Synthesis and characterization of Nanoporous Material via Rice husk

تحضير وتشخيص مادة مسامية نانوية عن طريق قشور الرز

Hayder Hamied Mihsen [1], Thana Jaafar Al-Hasani1[2] and Kasim Mohammed hello[3]

[1]Department of Chemistry, College of Science, University of Karbala
[2]Department of Chemistry, College of Science, University of Baghdad
3Department of Chemistry, College of Science, University of Al–Muthanna

Abstract

The idea of this research depended on the preparation of nanoporous material via rice husk based on the silica material. The silica material is prepared from the rice husks in appropriate chemical method. Where it is known that the rice husks are produced by the production of rice plants that are too large quantities and cause high pollution in environment. Instead, the husks is embedded or burn in the exposed atmosphere in urban and rural areas could benefit from it by the suitable chemical treatment and burning it in controlled conditions, it produces pure silica labeled as RHA (Rice Husk Ash) can be entered in chemical reactions for the production of Nanoporous Material labeled as RHAC-Pd$(DTO)_2$ .This Nanoporous Material is inorganic-organic hybrid. According to analysis of CHNS and FT-IR spectra can be conclude that the bis-dithiooxamidepalladium(II) chloride $[Pd(DTO)_2]Cl_2$ has successful incorporation on RHACCl . X-ray diffraction technique was used to determine the amorphous formula of $[Pd(DTO)_2]Cl_2$, while the Transmission electron microscopy (TEM) technique was used to confirm its nanostructure of compounds. The surface area measurements indicated that $[Pd(DTO)_2]Cl_2$ had a specific surface area of 70.83 m^2g^{1-} and a narrow average pore diameter of 3.25 nm. Thermogravimetric analysis (TGA-DTA) of RHAC-Pd$(DTO)_2$ indication that the physical adsorb water was lost between 30-160 °C which means it is weakly bonded in the silica matrix, while the residual parts of material decomposed up to 300 °C.

Keywords: Rice husk ,palladium complex , nanoporous material

الخلاصة

تعتمد فكرة البحث على تحضير مادة مسامية نانوية، المادة الاساس في تحضيرها هي السليكا التي يتم استخلاصها من قشور الرز بطريقة كيميائية مناسبة. حيث انه من المعروف ان قشور الرز التي تنتجها معامل انتاج الرز تكون بكميات كبيرة جدا مسببة تلوث عالي للبيئة، فبدلا ان تطمر تلك القشور او تحرق بالأجواء المكشوفة بالمدن والارياف يمكن الاستفادة منها بمعاملة كيميائية مناسبة وحرقها بظروف مسيطر عليها لتنتج سليكا نقية (ناصعة البياض) يرمز لها ب RHA مختصر Rice husk ash يمكن ادخالها في سلسلة تفاعلات كيميائية لتحضير مادة مسامية نانوية يرمز لها RHAC-Pd$(DTO)_2$ وهي هجين من مادة لاعضوية-عضوية. تم الاعتماد على نتائج كل من CHNS ودراسة اطياف الأشعة تحت الحمراء FT-IR باستنتاج الاندماج الناجح للمادة ثنائي- ثنائي ثايو اوكسمايد بلاديوم(II) كلورايد على المادة RHACCl ، كما تم التعرف على الطبيعة غير المتبلورة له من خلال تقنية حيود الأشعة السينية X-ray ، بينما أثبتت تقنية المجهر الالكتروني النافذ (TEM) أنه يمتلك طبيعة نانوية. في حين ان قياسات المساحة السطحية بينت ان المركب يمتلك مساحة سطحية تقدر ب 70.83 m^2g^{1-} وبمعدل قطر مسامي يقدر ب 3.25 nm، كما اوضحت التحاليل الحرارية بتقنية TGA-DTA ان الماء الممتز فيزيائيا يتفكك من المركب بين 30-160 م° بينما الاجزاء الاخرى العضوية واللاعضوية تتفكك فوق 300 °C .

