximum reaction rate (five times or more), whereas in the presence of stabilizers the reaction is much less violent and the volume expansion at the highest point is no more than twofold. This observation has a certain practical value, since reasonably small reaction vessels and furnaces (less than 1 l) can be used to obtain substantial amounts of titania (hundreds of grams), using stabilized melts.

### 3.2. Properties of the obtained solids

An important secondary reaction product was  $NH_4Cl$ , resulting from the exchange between chloride of  $TiOCl_2$  and ammonium from the melt. Ammonium chloride was sublimated on the cold part of the reaction vessel and therefore did not remain within the target oxide product. However, if the reaction temperature was 400 °C, non-negligible amounts of chloride (0.5–1 wt%) were detected in the solids even in the temperature of ammonium chloride sublimation is significantly lower (338 °C). By this reason only the samples prepared at 500 °C are further considered which are free from chloride impurity. After the reaction at 500 °C all the solids contained pure titania. Anatase (JCPDS No. 21-1272) was the only phase detected by XRD in the case of non-stabilized AN, oxalate, and urea-stabilized mixtures (Fig. 2a–c). In the melamine-stabilized mixture, a mixture of anatase with a smaller amount of rutile was observed (Fig. 2d). Analysis of the XRD lines width allowed determining mean particle size and showed that highly dispersed solids were obtained (Table 1). As compared to the non-stabilized reaction mixture (sample a), all stabilizers induce a significant decrease of mean particle size, the most important effect being observed for ammonium oxalate. However, the specific surface areas do not follow the changes of mean particle size. The highest specific surface area was obtained for the sample b issued from urea-stabilized melt whereas the lowest XRD-derived particle size was measured for the oxalate-doped sample c. This discrepancy can be explained by the differences in the agglomeration of nanoparticles. Indeed, in more agglomerated solids, even composed by smaller particles, the BET surface areas can be much lower than theory values, due to existence the extended areas corresponding to interfaces between particles and not available to gas adsorption.

Striking morphological differences were observed between the solids at the macroscopic and microscopic levels. The sample a issued from the non-stabilized melt was a low-density brittle foam-like mass, whereas the solids prepared using stabilized mixtures were compact soft powders. This can be clearly seen on the low- and medium-magnification SEM images (Fig. 3a and b). The solid a consists of layered particles, representing broken walls of macropores. Apparently these walls consist of densely packed primary nanoparticles, since no smaller agglomerate structures were detected by SEM up to the limit of SEM magnification of 200,000. The solids prepared in the stabilized mixtures contained rather shapeless porous agglomerates consisting of smaller particles, which are themselves agglomerates of primary nanoparticles, as exemplified by solid b (Fig. 3c and d). Such hierarchical structure is characteristic for molten salt preparations of oxides [25].



