



Thermal stability of polymeric carbon nitride (PCN)-Al₂O₃-ZrO₂ nanocomposites used in photocatalysis

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Abstract

Polymeric carbon nitride (PCN) was recently found to have extensive applications in the field of photocatalysis. Knowledge about thermal stability of PCN nanocomposites is crucial for this application and designing the final product. In this work, the thermal stability of PCN-Al₂O₃-ZrO₂ nanocomposites was investigated. PCN nanocomposites were obtained in two steps: (1) microwave hydrothermal synthesis of co-precipitated AlOOH and ZrO₂ precursors, followed by drying; (2) mixing the nanopowders with melamine powder and annealing in air in a tube furnace at 400, and 450 °C. The PCN nanocomposites were examined by attenuated total reflection technique of Fourier transformed infrared spectroscopy. Also, the evolved gas analysis was performed combining differential scanning calorimetry and thermogravimetry coupled with mass spectroscopy and FTIR. The results show that only PCN-Al₂O₃-ZrO₂ nanocomposite obtained at 400 °C is stable from room temperature up to 490 °C and during thermal decomposition, in one step releases ammonia (NH₃), cyanic acid (HNCO), water (H₂O), and carbon dioxide (CO₂). The limitation of the PCN-Al₂O₃-ZrO₂ thermal stability and performance is AlOOH-ZrO₂ used as a nanocomposite component.

Keywords Nanocomposite · Polymeric carbon nitride · Thermal decomposition · Gases analysis · DSC-TG-QMS-FTIR · Evolved gas analysis

Introduction

Recent research of scientists from different scientific fields are focused on manufacturing composites and heterojunctions containing carbon nitride called by graphitic carbon nitride (g-C₃N₄) [1], melon or polymeric carbon nitride (PCN) [2]. This material is usually obtained from the pyrolysis of urea, cyanamide, thiourea, and melamine [2]. PCN is characterized by optical bandgap of 2.7 eV, possess a 2D crystal structure and great chemical stability [1]. Due to physical and chemical properties of PCN it was used in the fields of photocatalysis, electrochemistry and photo-electrochemistry. PCN based compounds have attracted attention due to their promising applications to clean up air and water pollution by degradation of organic pollutants.

It was discovered recently that by addition of a metal oxide (ZnO, ZrO₂, TiO₂, Al₂O₃, etc.) to PCN, it is possible

to form a heterostructured composite. Such composite was characterized by long-term photostability, as well as thermal and mechanical stability [4, 5].

Analysis of literature shows that there is a lot of ambiguity as far as melamine thermal behavior. Synthesis of PCN from melamine was reported to occur in the broad temperature range from 400 to 700 °C [2, 6, 7]. During heating of melamine up to ~320 °C condensation reactions with evolution of NH₃ take place. Above 360 °C during condensation of melamine and its reaction with residual cyanamide (NH₂CN) melem (triaminotri-s-triazine, triamino-heptazine, C₆N₇(NH₂)₃) is formed. Melem was found to condense and form 1D chains of aminelinked heptazine units above 520 °C ([C₆N₇(NH₂)(NH)]_n—polymeric carbon nitride (PCN)) [2]. Melon, consist from layers made from 1D chains of NH-bridged melem (C₆N₇(NH₂)₃) monomers [8]. Praus et al. [6] recommend a higher than 600 °C temperature for PCN production from melamine. Authors [6] found, that at lower annealing temperature such as 550 °C and/or 575 °C PCN formation takes place, with the empirical formula C₆N₉H₃. At higher temperature this material decomposes. Melamine annealed at 600 °C leads to C₆N₉H₂ formation (which is

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very close to PCN) with the maximal C/N molar ratio of 0.68. This value indicates incomplete condensation of amino groups of PCN [6]. PCN is known as the most stable composition under ambient conditions among the family of carbon nitrides [2]. It was found [8] that the empirical PCN composition dependence on preparation method. Authors summarized that that melon structure is a mixture of molecules of different shapes and sizes. If so, PCN structure has rather amorphous character [8].

In previous work, it was demonstrated [7] that by using a tube furnace and applying the fast 50 °C/min heating rate during melamine and AlOOH-ZrO₂ annealing favorable PCN formation can be achieved at 400 °C. This temperature of PCN-nanocomposite formation is lower than reported in literature [7]. It was postulated that lower PCN formation temperature was probably due to the interaction of the melamine with the AlOOH/ γ -Al₂O₃ and ZrO₂ nanoparticles (NPs). The presence of AlOOH/ γ -Al₂O₃ and ZrO₂ NPs provide high specific surface areas and morphology beneficial for the formation of a PCN layer. The PCN nanocomposite was characterized by a 3 eV band gap and showed significant photocatalytic ability for degradation of common pollutants.

Simultaneous thermal analysis is widely used in investigation of various nanocomposites thermal behavior [9–13]. DSC–TG–FTIR–QMS method is applied to identify gases released during the thermal treatment of different materials [9, 10, 13, 14]. In the literature there is lack of complete studies about thermal decomposition of PCN or PCN-nanocomposites with analysis of released gases. Miller et al. [12] reported that during thermogravimetric analysis NH₃ is evolved from precursors such as melamine above approximately 450 °C, with C₂N₂ and C_xN_yH_z species. However, detailed analysis of PCN-materials using EGA have not been conducted. Systematic and complementary DSC–TG–QMS–FTIR experiments performed for PCN-nanocomposites provide knowledge about PCN based materials which will be crucial for their synthesis performance investigation and their further application. Therefore, the aim of the work is to (1) find optimum synthesis conditions for PCN-Al₂O₃–ZrO₂ nanocomposite photocatalysts; to (2) investigate the type of emitted gases during temperature program; and to (3) gain knowledge about interdependency between nanocomposite components.