1. Introduction

Agriculture of the rice covers 1% of the earth's surface and is a fundamental source of sustenance for billions of people and position second to wheat in terms of area and production [1]. Globally, nearly 500 million tons of rice vintage is produced each year. Production of rice is dominated by Asia, where rice is the only food crop that can be grown during the rainy season in the waterlogged tropical areas, but it can be grown during the summer season in Iraqi regions (particularly, middle and south regions)[2-3].
Rice husks (RH) are the hard protecting coverings of grains of rice. The main function of rice husk is protecting rice during the growing season. Rice husks are produced by the machines production of rice plants in a large quantities. In most cases the husks is embedded or burn in the exposed atmosphere in urban and rural areas and cause high pollution in environment, Fig.(1).

Fig. 1. The rice husk burned as a waste and used threat problems to the environment

Rice husks are known to have a relatively high content of inorganic compounds representing approximately 20% (wt) of the dry hull, while 80% (wt) of the residual are organic compounds which are cellulose and hemicellulose, 50% (wt), and lignin 26% (wt), with the remaining of 4% (wt) representing other organic compounds such as oil, proteins, etc. The percentages of organic and inorganic compositions are depending on several factors, including weather, soil and plant variety [3]. During growth, rice plants absorb silica from the soil and accumulate it into their structures. This silica can be concentrated by burning at high temperatures removing other elements, which make the ash so valuable.

Many researchers have concluded that the RH is an excellent source of high-grade amorphous silica [3-7]. The amorphous white silica (known as rice husk ash) that can be extracted from the husk and the straw of the rice plant; which may possess a very high specific surface area [3]. One important application of silica is due to its ability to be modified with different silylating agents, which can introduce basic groups through an anchored pendant chain. The traditional procedure for immobilization of 3-(chloropropyl)triethoxysilane (CPTES) onto different types of silica involves long reaction times, nonenvironmentally friendly organic solvents, harsh refluxing condition, and multiple steps [8-10]. Moreover, the vast majorities of these protocols call for expensive chemicals and techniques and cause environmental pollution. A more direct and simple method was introduced by Kassim et.al to immobilize CPTES onto silica to give a $–CH_2–Cl$ functionality on the silica surface labeled as RHACCl [11]. The product RHACCl had been used successfully to

reacted with different organic molecules contain $–NH_2$ group such as saccharine, melamine, and 7-amino-1-naphthalenesulfonic acid to produce heterogeneous catalysts[12-14]. Metal complexes that contain $–NH_2$ group as well as used to prepared nanomaterial composed [15]. The objective of the current study is to immobilized the $[Pd(DTO)_2]Cl_2$ comples onto the RHACCl compound to produce a hybrid of a silica-$[Pd(DTO)_2]Cl_2$ architecture that can be used for beneficial catalytic properties.

2. Materials And Methods

2.1 Raw materials

Sodium hydroxide (Fluka, 99%), Nitric acid (BDH, 65%), 3-(chloropropyl)triethoxysilane (CPTES) (Sigma–Aldrich, 95%), Dithiooxamid*e* (Fluka, >99%), Palladium (II) chloride (Fluka, (60)Pd%), toluene (Fluka, 99%), triethylamine (R&M Chemical, 99%), and dichloromethane (DCM) (BDH, 99%), were each used without further purification. The rice husk (RH) was collected from a rice mill in from the region of Al-Abbasya region, Kufa, Najaf, Iraq. $[Pd(DTO)_2]Cl_2$ complex was synthesized according to a reported method [16].