**Fig. 2.** XRD patterns of the  $TiO_2$  solids prepared in pure and stabilized AN.



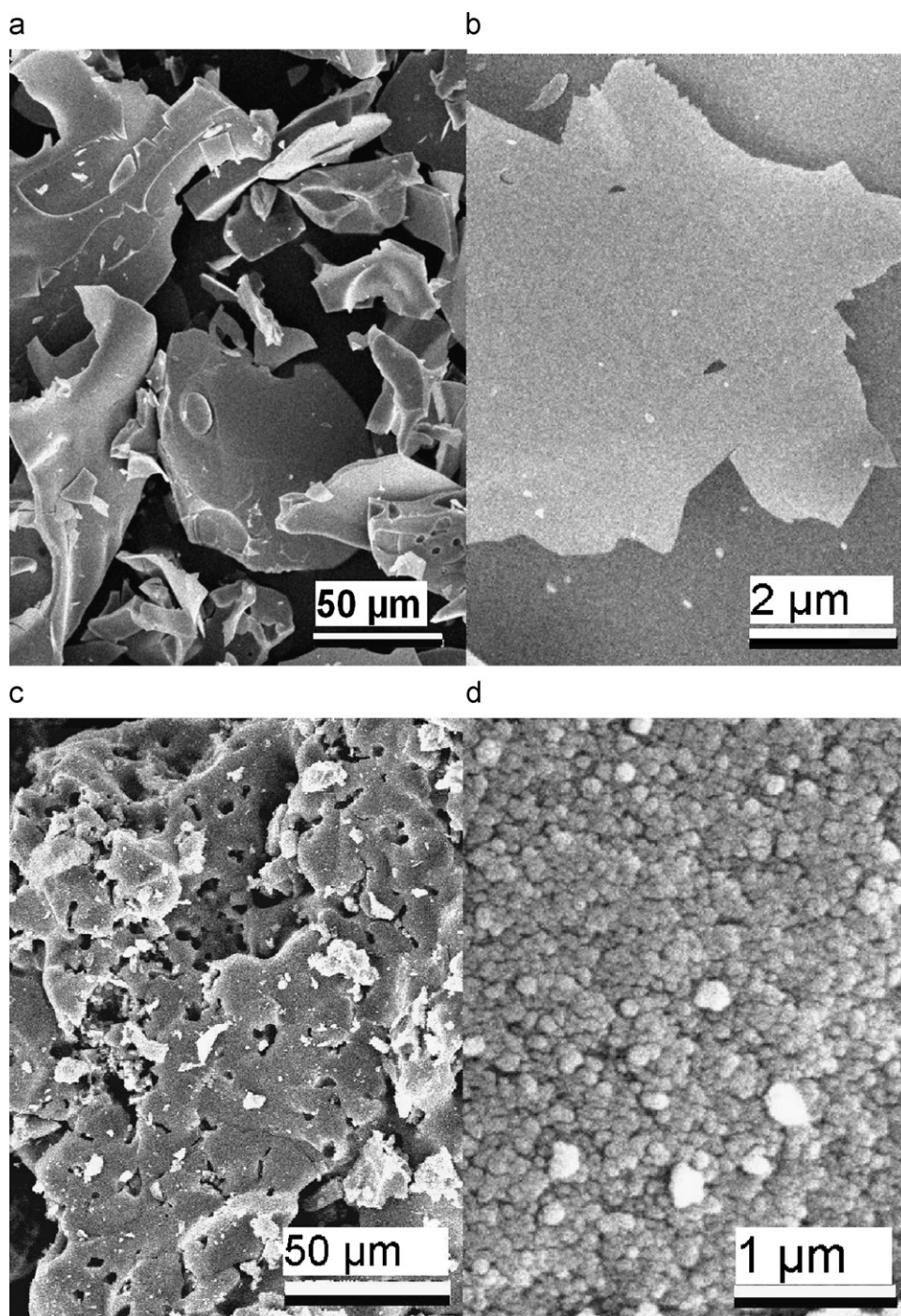


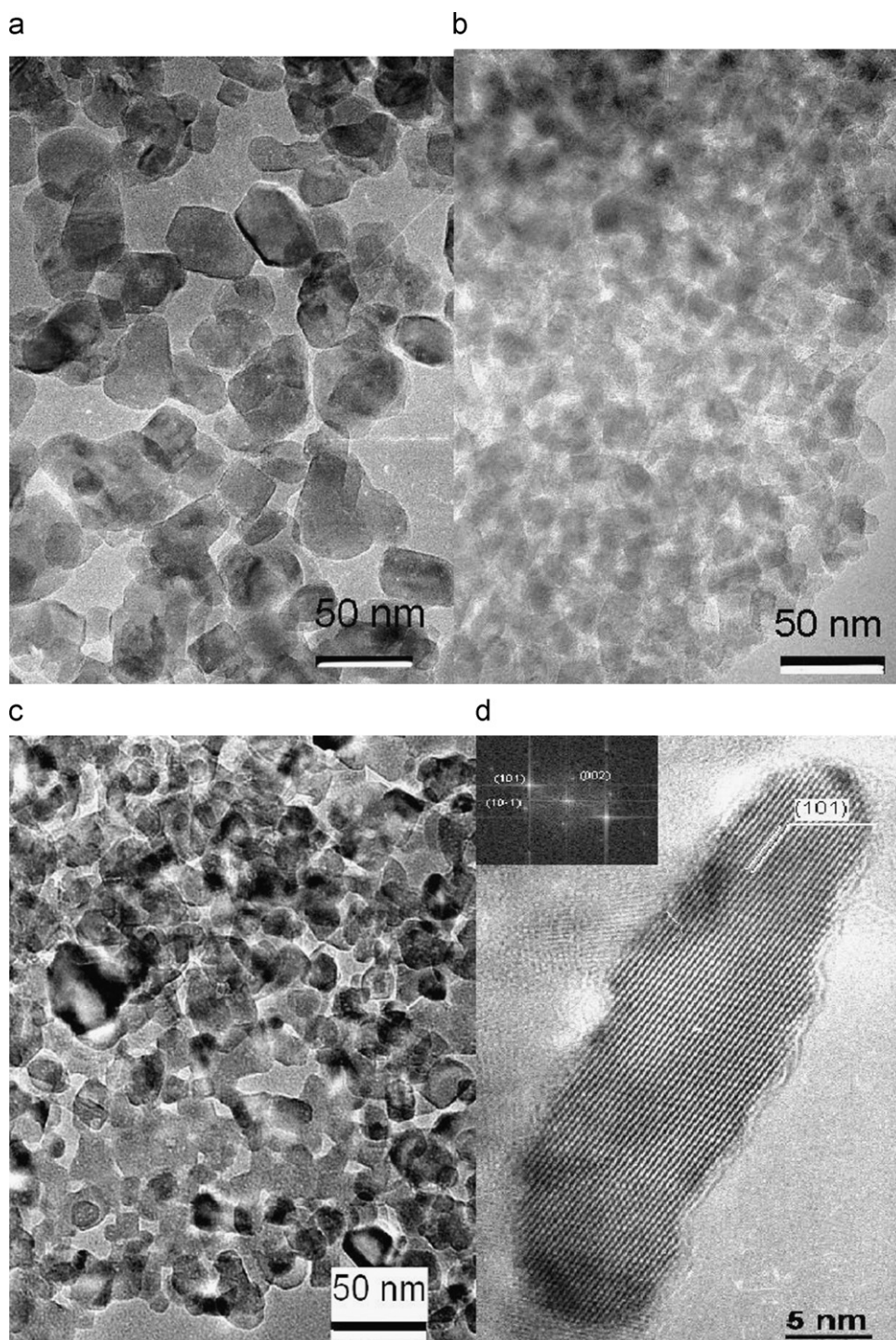
Fig. 3. SEM images of the titania samples: a, b—prepared in pure AN (a sample); c,d—prepared in urea-stabilized mixture (b sample).