Materials and methods

The microwave synthesis of nanopowder mixtures containing boehmite (AlOOH) with 20 mass% of ZrO₂ is described in details in previous works [7, 9, 10]. The PCN nanocomposites were made by hand mixing of AlOOH-20 mass%ZrO₂ nanopowder in zirconia mortar with 20 mass% of melamine (Sigma-Aldrich, CAS Number

108–78-1 (99%)). Further, prepared powder was annealed in a tube furnace in two temperatures: 400 °C and 450 °C for 5 h, in air. The heating rate applied was 50 °C min⁻¹.

The surface morphology of the investigated materials was observed using a scanning electron microscope (Zeiss, model Ultra Plus, Zeiss, Oberkochen, Germany).

All powders after synthesis were examined by a Fourier transform infrared spectrometer (Bruker Optics, Tensor 27, Bruker BioSpin GmbH, Rheinstetten, Germany) equipped with ATR accessory and gas cell connected to STA device. The ATR–FTIR spectra were recorded in the 4000–400 cm⁻¹ range, at room temperature. The resolution of spectra and their accuracy were as follows: 4 cm⁻¹ and 1 cm⁻¹, respectively.

Thermal stability of PCN-nanocomposites was investigated using DSC–TG–QMS–FTIR set of devices. The experiments were performed on a STA 449 F1 Jupiter by Netzsch equipped with SiC furnace. All tests were carried out with a heating rate of 10 °C min⁻¹ from room temperature up to 1000 °C, with constant flow of air (60 mL min⁻¹). The released gases during thermal heating of PCN-nanocomposites were detected by a mass spectrometer (QMS 403C Aeolos, Netzsch) and FTIR (Bruker Optics, Tensor 27,) coupled in line with the STA instrument. In order to avoid condensation of eventual melamine inside the equipment, maximum 20 mg of powder was placed into crucible for each measurement.

Results

Figure 1 shows FTIR–ATR spectra of pure as-synthesized mixture of AlOOH and 20 mass% ZrO₂ nanopowder (further denoted as AlOOH-20 mass% ZrO₂ nanopowder, which will be treated as reference sample), as well as PCN-nanocomposites annealed at 400 and 450 °C. The reference material was described by author previously [7, 9] and is characterized by strong bands 3099, 3311 cm⁻¹ which belong to asymmetric and symmetric O–H stretching vibrations from (O)Al–OH. Bands 1070, 1170 cm⁻¹ are assigned to (HO)–Al=O asymmetric stretching and the O–H bending, respectively. The strong band at ~737 cm⁻¹ can be attributed to Al–O–Al framework. AlOOH-20 mass% ZrO₂ in melamine presence and after annealing at 400 and 450 °C does not show any visible vibrations associated to AlOOH, ZrO₂ or Al₂O₃. In previous work [7] it was discussed already that PCN was identified only in the nanocomposite prepared at 400 °C. The confirmation of this fact was presence of PCN characteristic band at approximately 800 cm⁻¹ [8]. It was found that –NH₂ stretching vibrations of crystalline melamine (C₃N₃(NH₂)₃) at ~3475 and 3417 cm⁻¹ are similar to spectrum for melem (C₆N₇(NH₂)₃), containing the C₆N₇ central heptazine unit [12].

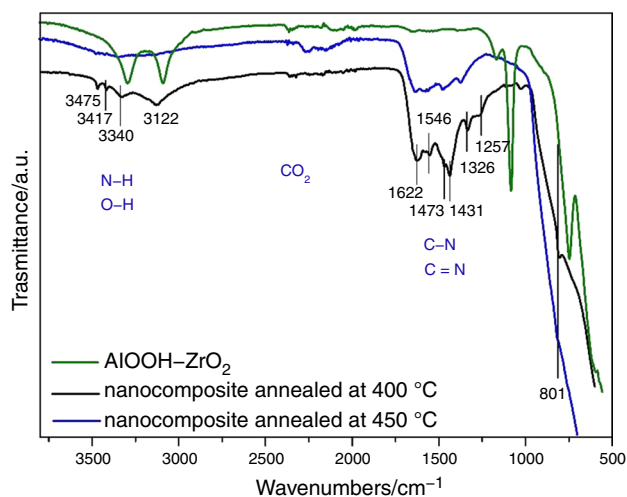


Fig. 1 FTIR-ATR spectra for AIOOH-20mass%ZrO₂ nanopowders, as well for nanocomposites with melamine annealed at 400 and 450 °C [7, 10]

Figure 2 shows morphology of obtained nanocomposites. Surface of the PCN nanocomposite obtained at 400 °C (Fig. 2a) looks like covered by thin organic layer what was discussed before in [7]. Nanocomposite obtained at 450 °C (Fig. 2b) represents morphology typical for Al₂O₃-ZrO₂ nanoparticles mixture.

