

GRAPHENE SUPPORTED CATALYST FOR ENHANCED BIOMASS HYDROLYSIS

N. Perkas, M. Klein, A. Gedanken

Department of Chemistry and the Center for Advanced Materials and Nanotechnology, Bar Ilan University, Ramat Gan, 52900 Israel

Nina.Perkas@biu.ac.il

Abstract: The present work reports on a new silicotungstic acid catalyst supported on graphene (HSiW/G). The deposition was performed by sonochemical method proven as an effective technique for the synthesis of the supported catalysts. The catalyst (HSiW/G) was characterized using a variety of physico-chemical methods as TEM, HR SEM, DLS, FTIR and Raman spectroscopy. Homogeneous distribution of HSiW on the surface of graphene was demonstrated. Hydrolysis of biomass for the production of glucose was studied. The hydrolysis of glycogen was performed with a HSiW/G catalyst by hydrothermal treatment. The yield of glucose (65 wt%) obtained was about 8 times higher than that obtained with the same amount of bare HSiW. Stability of the HSiW/graphene even after 3 repeated uses was confirmed. The mechanism of enhancement of the catalytic activity was discussed in terms of a special interaction between the graphene support and HSiW and also the appearance of hydrophobic cavities on the surface of graphene.

Keywords: SONOCHEMISTRY, NANOPARTICLES, GRAPHENE, GLYCOGEN, HYDROLYSIS

1. Introduction

Biomass is a sustainable source of organic carbon, which is considered as part of the solution for producing biofuels and chemicals.^{1,2} Biomass is obtainable world-wide in the form of organic materials such as grass, wood, agricultural crops and glycogen. Many studies have been done on the hydrolysis of biomass to glucose with mineral acids,^{3,5} but the large scale use of acids causes several problems such as reactor corrosion, further degradation of monomers, recovery of catalysts, and requires special treatment of the acid residue producing much waste.⁶

Solid acid catalysts have various advantages over liquid acid catalysts, such as: simple product separation, possible recycling, and less damage to the reactor. Lately, HPAs have been widely used as homogeneous catalysts for biomass conversion. Shimizu et al. reported H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀ for selective hydrolysis of cellobiose and cellulose to glucose in an aqueous phase.⁷ The heteropoly acids could be separated from the homogeneous solution and recycled by extraction with diethyl ether,⁸ but this process takes a long time, and the extraction is not complete. Some traces of the catalyst remain in the product.

Graphene has received much attention from researchers in the past few years due to its exceptional electronic, mechanical, and optical properties, high surface area, and biocompatibility. Graphene supported catalysts have also demonstrated high activity in biomass conversion.^{3,8} Kitano et al. reported on the enhancement of the hydrolysis of β -1,4-glucan on graphene-based amorphous carbon bearing SO₃H, COOH, and OH groups. Their results suggested that the synergistic combination of high densities of the functional groups bonded to amorphous carbon causes the efficient hydrolysis of β -1,4-glucan including cellulose.⁹

Glycogen, a water soluble polysaccharide of glucose, is a better feedstock for glucose production than lignocellulosic biomass as it needs no additional pre-treatment. The synthesis of glycogen from CO₂ by photosynthesis and its subsequent hydrolysis to glucose with high selectivity make glycogen an abundant and renewable feedstock for the production of glucose.¹⁰ Even though animal remains are the only source of glycogen as of now, currently immense research is underway to produce glycogen from cyanobacteria whereas CO₂ is used as feedstock for glycogen synthesis.¹⁰ Owing to such possibilities, strategies need to be developed for the effective conversion of glycogen to glucose, which was the objective of this study.

In this article we report on a new silicotungstic acid catalyst supported on graphene (HSiW/G). The catalyst preparation was performed by a sonochemical method.^{11,12} The catalytic activity of HSiW/G was studied for the hydrolysis of glycogen. This supported catalyst could be easily separated from the reaction mixture. The properties of the catalysts were studied by the following methods: X-ray diffraction (XRD), transmission and, high resolution scanning electron microscopy (TEM and HR-SEM), N₂ isothermal adsorption-desorption (BET), FT-IR and Raman spectroscopy,

inductively coupled plasma (ICP) analysis, and dynamic light scattering (DLS).