Inspecting the solids by TEM confirmed the difference of sizes found by XRD lines width analysis, and allowed explaining the discrepancy between the XRD and BET surface area measurements. The solid a forms separated isotropic particles in the size range 15–50 nm (Fig. 4a), whereas the particles size is strongly decreased in the preparations using stabilized melts. At the same time stronger agglomeration between primary particles was observed for the solids b–d. Agglomeration was pronounced in the oxalate-doped sample c (Fig. 4c). In urea stabilized solid b, elongated particles were observed, formed obviously by oriented agglomeration. The particle represented in Fig. 4d is oriented along the [101] direction and contains steps, produced probably due to oriented attachment of anatase nanocrystals

on high-surface-energy planes {001}, which is a preferential agglomeration mode for anatase growth [45].

This increased agglomeration is seen as growth of necks between the particles without substantial increase of their size. Such behaviour is characteristic for the initial stages of Ostwald ripening. The growth by Ostwald ripening may occur only in liquid medium whereas the only particles growth mechanism available for the oxide under inert gas atmosphere is that of sintering. The effect of stabilizers on the agglomeration can be explained by increase of temperature at which the reaction mixture still remains liquid and therefore allows Ostwald ripening. At the same time the reactivity in stabilized melts is obviously somewhat lowered, probably due to complexation with





**Fig. 4.** TEM images of the samples a, b and c at magnification 120,000 (a, b, c) and a particle of sample b at magnification 400,000 (d).

the nitrogen containing bases. As a result, smaller but more agglomerated particles are obtained. By contrast, the initial reactivity of  $\text{TiOCl}_2$  is higher in pure AN, which leads to a more rapid nucleation and growth. However, the melt decomposes sooner and the evolution of the solid proceeds as sintering leading to a foam-like solid with rigid and dense walls.

Yellowish colour of the solids suggested that some defects or impurities are present and allows suggesting some nitrogen or carbon doping. To study the optical response of  $\text{TiO}_2$  powders as-prepared, we measured the UV–vis absorption spectra, shown in Fig. 5. The absorption thresholds are estimated to be 390, 420, 395 and 425 nm, respectively, for the samples a–d, which is in

accordance with the yellow colour of the samples. The solid prepared in the presence of melamine (d) demonstrated a pronounced shoulder at 450 nm. This solid was the most intensely coloured (brown-yellow) among our preparations, and contained 0.2 wt% of residual carbon. In other solids no carbon impurity was detected.