Figure 3 presents thermal behavior of as-synthesized AIOOH-20 mass%ZrO₂, AIOOH-20 mass%ZrO₂ annealed at 400 °C, and melamine. All presented results refer to PCN-nanocomposite thermal decomposition. Figure 3a shows thermal behavior (DSC-TG) of pure melamine which fully decomposes at approximately 350 °C, which is in agreement with literature [6, 15, 16]. Figure 3b shows thermal behavior for sample of pure AIOOH-20 mass% ZrO₂ and transformation of AIOOH to Al₂O₃. The endothermic transition with peak at 300 °C can be associated to gibbsite transforming to χ -Al₂O₃ [17]. Further, exothermic peak at 410 °C can be explained by crystallization followed by boehmite (γ -AIOOH) transformation to γ -Al₂O₃ [17]. The all phase

transformations are associated with OH⁻ groups detachments. The total mass loss of this sample was 18 mass%. The phase transitions of AIOOH-ZrO₂ materials in relation to annealing temperatures were discussed before [7, 9, 9, 18]. Thermal analysis results for AIOOH-20 mass%ZrO₂ nanopowders annealed at 400 °C are presented at Fig. 3c, d. DSC curve shows exothermic event at ~230 °C (Fig. 3c) which is related to CO₂ and H₂O release (Fig. 3d) and may be associated with crystallization process of γ -Al₂O₃. At 400 °C annealing temperature AIOOH should already transforms to Al₂O₃. However, it is clear that nano powder after thermal treatment at 400 °C still contains some AIOOH phase (boehmite or diaspore [17]). The broad endothermic transition with onset at 430 °C ($T_{\text{peak}}=490$ °C) is caused by further decomposition of AIOOH residues and phase transformation to alumina. The total mass loss for this material was 11 mass% related mainly to OH⁻ groups release.

The DSC-TG curves of PCN-Al₂O₃-ZrO₂ nanocomposites prepared at 400 °C and 450 °C are presented in Fig. 4. Nanocomposite prepared at 400 °C is characterized by narrow exothermic event in the temperature range: from 480 to 550 °C, while the sample prepared at 450 °C shows broad exothermic peak in the range 400–600 °C. The temperature stability of the nanocomposite prepared at 450 °C is similar to the reference material (Fig. 3a). The total mass loss observed during thermal decomposition was 19 and 9.5% for nanocomposite annealed at 400 and 450 °C, respectively.

Figure 5 shows mass spectra collected during thermal decomposition of PCN-Al₂O₃-ZrO₂ nanocomposites prepared at 400 °C and 450 °C. The evolved gases during analysis of nanocomposite prepared at 400 °C were following: H₂ ($m/Z=2$), NO₂, ($m/Z=14, 16, 30, 46$), NO ($m/Z=14, 30$), N₂O ($m/Z=12, 14, 16, 30, 45$), NH₃ ($m/Z=14, 15, 16, 17$), H₂O ($m/Z=17, 18$), HNCO ($m/Z=30, 43$), CO₂ ($m/Z=12, 44$) (Fig. 5a, b). Sample prepared at 450 °C during thermal decomposition released CN⁻/HCN ($m/Z=26, 27$) in addition to the gases listed above and rather did not evolved NO_x. It should be noticed, that material obtained by annealing of AIOOH-ZrO₂ and melamine at 450 °C is less stable than

Fig. 2 SEM images of PCN-Al₂O₃-ZrO₂ nanocomposites obtained at 400 (a) and 450 °C (b)

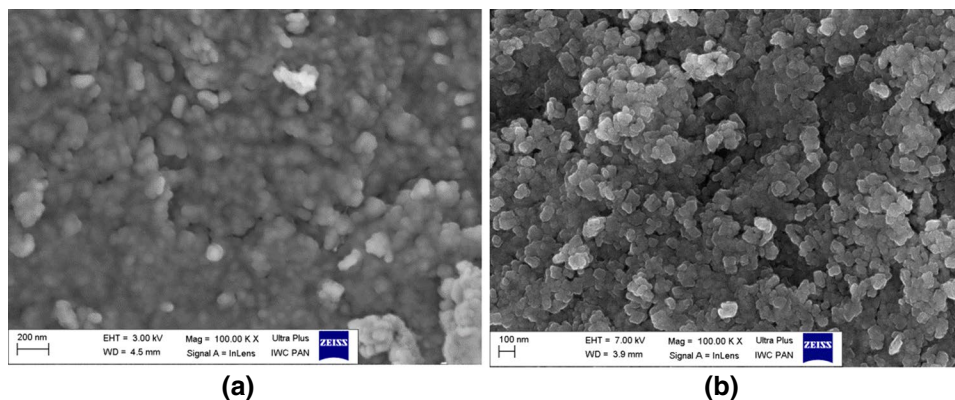


Fig. 3 DSC–TG curves for as-received melamine (a), AlOOH-20mass% ZrO₂ (b) and DSC–TG curves for Al₂O₃-20mass% ZrO₂ annealed at 400 °C (c); QMS spectra recorded during thermal analysis of Al₂O₃-20mass% ZrO₂ annealed at 400 °C, where $m/Z = 18$ characterizes H₂O and $m/Z = 44$ CO₂ (d)