2.2 Samples Characterization

The RHAC-$Pd(DTO)_2$ was characterized by elemental analysis(CHNS) using (EuroEA Elemental Analyzer). Powder X-ray diffraction of the complex was collected from (XRD-6000, Shimadzu), Nitrogen adsorption porosimetry (ASAP 20 Automatic Chemisorption Analyzer), The specific surface area of the prepared complex were calculated using the BET model. Infrared spectra were obtained by KBr disc over the wave number range of 4000–400 cm^{-1} using (FTIR–8400S Shimadzu). Energy dispersive spectrometry, EDX (Edax Falcon System). The TEM micrographs were obtained using Philips CM12 equipment.

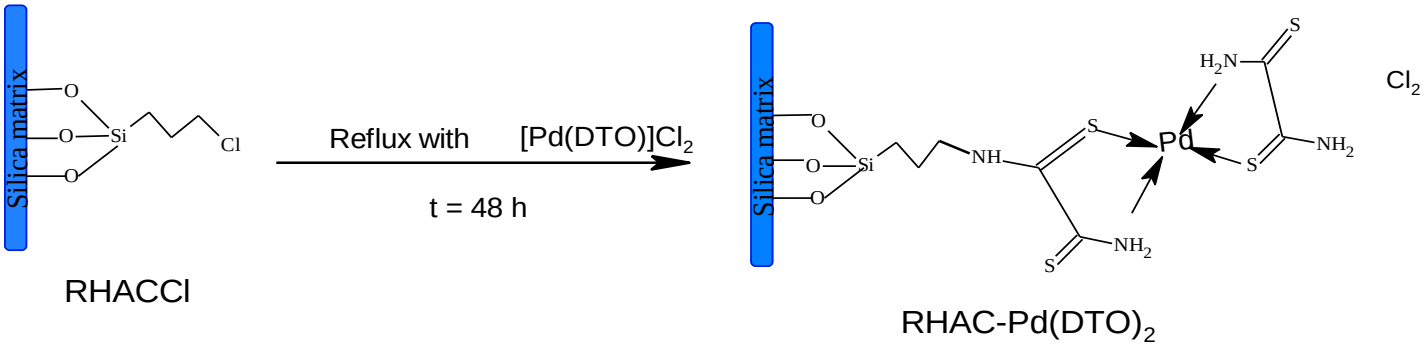
2.3 Synthesis

2.3.1 Sources of silica

The rice husk ash (RHA) was select as the origin of amorphous silica as it was available in abundance. The silica was removed from rice husk according to a informed method [17,18].

2.3.2 Preparation of silica–palladium nano catalyst, RHAC-$Pd(DTO)_2$

RHACCl and $[Pd(DTO)_2]Cl_2$ have been prepared according to the reported method [11] and [16], respectively. To prepared RHAC-$Pd(DTO)_2$, a solution mixture of 0.53 g (1.26 mmol) of $[Pd(DTO)_2]Cl_2$, 1.26 mmol of Et_3N and 0.53 g of RHACCl in (30 mL) toluene were refluxed at 110 °C in an oil bath for 48 h. The separated solid was filtered, washed with acidic ethanol then with acetone, dried at 100 °C for 24 h and finally labeled as RHAC-$Pd(DTO)_2$. About 0.7 g of the RHAC-$Pd(DTO)_2$ was collected using this method. Scheme 1 showed the immobilization of $[Pd(DTO)_2]Cl_2$ onto RHACCl to form RHAC-$Pd(DTO)_2$.



RHACCl

RHAC-Pd(DTO)$_2$

Scheme 1: The reaction Scheme for the immobilization of $[Pd(DTO)_2]Cl_2$ onto RHACCl to form RHAC-Pd(DTO)$_2$.

3. Results And Discussion

3.1 Elemental analysis

The elemental analysis of RHA , RHACCl and RHAC-Pd(DTO)$_2$ were shown in Table 1 . RHAC-Pd(DTO)$_2$ contained 6.07 % of N and 14.62 % of S. The percentage of C and H for RHAC-Pd(DTO)$_2$ were significantly higher than that of both RHACCl and RHA, as was expected. These results clearly indicate the successful immobilization of $[Pd(DTO)_2]Cl_2$ onto RHACCl.