2. Experimental Procedure

Catalysts Preparation

Tungstosilicic acid hydrate (H₄SiW₁₂O₄₀·nH₂O, HSiW, 99%), and glycogen from bovine liver were purchased from Sigma-Aldrich Co. The graphene nanoplatelets (6–8 nm thick ×15 microns wide) were purchased from STREM chemicals, Newburyport, MA, USA. An ultrasound-assisted method was used to prepare the supported HSiW/G catalysts. Typically, the procedure was followed: HSiW was first dissolved in ethanol then graphene was added. The sonochemical irradiation was performed in a glass beaker reactor with 1 cm² Ti horn immersed the (Sonicator 20 kHz, Sonics & Materials, VCX-750) for 1 h. The product was then separated by centrifugation and dried in a vacuum overnight.

In addition to the sonochemical route, the conventional impregnation method was also used for the preparation of the HSiW/G catalyst. The mixture of the reagents was kept for 4 h of stirring. Then the solvent was evaporated using a water bath followed by drying of the catalyst under vacuum overnight. The catalysts prepared in the two aforementioned routes were compared in the glycogen hydrolysis reaction.

Glycogen hydrolysis reaction

For the glycogen hydrolysis process a stainless steel homemade autoclave of 50 mL volume was used. Typically, 1 g glycogen and 1 g catalyst were dispersed in 20 mL water and placed in the autoclave for hydrothermal treatment. Reaction parameters such as time, temperature of heating, weight ratio of the catalyst and glycogen were varied to optimize the hydrolysis process. After the reaction, the catalyst was separated from the solution by centrifugation and dried under vacuum overnight. The catalyst was used for a second run without regeneration under identical hydrothermal reaction conditions. The reusability was tested for 3 times.

The progress of the glycogen hydrolysis reaction was monitored using ¹³C NMR spectroscopic analysis on a Bruker Avance DPX 300 instrument. D₂O was used as the solvent. The water soluble products of catalyzed hydrolysis reactions were analyzed by HPLC (Merck-Hitachi LaChrom System L-7000 equipped with L-7455 Diode Array Detector and Schambeck SFD RI 2000 Refractive Index Detector, Bad Honnef, Germany). Analyses were carried out using a 300 × 7.8 mm Rezex-ROA ion exclusion chromatography column (Torrance, CA, USA) equipped with a matching guard column. The mobile phase was 0.005 N H₂SO₄ under isocratic elution for 45 min at a flow rate of 0.5 mL min⁻¹ at ambient temperature, with an injection volume of 10 μ L. EZ Chrom Elite v. 3.1.7 software was used for data acquisition and processing, with the RI signal acquired using an external analog input.

3. Results and discussion

3.1. Catalysts characterization

The morphology of the catalyst HSiW/G was studied by using HR-SEM. Sheets with layered structures were observed in the case of commercial graphene (Fig. 1a). The HSiW/G catalyst showed randomly oriented spherical particles of HSiW, in the range of 100–250 nm, on the graphene sheets (Fig. 1b). It could be seen that the original smooth surface of graphene was partly changed after deposition of HSiW, but the layered structure of graphene was not destroyed. The amount of HSiW on graphene was found to be 2.5 wt% by ICP analysis.

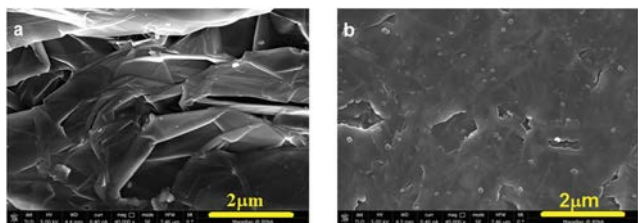


Fig. 1. HR-SEM images of (a) commercial graphene and (b) graphene coated with HSiW using the sonochemical method.

The influence of sonication on the morphology and size of HSiW was studied by TEM and DLS analysis. The TEM image indicated that after 1 h of sonication of HSiW in ethanol without graphene, spherical HSiW nanoparticles were formed with sizes in the range of 100–400 nm (Fig. 2b). After the same period (1 h) of regular stirring of HSiW in ethanol the spherical particles of a slightly larger size in the range of 200–500 nm were found (Fig. 2a). Besides the large particles, very small particles were also observed in both treatments.