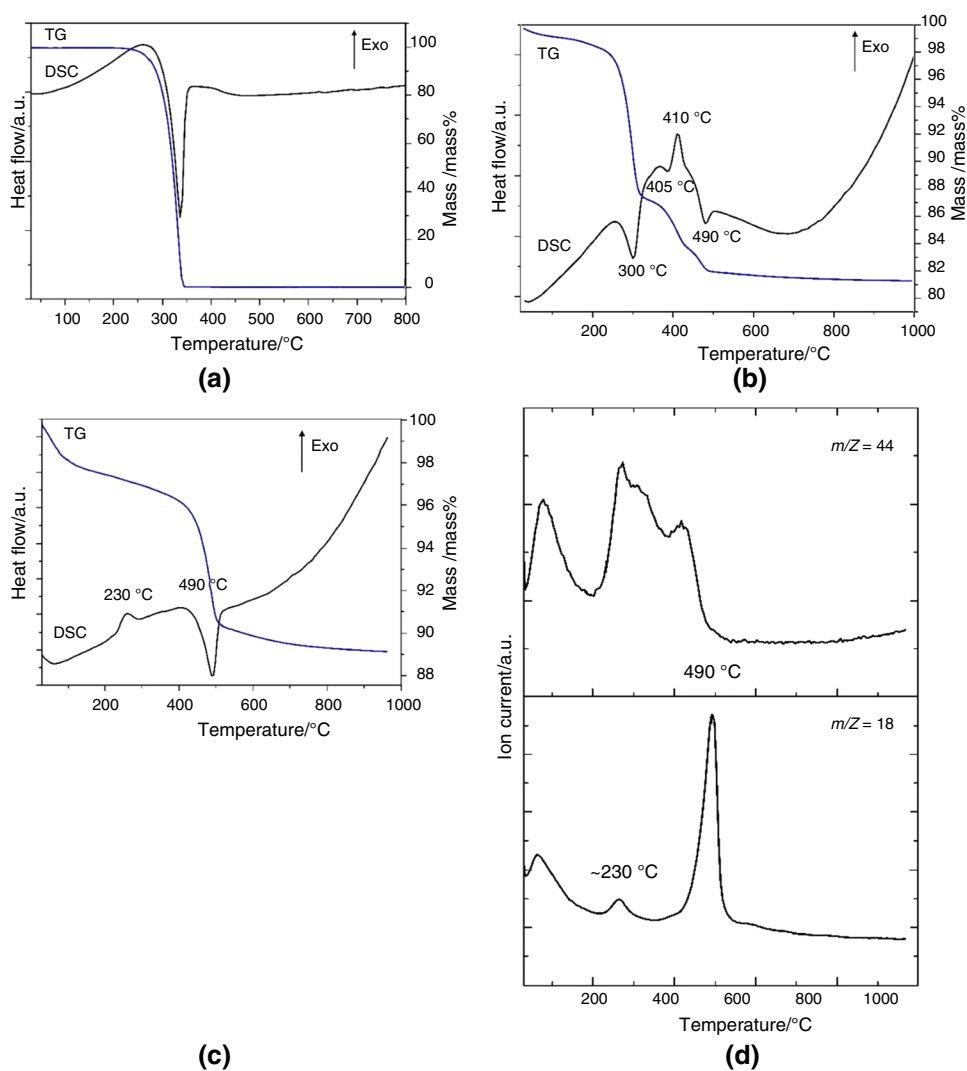
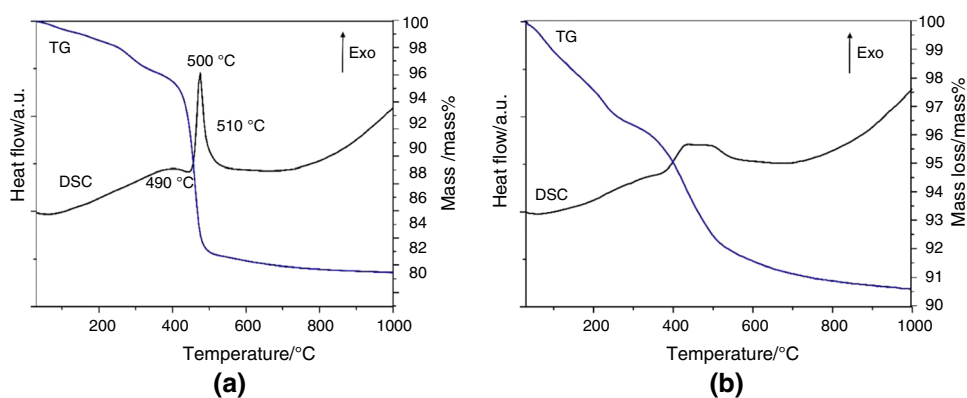


