

## EFFECT OF PROCESSING TEMPERATURE ON THE PHOTOCATALYTIC ACTIVITY OF G-C<sub>3</sub>N<sub>4</sub>/MONTMORILLONITE COMPOSITES

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### Abstract

The aim of the present work was the preparation of photoactive composites of g-C<sub>3</sub>N<sub>4</sub>/MMT type. In this work, g-C<sub>3</sub>N<sub>4</sub>/MMT photocatalysts were prepared by thermal polycondensation of the mechanical mixture of melamine and MMT at different temperatures (450, 550, 600, 620, 650, and 700°C). Using wide range of analytical methods (X-ray diffraction, infrared spectroscopy, diffuse reflectance spectroscopy, and photoluminescence) a significant differences in crystalline structure, morphology, and optical properties between the prepared composites were found. Furthermore, composites prepared at 550-650 °C were tested for the photocatalytic decomposition of N<sub>2</sub>O. Photocatalytic experiments showed very similar activity of all samples synthesized at 550-650°C. The best photoactivity was exhibited by the sample prepared at the highest temperature (620°C and 650°C). The N<sub>2</sub>O conversion in presence of sample prepared at 620°C and 650°C was 45 % after 20 hours of UVA irradiation.

**Keywords:** Melamine, g-C<sub>3</sub>N<sub>4</sub>, montmorillonite, composites, photocatalytic activity

### 1. INTRODUCTION

Nitrous oxide is compound damaging the stratospheric ozone layer and contributing to the greenhouse effect. One of the promising methods of photocatalytic decomposition of N<sub>2</sub>O is semiconductor photocatalysts efficient under UV or VIS irradiation. At present time, most research focuses on photocatalysts containing metallic compounds, such as metal oxides, metal sulfides, etc. [1]. A new type of non-metallic polymeric semiconductor material is graphitized carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) having high thermal and chemical stability, but also interesting electronic and optical properties which make appropriate for a wide range of applications [2], such as H<sub>2</sub> production [3,4], environmental purification [5], CO<sub>2</sub> reduction [6] and just for photocatalytic decomposition of N<sub>2</sub>O [7]. A band gap (~2.7 eV) of g-C<sub>3</sub>N<sub>4</sub> indicates that can absorb light up to 450 nm. The easy agglomeration and weak adsorption ability of pristine g-C<sub>3</sub>N<sub>4</sub> limit its practical applications. These problems could be solved by phyllosilicate - montmorillonite (MMT) as a suitable photocatalyst carrier [8]. In this work, g-C<sub>3</sub>N<sub>4</sub>/MMT photocatalysts were prepared by thermal polycondensation of melamine/MMT at different temperatures and photocatalytic decomposition of N<sub>2</sub>O was examined under UV and VIS light irradiation. The differences on structure, morphology, optical properties and photocatalytic efficiency between the prepared materials were found.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of the samples

Melamine (ML) was used as received from Lach-Ner Co.. Na-MMT Portaclay® (Ankerpoort NV) having formula  $(\text{Si}_8)(\text{Al}_{2.85}\text{Mg}_{0.71}\text{Ti}_{0.02}\text{Fe}^{3+}_{0.42})\text{O}_{20}(\text{OH})_4$  with layer charge  $\sim 0.7$  el. per unit cell was used to prepare ML/MMT composite via dry technique. In the first step, a mixture of MMT and solid ML (1:4 w/w) was grounded in a planetary micro mill (Pulverisette 7, FRITSCH) for 15 min (rotation speed 700 rpm). The sample was named 1\_0. Composites g-C<sub>3</sub>N<sub>4</sub>/MMT were synthesized from 6 g of ML/MMT composite (sample 1\_0) in close alumina crucible by thermal polycondensation in furnace heated at temperatures 450°C, 550°C, 600°C, 620°C, 650°C, and 700°C in air, at a fast rate of 5°C/min. Temperature was applied for 2 hours. Prepared materials were ground to powder and final yields showed decrease with increasing temperature: 3.39 g (450°C), 3.46 g (550°C), 2.52 g (600°C), 1.87 g (620°C), 1.22 g (650°C), 1.16 g (700°C). Samples, denoted according to the temperature, are shown in (Figure 1).