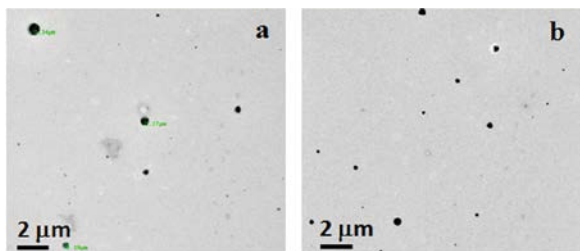


Fig. 2. TEM images of the HSiW after (a) 1 h stirring and (b) 1 h sonication. images of (a) commercial graphene and (b) graphene coated with HSiW using the sonochemical method.

In addition to TEM, DLS analysis was also employed to measure the particle size of HSiW upon different treatments (Fig. 3). The results were in agreement with the TEM images. It was found that with an increase in the sonication time from 15 to 60 min the average particle size decreased from 380 to 340 nm. Such a reduction of particle size results in an improved catalytic performance of HSiW/G in the hydrolysis process.

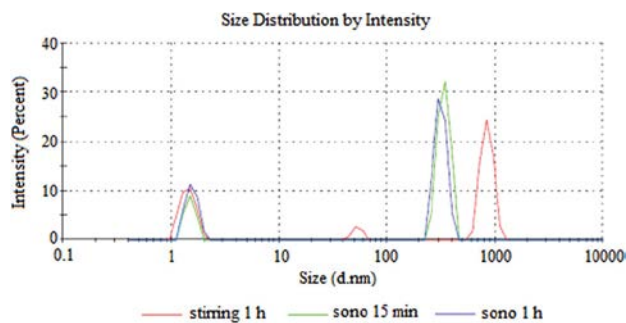


Fig. 3. DLS plot depicting the size distribution of HSiW particles after 15 min and 1 h sonication and 1 h stirring.

The FT-IR spectra of the bare graphene, HSiW and HSiW/G catalyst are shown in Fig. 4. The FT-IR spectrum of HSiW demonstrated four characteristic peaks at 1020, 982, 921, and 798 cm^{-1} assigned to the stretching modes of Si–O, W=O, W–Oe–W, and W–Oc–W, respectively.¹³ In the spectrum of HSiW/G the peaks in the region of 1020–780 cm^{-1} are very weak and slightly shifted to lower wavelengths. This shift indicates a strong interaction between graphene and the catalyst, causing the weakening of the various bonds. A similar effect was observed by Chen et al.¹³ upon stabilization of HSiW by organic molecules. The FT-IR results clearly demonstrated the fact that HSiW was effectively deposited on graphene and its strong interaction with the support.

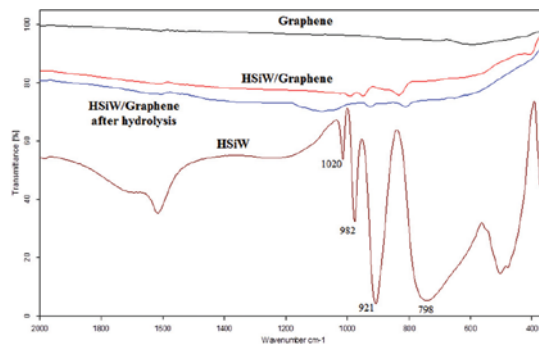


Fig. 4. FT-IR spectra of graphene, HSiW/G and HSiW.

The Raman spectra of the bare graphene, HSiW and HSiW/G catalyst are shown in Fig. 5.