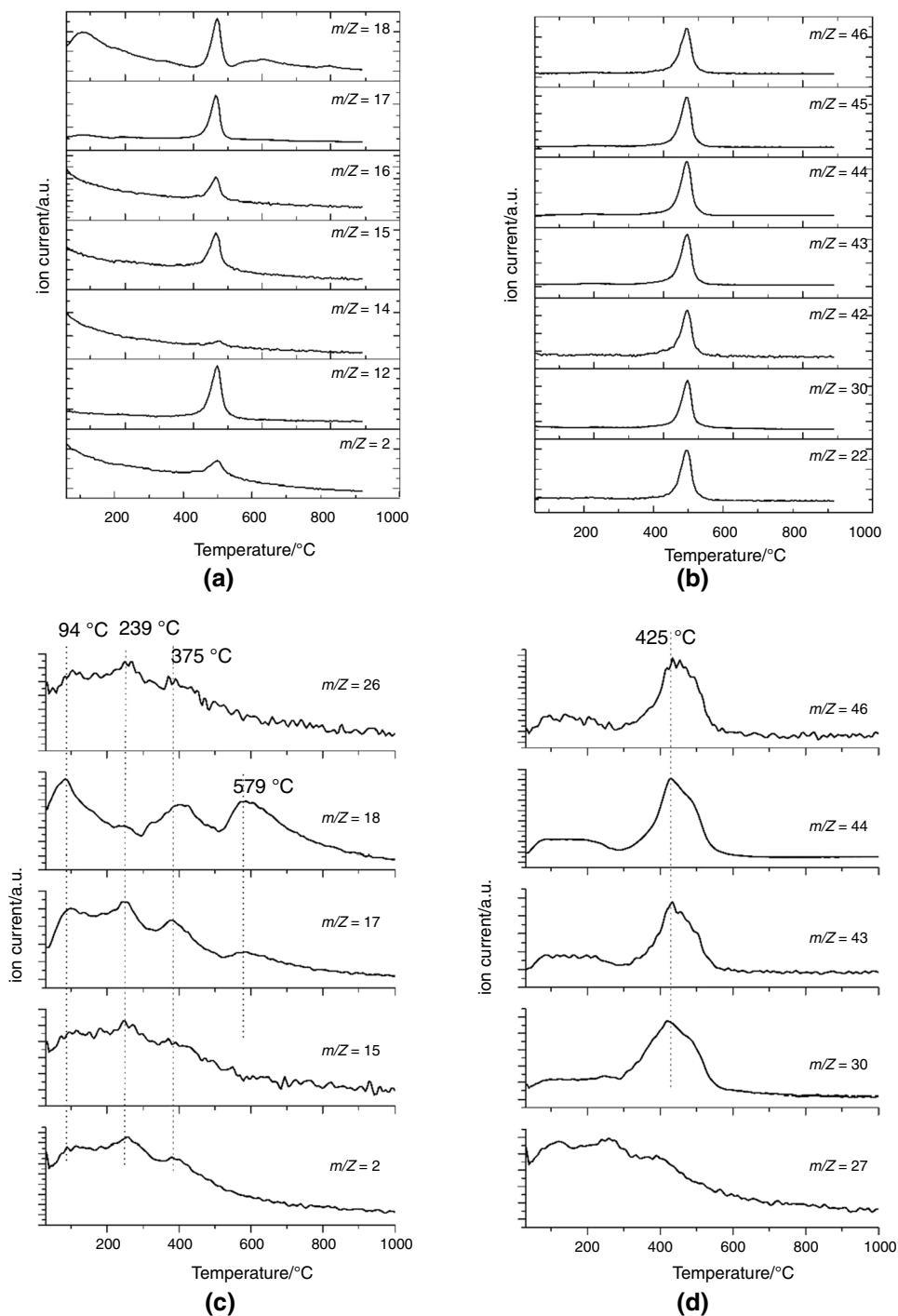
Fig. 4 DSC–TG curves for PCN-Al₂O₃-ZrO₂ nanocomposites prepared at 400 °C (a); and at 450 °C (b)



the one annealed at 400 °C. Five different maxima can be distinguished (Fig. 5c, d): peaks at 94 °C and 375 °C where H₂O and H₂ are released, at 239 °C with H₂ and NH₃ evolution, and 425 °C with CO₂ evolution. At 579 °C, only water was released from the nanocomposite.

Figure 6 illustrates the 3D FTIR spectra for the gases evolved during thermal decomposition of PCN-Al₂O₃-ZrO₂ nanocomposites in DSC–TG–FTIR–QMS experiment. The time axis seen on the map is related to the change of temperature, which can be visible on the subtracted spectra.

Fig. 5 Mass spectra recorded during thermal analysis of nanocomposites annealed at 400 °C for 5 h (a, b); and annealed at 450 °C for 5 h (c, d)



The main signals visible on FTIR maps belong to NH₃ (930–960 cm⁻¹) and CO₂ release (~2300 cm⁻¹) which is in agreement with literature [19]. On subtracted spectra from the maps the additional signals can be distinguished: CO (2250–2300 cm⁻¹), hydrocarbons (2800–3100 cm⁻¹), HNCO (2260 cm⁻¹- only in the sample prepared at 400 °C), H₂O/OH⁻ (~3300 cm⁻¹), N₂O (2150 cm⁻¹). It is important to note that the FTIR spectra not only provide the information about the species of the released gas, but also show the

relative intensities of the released gases. The emission of ammonia (NH₃) is confirmed by the presence of absorption bands at 3335, and 966 cm⁻¹ [11]. The cyanic acid (HNCO) bands were found at 1095 and at 3474 [11].