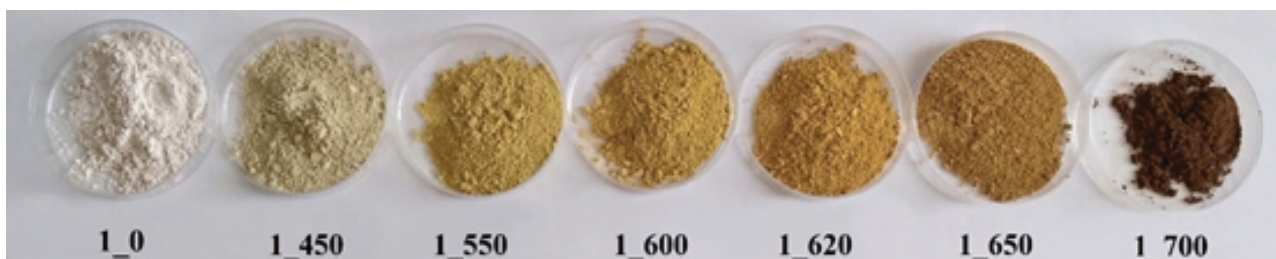


Figure 1 Different colors of the prepared samples (0-700°C)

### 2.2. Characterization methods

XRPD patterns were recorded under CoK $\alpha$  irradiation ( $\lambda = 1.789 \text{ \AA}$ ) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VANTEC 1. Measurements were carried out in the reflection mode, powder samples were pressed in a rotational holder, goniometer with the Bragg-Brentano geometry in  $2\theta$  ranges from 3 to 40°, step size 0.03°. Phase composition was evaluated using database PDF 2 Release 2014 (International Centre for Diffraction Data).

The IR spectra were collected by a FTIR spectrometer Nexus 470 (ThermoScientific) with a DTGS detector using the KBr pellets technique. Exactly 1.0 mg of sample was ground with 200 mg of dried KBr. Pellets were pressed with the pressure corresponding to 8 tons for 30 s under vacuum. Measurement parameters: the spectral region 4000-400 cm<sup>-1</sup>, the spectral resolution 4 cm<sup>-1</sup>, 64 scans; the Happ-Genzel apodization. The treatment of spectra: polynomial (second order) baseline, subtraction spectrum of pure KBr.

The UV-Vis DRS (diffuse reflectance spectra) of powder samples from the dry pressed disk samples were recorded within the range of 220-800 nm at room temperature on the Shimadzu UV-2600 Series (Shimadzu Ltd). The diameter of the integrating sphere assembly was 60 mm. BaSO<sub>4</sub> powder as reference sample and an external 2D detector were used. The Kubelka-Munk (K.-M.) function for determination of values of the direct band gap energy ( $E_g$ ) was used. The  $E_g$  values were determined by extrapolating the plot of  $(F(R)h\nu)^{1/2}$  on the depending  $h\nu/F(R)h\nu=A(h\nu-E_g)^2$ . K.-M. function  $F(R)=(1-R)^2/2R$  from the reflectance spectrum was obtained. K.-M. function depending on the  $h\nu$  (photon energy in eV) can be obtained Tauc curve.

The photoluminescence (PL) emission spectra (samples from 1\_550 to 1\_650) were measured by a spectrometer FLSP920 Series (Edinburgh Instrument Ltd) in the wavelength 335-760 nm at room temperature. Spectrometer was equipped with a 450 W non ozone xenon lamp (Steady state Xe900 lamp) and R928P type detector (PMT detector). Czerny-Turner configuration was used. The excitation wavelength was 365 nm. The widths of excitation and emission slits were 1 nm.