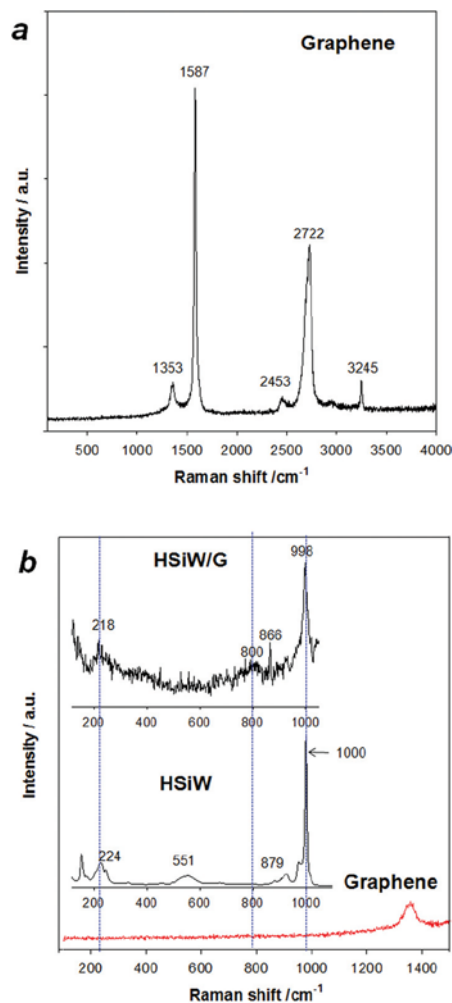
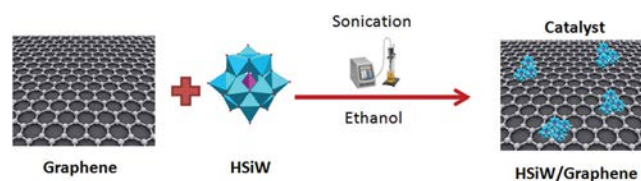


Fig. 5. Raman spectrum of graphene in full range (a), and Raman spectra of graphene, HSiW and HSiW/G (b). Dashed blue lines are eyeguides.

The most prominent features in the Raman spectra of graphene are the G-band appearing at 1587 cm^{-1} and the D-band appearing at 1353 cm^{-1} (Fig. 5a). The Raman spectroscopy technique was used extensively for observing the Keggin structure of heteropoly acids and also for proving its presence on the graphene.^{14,16} The Raman spectrum of commercial HSiW (Fig. 5b) showed the most intense bands at 1000 , 974 , 551 and 224 cm^{-1} assigned to stretching of $\text{W}=\text{O}$, bending of $\text{W}-\text{O}-\text{W}$, $\text{O}-\text{Si}-\text{O}$, and WO_3 vibrations, respectively. These signals are typical of Keggin structure.¹⁴ The Raman spectrum of HSiW/G is similar to that of the bare heteropoly acid (Fig. 5b). The spectrum showed peaks at 998 , 866 and 218 cm^{-1} for the $\text{W}=\text{O}$ stretching, $\text{W}-\text{O}-\text{W}$ bending mode, and WO_3 bending, indicating the preservation of the Keggin structure of the HSiW on the surface of graphene. However, a shift in two bending modes from 879 to 866 cm^{-1} and from 224 to 218 cm^{-1} , respectively might be due to the strong interaction of HSiW with the graphene support, which correlates with the FT-IR result.

The Raman and HR-SEM studies indicated that the graphene layers are not damaged during sonochemical synthesis of the HSiW/G catalyst. Based on the Raman results it could also be argued that the units of the HSiW were not destroyed during the deposition and they are well dispersed on the surface of graphene. The HSiW is homogeneously distributed on the surface of graphene and strongly anchored to the support. Even after the catalytic hydrolysis of glycogen, the bands corresponding to HSiW were observed in the FT-IR spectra (Fig. 4). The sonochemical deposition of HSiW on the graphene substrate is presented in Scheme 1.



Scheme 1. Synthesis of the HSiW/G catalyst by the sonochemical method.

Our explanation of the ultrasound assisted coating is based on the phenomena of cavitation, formation, growth and implosive collapse of the acoustic bubbles in the liquids. The nanoparticles (NPs) of HSiW created in the liquid under ultrasound waves are thrown to the solid by microjets and shock waves which are the after effects of the cavitation collapse.^{17,18} The speed and power of the microjets are extremely high ($>500\text{ m s}^{-1}$), causing the strong anchoring of the NPs to the surface of the substrate.

3.1. Glycogen hydrolysis under hydrothermal reaction conditions

The glycogen hydrolysis was carried out under hydrothermal conditions in an autoclave. ^{13}C NMR spectra of the products obtained with three types of catalysts (bare HSiW, bare graphene and HSiW/G) are shown in Fig. 6.