Figure 7 presents scheme of the PCN nanocomposites thermal decomposition prepared based on results from DSC-TG-QMS-FTIR experiment. Upon TG values analysis it can be concluded that as-synthesized AlOOH-ZrO₂ nanopowders loses 18 mass% of mass during thermal

Fig. 6 Evolved gas analysis showing FTIR map of PCN- Al_2O_3 - ZrO_2 nanocomposites prepared at 400 °C (a) and subtracted spectra (b); FTIR map for nanocomposite annealed at 450 °C (c) and subtracted spectra (d)

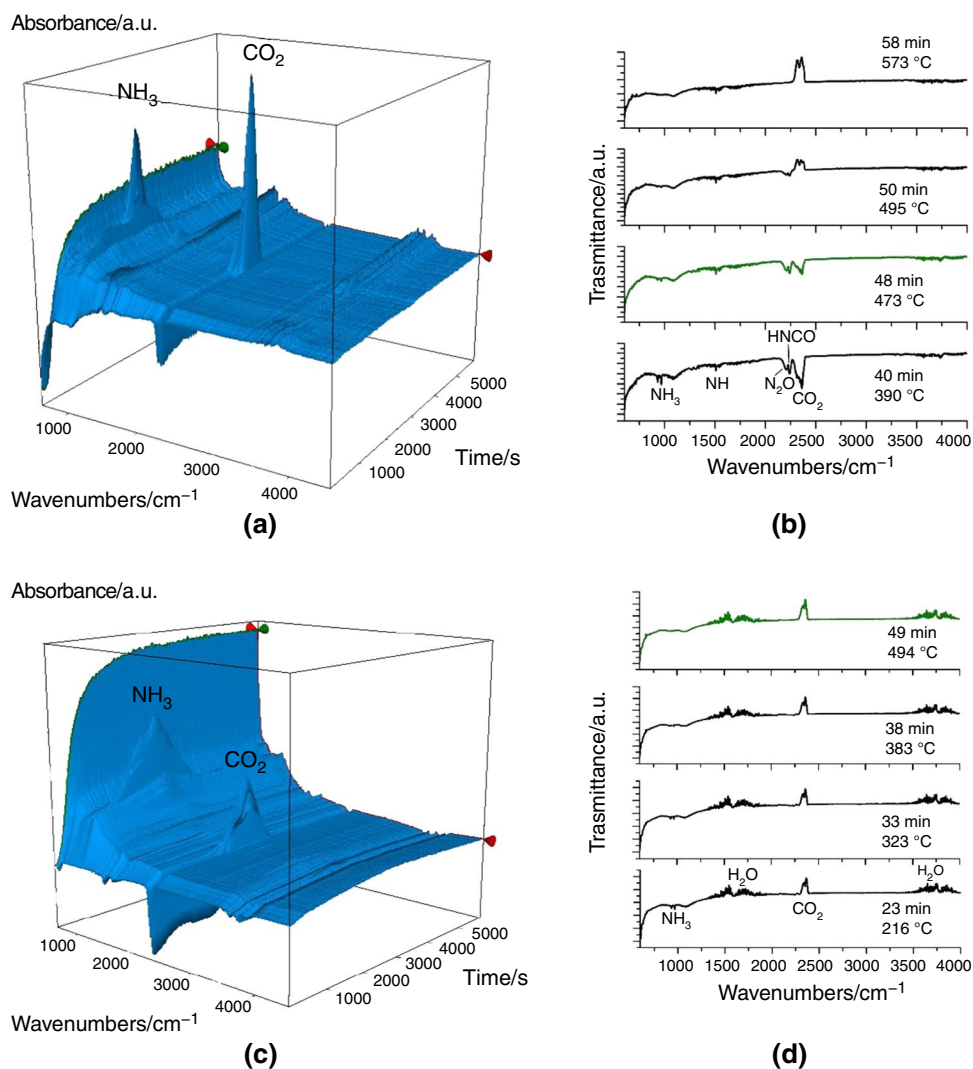
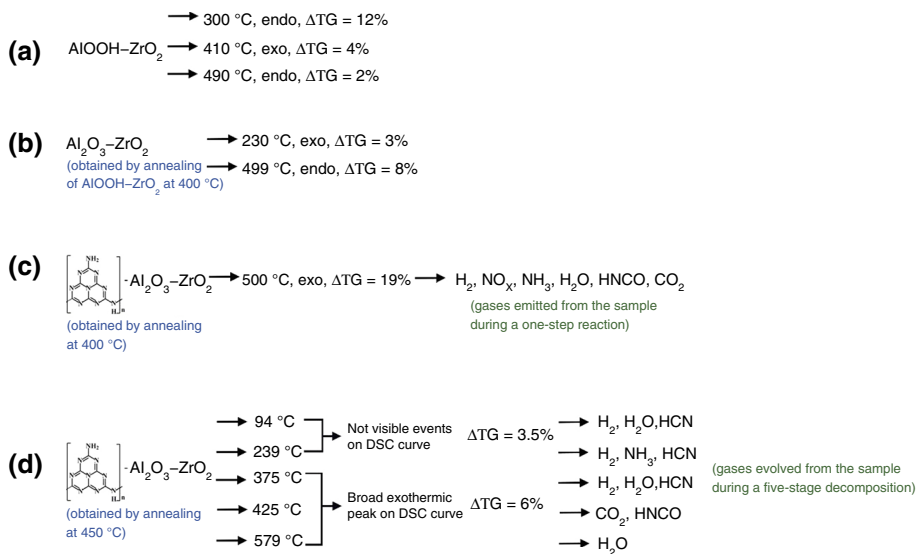


Fig. 7 AlOOH-ZrO_2 (a), Al_2O_3 - ZrO_2 (b), and PCN- Al_2O_3 - ZrO_2 nanocomposites (c, d) decomposition scheme



treatment, while this material annealed at 400 °C loses only 11 mass%. It may lead to conclusion that while AlOOH-ZrO₂ is mixed with 20 mass% of melamine and annealed at 400 °C ~ 11 mass% mass loss may origin form AlOOH-ZrO₂ and only ~ 8 mass% from PCN. This means, that final PCN-nanocomposite may contain only 8 mass% of PCN. It expected then, that nanocomposite produced at higher temperature (450 °C) will contain even less melamine condensation products then its counterpart prepared at 400 °C.