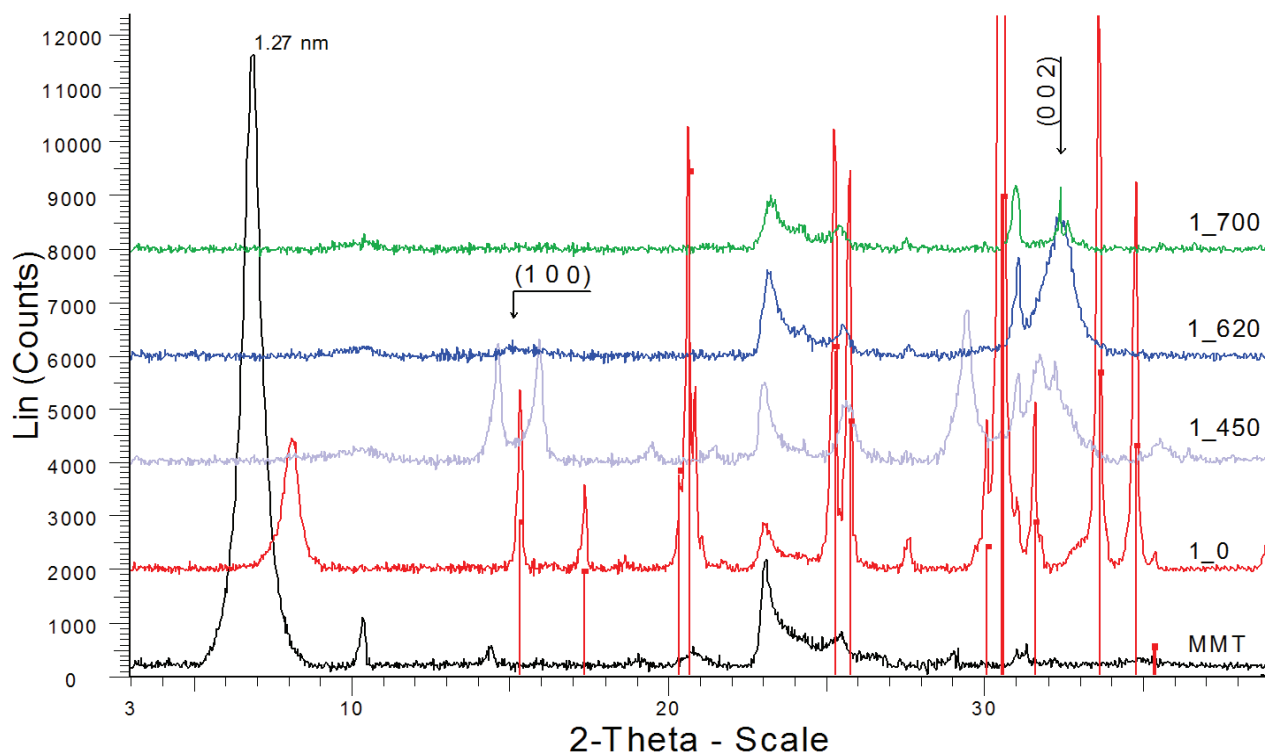
The N<sub>2</sub>O photocatalytic decomposition was carried out in a homemade stainless steel experimental apparatus. An 8 W Hg lamp with  $\lambda = 365$  nm (UVA) was situated in horizontal position on top of the quartz glass visor. The batch photoreactor with circulating mixing and with photocatalyst (0.1 g) placed on the bottom, was filled with N<sub>2</sub>O/He mixture (998 ppm) and pressurized to 1700 mbar. The gas chromatograph with barrier discharge ionization detector (GC/BID) was used to determine the N<sub>2</sub>O concentration which was measured before switching on the UVA lamp and during the irradiation. The reproducibility of photocatalytic experiments was checked by repeated tests. The N<sub>2</sub>O conversion was determined according to

$$X_A = (c_{A0} - c_A) / c_{A0} \quad (1)$$

where  $c_{A0}$ ,  $c_A$ , is the N<sub>2</sub>O concentration at the beginning of reaction ( $t = 0$ ) and at different times during the photocatalytic reaction, respectively. Volume was kept constant.

### 3. RESULTS AND DISCUSSION

XRPD patterns of MMT and 1\_0, 1\_450, 1\_620, 1\_700 composites are shown in **Figure 2**. In 1\_0 sample, ML and MMT were identified and it can be observed that the ML was not intercalated into MMT interlayer. At 450°C melem was formed (regions  $2\theta = 13-17^\circ$  and  $31-34^\circ$ ). For pure g-C<sub>3</sub>N<sub>4</sub> the characteristic reflections at  $15.3^\circ$  and  $32.5^\circ$  indexed as (100) and (002) diffraction planes (JCPDS 87-1526) were found. These reflections are observed in samples 1\_550 - 1\_650, thus only the spectrum of 1\_620 is shown (**Figure 2**). Comparing the intensities of (002) g-C<sub>3</sub>N<sub>4</sub> plane, temperatures 600 and 620 °C are the most appropriate.