3.2 The nitrogen adsorption analysis

The specific surface area of RHAC-Pd-(DTO)$_2$ was 70.83 $m^2.g^{-1}$ which is lower than the specific surface area of RHACCl .This was probably due to the presence of Palladium ion inside the silica matrix . The open loop in adsorption and desorption isotherms of RHAC-Pd(DTO)$_2$ in Fig.1 as a result of the compound formation has "ink-bottle " shape pores that can trap adsorbate nitrogen. However, the irreversible change may occur in the pore structure on adsorption, so that the desorption situation is truly differ from the adsorption one [19]. The average pore diameter and the average pore volume were 3.25 nm and 0.057 cm^3g^{-1} respectively, which were less than that of RHACCl (Table 1), this could be due to blockage of the pore by palladium complex moiety [20]. The RHAC-Pd(DTO)$_2$ (Fig. 1) showed a sharp pore size range from 1 to 3 nm which is in the nanoporous range.

Table 1: The physical parameters obtained for RHAC-Pd(DTO)$_2$.The percentage of elements content determined by elemental analysis. The result of BET analysis was also shown.

Sample	Elemental analysis (%)				Specific surface area (m^2 g^{-1})	Average pore volume (cm^3 g^{-1})	Average pore diameter (nm)
	C	H	N	S			
RHA [a]	1.6	0.84	-	-	347	0.87	10.4
RHACCl [a]	9.98	1.61	-	-	633	0.70	6.07
RHAC-Pd(DTO)$_2$	18.65	3.22	6.07	14.62	70.83	0.057	3.25

[a] [11]

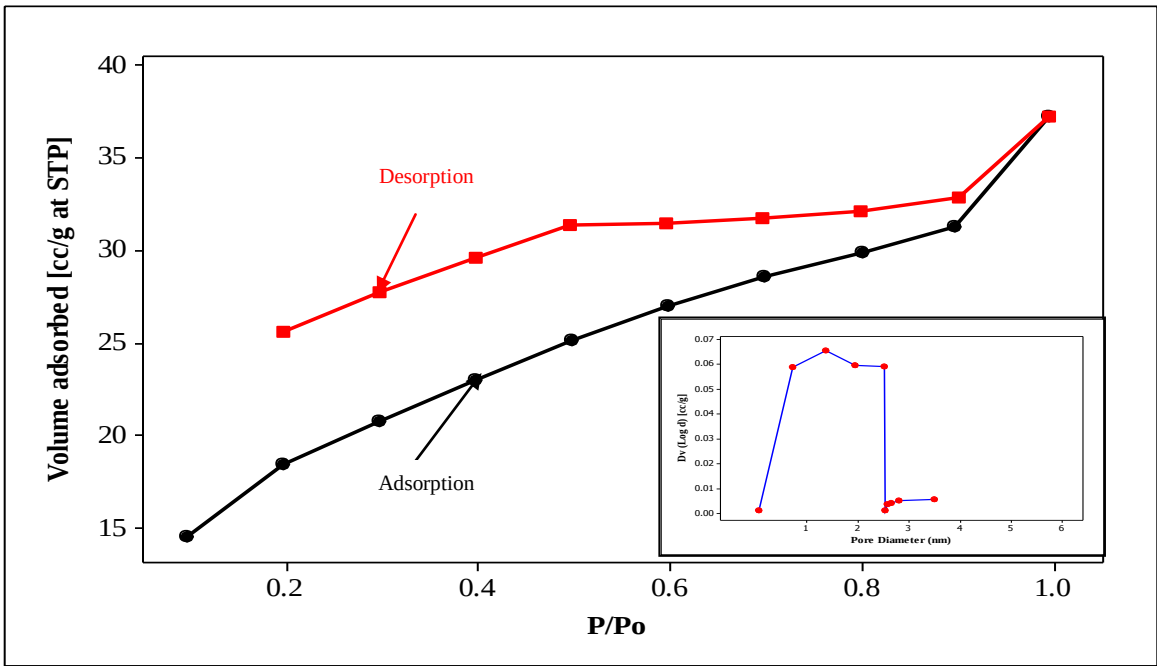


Fig.1: The nitrogen adsorption–desorption isotherms of RHAC-Pd-(DTO)$_2$. The inset shows the corresponding pore size distribution.