Discussion

It was shown recently [7] that the PCN-nanocomposite obtained at 400 °C has very promising photocatalytic properties. The temperature 400 °C was surprising for PCN formation since according to literature [6] melamine undergoes transition to PCN above 500 °C. In this case the PCN formation at 400 °C takes place due to the presence of nano-sized metal oxide in the nanocomposite and rapid heating (50 °C min⁻¹). Additionally, in the heterogeneous surface processes that may not occur easily in a pure melamine used by others or in different experimental procedure [1]. As a result, the conversion temperatures of melamine to PCN presented in literature are much higher due to the need to overheat the system for a transformation to occur. It is postulated that in this work PCN formation from melamine takes place at or around the true transition temperature. It can also be assumed that the formation of PCN on the surface of the nanopowder may be accelerated by water release during the phase transition AlOOH to Al₂O₃.

Based on results presented in Fig. 3, it is clear that thermal stability of PCN-nanocomposite depends on the stability of AlOOH-ZrO₂ which is present in nanoscale form. Annealing of AlOOH-ZrO₂ with melamine at 400 °C causes several chemical reactions during that process. At 400 °C AlOOH-ZrO₂ nanopowder undergoes already endothermic reaction due to water release (Fig. 3b), while melamine itself should already decompose (Fig. 3a). Thus, thermal stability of PCN-nanocomposite is the same as Al₂O₃-ZrO₂ stability (while comparing Figs. 3c and 4a) with the maximum of peak at ~ 500 °C.

Nanocomposite prepared at 450 °C does not show any presence of PCN but various melamine decomposition products what was described before [7]. Also, the amount of melamine decomposition products is lower than in case of nanocomposite prepared at 400 °C. Once the DSC curve of AlOOH-ZrO₂ is analyzed (Fig. 3b), it confirms lower stability of material in comparison to PCN-nanocomposite obtained at 400 °C. At 450 °C, AlOOH-ZrO₂ water released already (~ 300 °C, Fig. 3b) and material started crystallizing to form γ -Al₂O₃. It appears that exceeding crystallization

temperature of Al₂O₃ in AlOOH-ZrO₂ nanopowder influences dramatically PCN formation on Al₂O₃-ZrO₂ surface.

The annealing of the mixture containing AlOOH, ZrO₂ and melamine at 400 °C leads to a rather rapid process of bubbling off excess melamine, NH₃, NO_x and H₂. In the same time, each solid particle of ZrO₂ and AlOOH/Al₂O₃ act as nucleation centers for this bubbling process [7]. It is possible that, smaller and sharper particles may facilitate controlled interconversion of melamine at lower temperature and creating PCN layer around AlOOH and ZrO₂ particles. Evolved gas analysis showed different thermal stability of investigated materials. Nanocomposite prepared at 450 °C starts gradually decomposing already at 94 °C, while PCN-nanocomposite obtained at 400 °C is stable from room temperature up to ~ 490 °C (when the final transformation AlOOH to Al₂O₃ takes place). Decomposition of this material causes following gases release: ammonia (NH₃), water (H₂O), cyanic acid (HNCO), carbon dioxide (CO₂), nitric oxides (NO, NO₂, N₂O). These findings are in agreement with Praus et al. [6] who performed elemental analysis of the melamine condensation products at different temperatures. They showed [6] that all melamine condensation products contain nitrogen and hydrogen.

The evolution of gaseous carbon-containing species may indicate the fact that PCN does not exist in ideal C₃N₄ stoichiometry, which could be assumed as result when NH₃ component will be removed from the N-rich compound. Instead, the stoichiometry of PCN materials seem to be close to C₂N₃H, corresponding to melon (C₆N₇(NH)(NH₂)) or hydromelonic acid (C₆N₇(NCNH₃)) [12].

Conclusions

The thermal stability of PCN-nanocomposites was studied for the first time using the DSC-TG-FTIR-QMS method. Designed experiments allowed confirming optimum synthesis conditions for PCN-Al₂O₃-ZrO₂ nanocomposite photocatalysts. PCN-nanocomposite obtained at 400 °C was found to be thermally stable from room temperature up to ~ 490 °C. At 500 °C, full decomposition of the material takes place with evolution of ammonia (NH₃), water (H₂O), cyanic acid (HNCO), nitric oxides (NO, NO₂, N₂O).