**Figure 2** XRD patterns of pure MMT and samples 1\_0, 1\_450, 1\_620, 1\_700

In FTIR spectra (**Figure 3**), spectral band described in the spectrum of sample 1\_0 can be assigned to vibrational bands of ML [9]. Spectrum of sample 1\_450 contains mainly bands of melem. Especially very strong bands at  $1608\text{ cm}^{-1}$  and  $1468\text{ cm}^{-1}$  are very significant for melem [10]. Weak bands at  $1053\text{ cm}^{-1}$ ,  $525\text{ cm}^{-1}$ , and  $469\text{ cm}^{-1}$  are bands of MMT. Spectral bands presented in the spectrum of sample 1\_650 are typical for melon or g-C<sub>3</sub>N<sub>4</sub>; especially bands between  $1700\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  [10]. Spectral difference between melom

and g-C<sub>3</sub>N<sub>4</sub> are only in overlapping of bands; bands of melom are much overlapped, whereas bands of g-C<sub>3</sub>N<sub>4</sub> are relatively separated. The spectral bands in the spectra of the samples 1\_550-1\_650 are very similar, for this reason, only the spectrum 1\_650 is shown. For a sample 1\_700 could be observed degradation product of MMT, for example amorphous silica or high-temperature form of quartz (cristobalite and tridymite). The same bands are present in the spectrum of sample 1\_650 (1045 cm<sup>-1</sup>, 567 cm<sup>-1</sup>, and 482 cm<sup>-1</sup>).

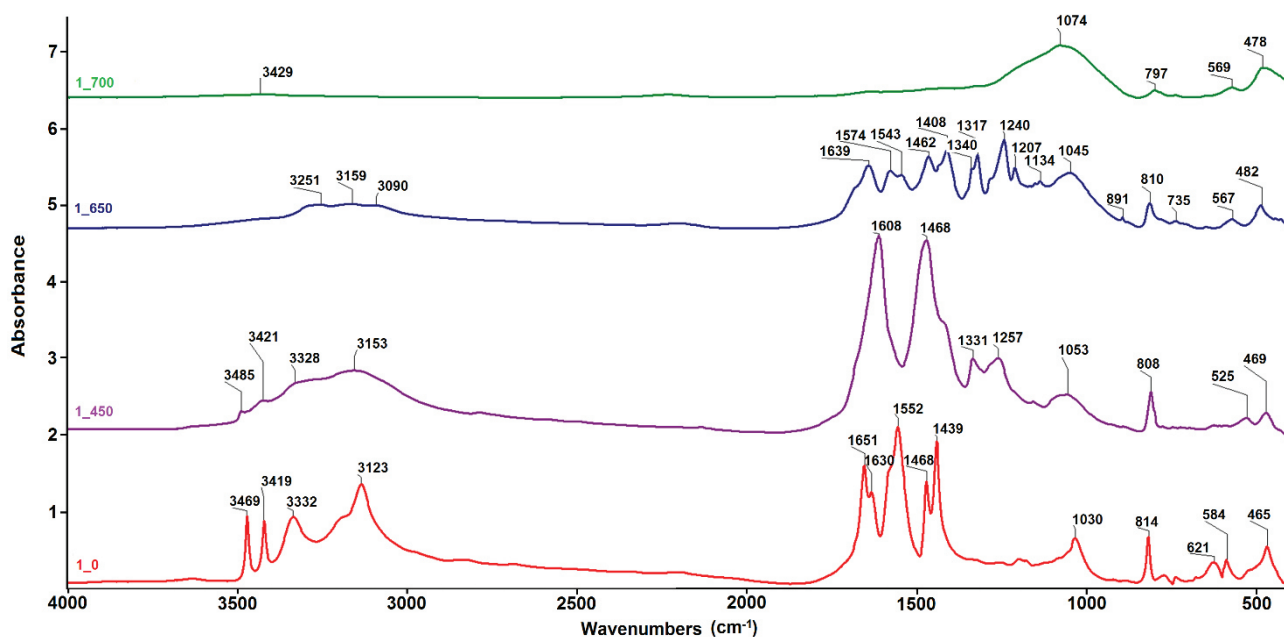


Figure 3 FTIR spectra of samples 1\_0, 1\_450, 1\_650, and 1\_700

DRS analysis (Figure 4A) revealed that absorption edge is around 420-430 nm. The MMT has weak light absorption ability within the scope of full spectrum. Sample 1\_0 has very low absorption edge value about at 255 nm and is very difficult to determine the value of band gap energy. Figure 4B shows Tauc curves from which it is possible to determine the values of the band gap energy.