The optical absorption edge of the samples shows a slight but appreciable shift between different preparations. The energy band gaps ( $E_g$ ) of the samples can be calculated from the intercept of UV–vis spectra using linearization of different powers of  $(\alpha h\nu)$  vs.  $h\nu$  where  $\alpha$  is measured absorption value [46]. The linear part of the curve for the P25 gives a direct band gap of 3.22 eV, which is

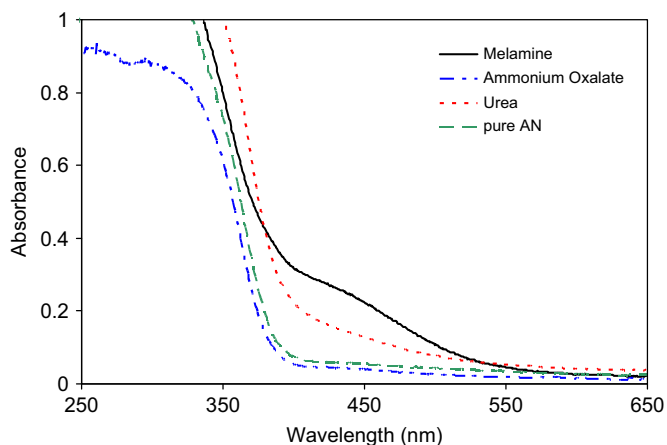


Fig. 5. UV-visible spectra of the solids prepared at 500 °C as a function of stabilizer used.

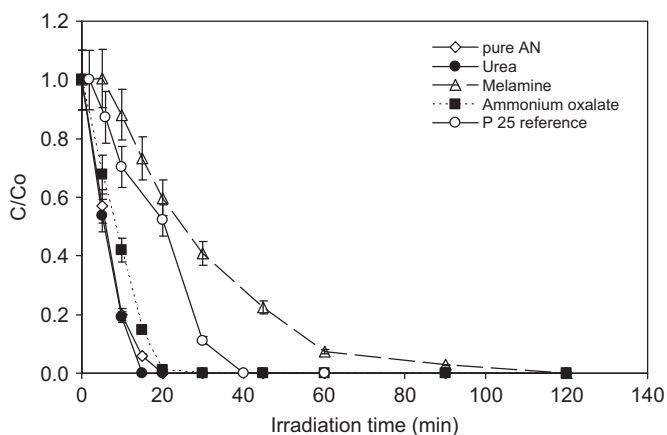


Fig. 6. Time dependence of the degree of formic acid photooxidation in the presence of TiO<sub>2</sub> samples.

close to the values reported for commercial Degussa P25 (3–3.2 eV). The band gap energies of molten salt preparations samples were found to be 3.21, 3.16, 3.20 and 3.12 eV for a, b, c and d, respectively.

Formic acid is a ubiquitous anthropogenic and biogenic pollutant, which has no absorption in the visible region [47,48]. At the same time formic acid is the simplest of carboxylic acids. Consequently, it was chosen as a model target pollutant to assess the photocatalytic activity of TiO<sub>2</sub> samples under UV-visible light irradiation. The catalytic tests revealed high photooxidation activity of the solids as-prepared, at the same level or better than the P25 reference (Fig. 6). Only the solid d despite its lowest  $E_g$  value showed quite poor photooxidation activity. Therefore, the low energy absorption tail in melamine-doped sample (Fig. 5) is probably related to the pollution of the surface rather than to doping of titania bulk with light elements. The most active solid was the b one, prepared in urea-stabilized mixture. It seems that urea induces nitrogen doping of the solid b, but detailed study of this question is beyond the scope of the present preparation-focused work. Note that a beneficial effect of urea was earlier observed in titania preparations [49–51], in which similar to our values of specific surface areas were observed for the calcined TiO<sub>2</sub> solids. It is well known that for titania to be a good photocatalyst, it must contain a minimal amount of impurities or defects causing recombination of electron-hole pairs [52]. The solids prepared using AN melts obviously meet such criteria.

Overall, the tests of photooxidation show that the TiO<sub>2</sub> samples prepared using AN melts have the properties very favourable for their catalytic use.

#### 4. Conclusion

An expedite one-step technique using simple precursors has been proposed, consisting in heating of organics-stabilized ammonium nitrate melts with a dissolved metal salt precursor above their decomposition temperature. It allows obtaining pure and highly dispersed oxide solids, as exemplified by titania preparations. Certain similarity of MS technique to the combustion syntheses using nitrates [53] can be noted, but in the molten salt process there is no strong local overheating immanent to the combustion technique. The as-prepared titania has large specific surface area and shows a red-shift in the optical spectra. The crystallites of the resulting TiO<sub>2</sub> demonstrate varying shape as a function of the stabilizer nature. Their activity in formic acid photooxidation also depends on the nature of the stabilizer. The best of the prepared catalysts showed formic acid decomposition rates superior to that of the P25 reference. Nitrogen containing stabilizers play a double role of increasing the process safety and modifying the properties of the solid product. The stabilizer allows also increasing working temperature by 30–50 °C which proves to be useful for improving morphological properties of the resulting oxide. As our preliminary data showed, the same technique can be successfully used to prepare titania doped with other metals and nanocrystalline mixed oxides.

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