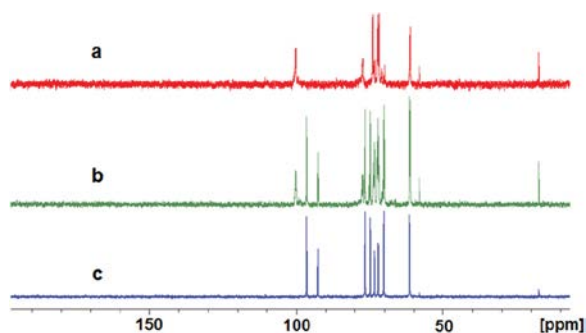


Fig. 6. ^{13}C NMR spectra of hydrolyzate obtained with (a) bare graphene, (b) HSiW/G and (c) HSiW (reaction conditions: 0.1 g glycogen; 0.1 g catalyst; 2 mL water; $100\text{ }^\circ\text{C}$; 1 h).

As suspected, no glycogen conversion was observed when only graphene was used as the catalyst (Fig. 6a). With HSiW, complete conversion of glycogen to glucose was obtained (Fig. 6c). With the HSiW/G catalyst, in addition to glucose, some traces of unreacted glycogen were also noticed (Fig. 6b), indicating that the hydrolysis is not complete. This fact can be explained because of the low content of the HSiW in the catalyst. According to the ICP analysis, the content of HSiW in the HSiW/G catalyst was found to be $2.5\text{ wt}\%$. In other words, the amount of HSiW in the 0.1 g HSiW/G catalyst used for the hydrolysis reaction is 0.0025 g . It is interesting to note that even at such a low loading of the solid acid, the synthesized catalyst is effective for the hydrolysis of glycogen. In addition, under the reaction conditions used, the hydrolysis of glycogen was selective. No by-products such as hydroxymethylfurfural (HMF), levulinic acid and formic acid were formed.

For optimizing the glycogen hydrolysis process with HSiW/G and detailed study, the reaction was performed in a larger reaction batch of 20 mL at different reaction times, temperatures and wt/wt% ratio of catalyst and glycogen. The products obtained under various reaction conditions were analyzed by HPLC analysis, and the results are presented in Fig. 7.

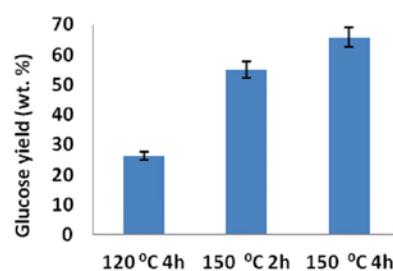


Fig. 7. Glucose yield (wt%) from glycogen hydrolysis as a function of reaction time and temperature (reaction conditions: 1 g glycogen; 1 g HSiW/G catalyst; 20 mL water).

The maximum yield of glucose (65%) was obtained at $150\text{ }^\circ\text{C}$ with prolonging the reaction time to 4 h .

The weight ratio of the catalyst (HSiW/G) to glycogen was varied in the range $1-0.25$. The yields of glucose generated from hydrolysis of glycogen with various amounts of catalyst are depicted in Fig. 8.

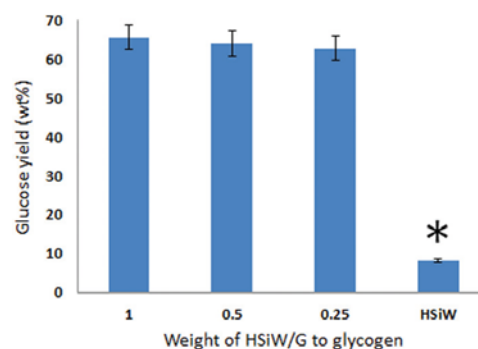


Fig. 8. Glucose yield from glycogen hydrolysis at different weight ratios of HSiW/G to glycogen (glycogen – 1 g ; HSiW/G – 1 , 0.5 and 0.25 g ; time – 4 h ; temperature – $150\text{ }^\circ\text{C}$). *Bare HSiW – 0.025 g (this corresponds to the amount of HSiW present in the HSiW/G catalyst at a ratio of HSiW/G to glycogen $1 : 1$).