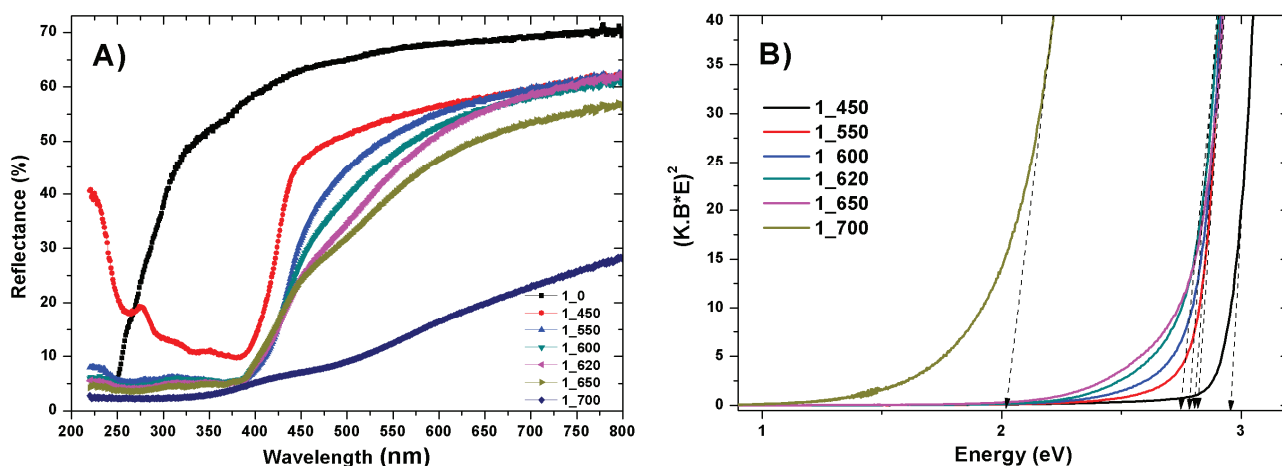


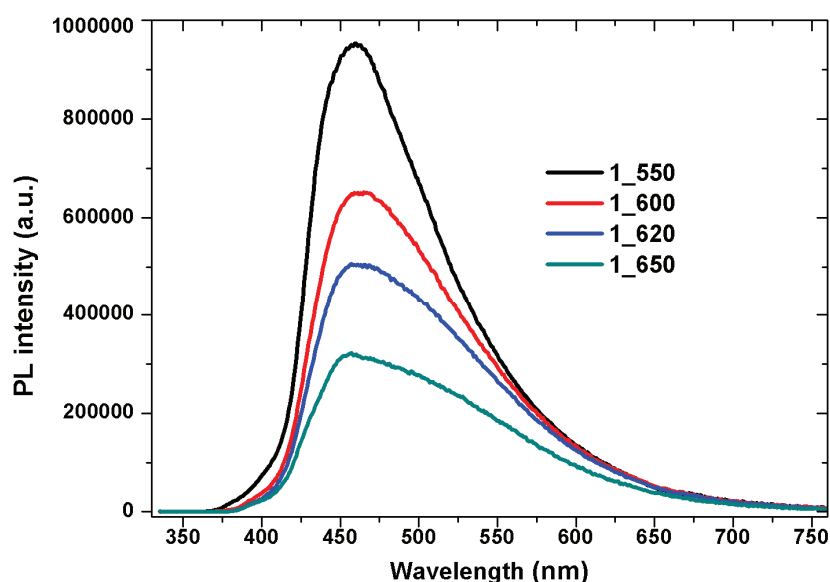
Figure 4 Diffuse reflectance spectra of samples (A); Tauc curves obtained from reflectance spectra of samples (K.-M. function) and determination of direct band gap energy (B)

With increasing temperature at which the samples were prepared, the band gap decreases (see **Table 1**). Similar results were reported by Li et al. [8] when the band gaps mixtures of g-C<sub>3</sub>N<sub>4</sub>/clay have values in the range 2.72-2.80 eV, which are a little larger than that of g-C<sub>3</sub>N<sub>4</sub> due to its extended  $\pi$ -conjugated frameworks connected by the sp<sup>2</sup> hybridization of carbon and nitrogen. For the sample 1\_700, the band gap differs significantly (2.10 eV - transition n- $\pi^*$  type and 3.04 eV - transition  $\pi$ - $\pi^*$  type). A very small amount of g-C<sub>3</sub>N<sub>4</sub> is in sample 1\_700.