In contrast to 400 °C route, nanocomposite prepared at 450 °C was thermally unstable with gradual decomposition starting already below 100 °C. The main difference in the type of emitted gases during thermal decomposition of the investigated nanocomposites was the presence of HCN/CN⁻. This compound was released in addition to NH₃, H₂, H₂O, and HNCO in the case of nanocomposite obtained at 450 °C. The presence of HCN/CN⁻ indicates poor stability of the nanocomposite produced at 450 °C.

The obtained results allow to conclude that in case of PCN-nanocomposites usage of AlOOH-ZrO_2 as a composite components mixture play a major role. The results showed, that obtained in microwave synthesis AlOOH-ZrO_2 uniformly mixed nanopowder undergoes several transitions of AlOOH to Al_2O_3 . The final phase transition at 490°C leads to complete decomposition of PCN. Even being close to this temperature (like in a case of nanocomposite annealed at 450°C) is not beneficial for further thermal stability and performance of the nanocomposite. This could be explained by changing of morphology and internal rearrangements of nanoparticles leading to breaking continuity of PCN layer on $\text{Al}_2\text{O}_3\text{-ZrO}_2$.

In the future, the mechanism of the PCN-nanocomposite formation will be investigated. However, currently it can be assumed that the formation of PCN in the nanocomposite is initiated by the disintegration of AlOOH and Al_2O_3 formation at approximately 400°C in the presence of AlOOH , ZrO_2 and melamine mixture.

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Author contributions IK conceived and designed experiments, wrote the paper, synthesized materials, and performed DSC–TG–QS–FTIR and FTIR–ATR tests/analysis of results; this publication is part of Iwona Koltsov's habilitation thesis.

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Declarations

Conflict of interest The authors declare no conflict of interest.

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Availability of data and material Samples of the all compounds described in this work are available from I.K.

Code availability Not applicable.

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References

1. Wang X, Maeda K, Thomas A, Takanabe K, Xin G, Carlsson JM, Domen K, Antonietti M. *Nat Mater.* 2009;8:76–80.
2. Kessler FK, Zheng Y, Schwarz D, Merschjann C, Schnick W, Wang X, Bojdys MJ. *Nature Rev Mater.* 2017. <https://doi.org/10.1038/natrevmats.2017.30>.
3. Sano T, Tsutsui S, Koike K, Hirakawa T, Teramoto Y, Negishi N, Takeuchi K. *Mater Chem A.* 2013;1:6489–96.
4. Jo W, Natarajan TS. *J Colloid Interface Sci.* 2016;482:58–72.
5. Jo W, Selvam NCS. *J Hazard Mater.* 2015;299:462–70.
6. Praus P, Svoboda L, Ritz M, Troppov I, Sihor M, Kocí K. *Mater Chem Phys.* 2017;193:438–46.
7. Koltsov I, Wojnarowicz J, Nyga P, Smalc-Koziorowska J, Stelmakh S, Babyszko A, Morawski A, Lojkowski W. *Molecules.* 2019. <https://doi.org/10.3390/molecules24050874>.
8. Lotsch BV, Döblinger M, Sehnert J, Seyfarth L, Senker J, Oeckler O, Schnick W. *Chem Eur J.* 2007. <https://doi.org/10.1002/chem.200601759>.
9. Koltsov I, Przesniak-Welenc M, Wojnarowicz J, Rogowska A, Mizeracki J, Malysa M, Kimmel G. *J Therm Anal Calorim.* 2017;131:2273–84.
10. Malka IE, Danelska A, Kimmel G. *Mater Today Proc.* 2016. <https://doi.org/10.1016/j.matpr.2016.06.018>.
11. Cheng H, Liu Q, Liu J, Sun B, Kang S, Frost RL. *J Therm Anal Calorim.* 2014;116:195–203.
12. Miller TS, Belen Jorge A, Suter TM, Sella A, Cora F. *Phys Chem Chem Phys.* 2017. <https://doi.org/10.1039/C7CP02711G>.
13. Alshehri AJ. *Hazard Mater.* 2012;200–8:199–200.
14. Madarasz J, Bombicz P, Okuya M, Kaneko S, Pokol G. *J Anal Appl Pyrolysis.* 2004;72(2):209–14.
15. Aditya T, Jana J, Pal A, Pal T. *ACS Omega.* 2018. <https://doi.org/10.1021/acsomega.8b00968>.
16. Jiang Z, Liu G. *RSC Adv.* 2015. <https://doi.org/10.1039/c5ra14586d>.
17. Xie Y, Kocaefe D, Kocaefe Y, Cheng J, Liu W. *Nanoscale Res Lett.* 2016. <https://doi.org/10.1186/s11671-016-1472-z>.
18. Koltsov I, Kimmel G, Stelmakh S, Sobczak K, Lojkowski W. *Sci Rep.* 2019. <https://doi.org/10.1038/s41598-019-42058-417>.
19. Koltsov I, Smalc-Koziorowska J, Przesniak-Welenc M, Malysa M, Kimmel G, McGlynn J, Ganin A, Stelmakh S. *Materials.* 2018. <https://doi.org/10.3390/ma11050829>.
20. Wang X, Maeda K, Thomas A, Takanabe K, Xin G, Carlsson JM, Domen K, Antonietti M. *Nat Mater.* 2009. <https://doi.org/10.1038/nmat2317>.
21. Wang YS, Wu R, Yuan MZ. *Appl Surf Sci.* 2015;20:21. <https://doi.org/10.1016/j.apsusc.2015.08.173>.

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