It was observed that at a hydrolysis temperature of $150\text{ }^\circ\text{C}$ for 4 h , the yield of glucose for all of the examined ratios of HSiW/G to glycogen ($1 : 1$; $0.5 : 1$ and $0.25 : 1$) was almost the same ($65\text{ wt}\%$). When same amount of bare HSiW as that present in the supported catalyst (HSiW/G) was used as a catalyst, the glucose yield was dramatically low (8.2%). Thus, the bare HSiW is about 8 times less active than HSiW deposited on graphene. The increase of the catalytic activity of the supported HSiW compared to the bare HSiW could be due to the effective and uniform distribution of the heteropoly acid on the surface of graphene. Moreover, the HSiW/G

catalyst has a larger specific surface area ($52 \text{ m}^2/\text{g}$) compared to bare HSiW ($1.8 \text{ m}^2/\text{g}$). The large surface area enables an effective contact between the uniformly distributed acid sites on the graphene surface and the glycogen that promotes the rapid and efficient catalytic reaction.

The observed enhanced activity of HSiW/G could be due to the strong binding of the heteropoly anions to the aromatic π -cloud on the graphene surface (similar to π - π interactions) leading to higher accessibility of the protons for the cleavage of the glycosidic bond in glycogen. Kim et al. reported similar strong electrostatic interactions between polyoxometalate and rGO.¹⁹ In contrast, in the case of bare HSiW, the protons of the polyanion rotate freely in the reaction medium and are in constant motion. As a result, the probable interaction between the protons and the reactant (glycogen) is low, resulting in lower yields of glucose.

We have further evaluated the stability of HSiW/G in the hydrolysis of glycogen. After the first run under optimal hydrothermal conditions (1 g HSiW/G, 1 g glycogen, 20 mL water, 150°C , 4 h) the HSiW/G was separated from the aqueous product mixture by centrifugation. The collected catalyst was dried under vacuum overnight and subsequently reused for the second and third runs under identical reaction conditions. The results as measured by HPLC analysis are presented in Fig. 9.

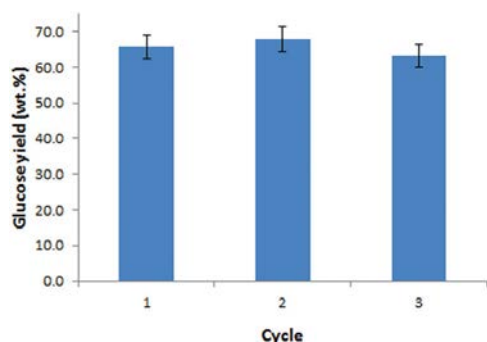


Fig. 9. Recyclability of the HSiW/G catalyst in the hydrolysis of glycogen (reaction conditions: 1 g of glycogen; 1 g of the solid acid catalyst; 20 mL of H₂O; 150°C ; 4 h). The catalyst was recovered by 9000 rpm centrifugation for reuse.

The glucose yield after three reaction cycles was still high (63.3 wt%) indicating that HSiW can be reused without loss in catalytic activity. Even after three repeated runs, the amount of HSiW on graphene was found to be 2.2 wt%. This indicates that the catalyst is not just a physical mixture but a supported system wherein the active component (HSiW) is strongly adhered to the support (graphene). The good catalyst stability could be due to the use of the sonochemical deposition method which leads to the strong adherence of HSiW to the support.^{20,21}

4. Conclusions

Polyoxometalate (HSiW) was deposited on the surface of graphene by the sonochemical method. Physico-chemical characterization of the HSiW/G catalyst was done using HR-SEM, TEM and XRD, which demonstrated a homogeneous distribution of HSiW on the surface of graphene supports. The catalytic performance of the synthesized catalyst was evaluated for the hydrolysis of the glycosidic bond of biomass to glucose. The following conclusions have been drawn: the catalytic activity of HSiW/G is significantly higher than that of the bare HSiW. The hydrolysis process with HSiW/G is selective, fast and green with a high yield of glucose (66 wt%). The sonochemical method provided strong anchoring of HSiW to graphene and high stability of the catalyst. The reuse of the HSiW/G catalyst in 3 cycles was demonstrated. The glucose yield after three reaction cycles was not altered significantly, showing that HSiW/G is a reusable, economically viable and green catalyst.

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