**Table 1** Direct band gap ( $E_g$ ) of prepared samples (+transition  $\pi$ - $\pi^*$ ; \*transition n- $\pi^*$ ) at different temperature

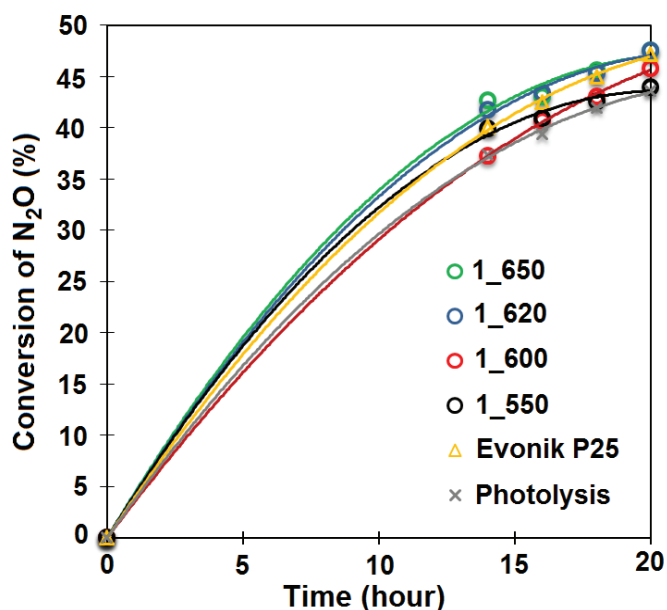
sample	$E_g$ (eV)	sample	$E_g$ (eV)	sample	$E_g$ (eV)
1_450	2.92	1_600	2.75	1_650	2.79
1_550	2.86	1_620	2.76	1_700	+3.04 (*2.10)

From the PL emission spectra (**Figure 5**) it is evident that sample 1\_550 has a maximum emission wavelength at 460 nm, 1\_600 at 464 nm, 1\_620 at 461 nm and 1\_650 at 457 nm. With the increasing temperature to 600°C of prepared samples is observed slight bathochromic shift for emission maximum of bands (about 4 nm) and band gap energy value for this materials decreases (see **Table 1**). This fact can be attributed to the expansion of the g-C<sub>3</sub>N<sub>4</sub> clusters network by connecting more tri-s-triazine units and increasing the sp<sup>2</sup> clusters and increase bond length between C and N atoms at higher preparation temperatures [11], thereby improving the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>. For samples prepared from 600 to 650°C it is evident hypsochromic shift from 464 to 457 nm (about 7 nm). The highest emission intensity has been found for sample 1\_550 which agrees with the results of the studies [11] and contrast the smallest emission intensity is for the sample 1\_650. For a pure g-C<sub>3</sub>N<sub>4</sub>, a strong emission band is about 465 nm [8], while for the mixture of g-C<sub>3</sub>N<sub>4</sub> prepared at 550°C with MMT the peak of the emission PL band has a lower intensity (about 455 nm), which means that the interfacial charge between MMT and g-C<sub>3</sub>N<sub>4</sub> in the composite is improved.



**Figure 5** PL emission spectra of samples prepared at 550-650°C

The time dependences of the N<sub>2</sub>O conversion of all prepared samples under UVA ( $\lambda = 365$  nm) irradiation during a time period of 0-20 h are shown in **Figure 6**. The N<sub>2</sub>O conversion is very similar over the all prepared samples. The samples synthesized at higher temperature (620°C and 650°C) showed moderate improvement compared to sample prepared at 550°C. The highest N<sub>2</sub>O conversion after 20 hours of UVA irradiation (45 %) was achieved in the presence of the samples prepared at 620°C and 650°C.



**Figure 6** The time dependences of N<sub>2</sub>O conversion over of the prepared photocatalysts (550°C-650°C) under UVA ( $\lambda = 365$  nm) irradiation

#### 4. CONCLUSION

g-C<sub>3</sub>N<sub>4</sub>/MMT type photocatalysts were prepared by thermal polycondensation of ML/MMT composite at different temperatures. Presence of melem and its derivatives after low temperature (450°C) processing was evidenced by the XRD and FTIR analysis indicating incomplete ML to g-C<sub>3</sub>N<sub>4</sub> transformation. Preparation of composites at 550- 650°C resulted in the creation and extension of g-C<sub>3</sub>N<sub>4</sub> networks that was confirmed by the significant peak differences in their FTIR spectra and also characteristic peaks at XRD patterns. These composites have been tested for the photocatalytic decomposition of N<sub>2</sub>O. Photocatalytic experiments showed very similar activity of all samples synthesized at 550-650°C. The best photocatalytic activity was exhibited by the sample prepared at the highest temperature (620°C and 650°C). The N<sub>2</sub>O conversion in presence of sample prepared at 620°C and 650°C was 45 % after 20 hours of UVA irradiation. These results make g-C<sub>3</sub>N<sub>4</sub>/MMT promising photocatalytic materials.

#### ACKNOWLEDGEMENTS

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