3.3 Thermogravimetric analysis (TGA/Differential thermal analysis (DTA)

The TGA-DTA of RHAC-Pd(DTO)$_2$ (Fig. 2) showed three characteristic decomposition stages. The first at 29.5–148 ºC, with a maximum at 60 °C which was assigned to the physical adsorb water loss (ca. 4.32 %) [13].The second mass loss (ca. 20.05 %) occurred between 148 – 468 ºC, with a maximum at 315 °C assigned to the decomposition of the [Pd(DTO)$_2$]Cl$_2$ complex and degradation of propyl group chain attached to silica matrices in polymer structure [12]. The third step decomposition starts from 468.7-896.7 °C (ca 13.31%) corresponding to loss of remaining of

chloropropyl and of dithiooxamide moiety [11], as well as the condensation of silanol groups and release of palladium.

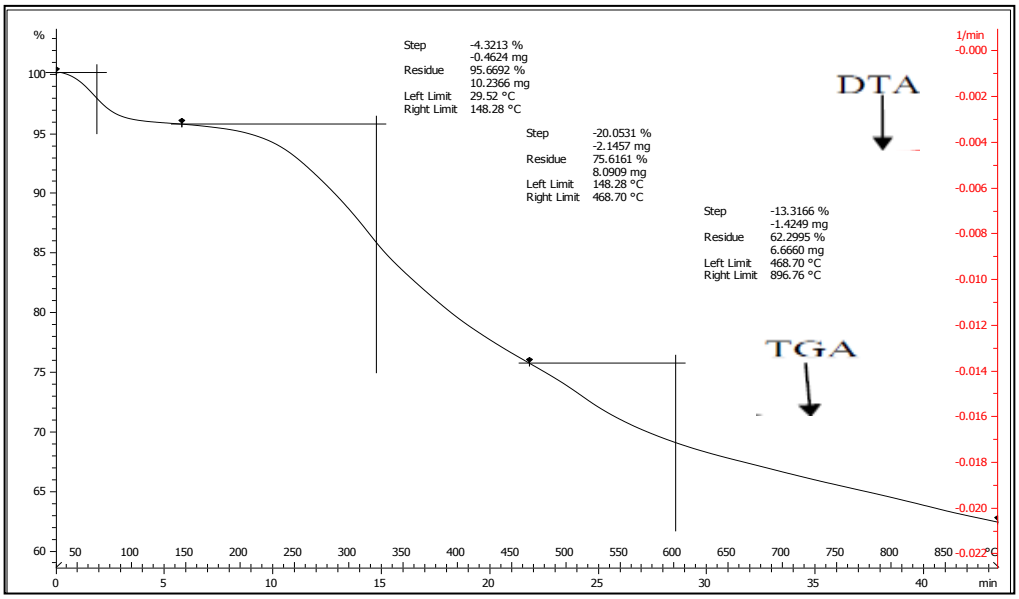


Fig. 2: Thermogravimetric analysis (TGA)/differential thermal analysis (DTA) for RHAC-Pd(DTO)$_2$.Three characteristic decomposition stages are shown.

3.4 Powder X–ray diffraction (XRD)

X-ray diffraction pattern of RHAC-Pd(DTO)$_2$ is shown in Fig. 3., from which amorphous characteristic of RHAC-Pd(DTO)$_2$ has been observed with 2-theta ca. 25°.

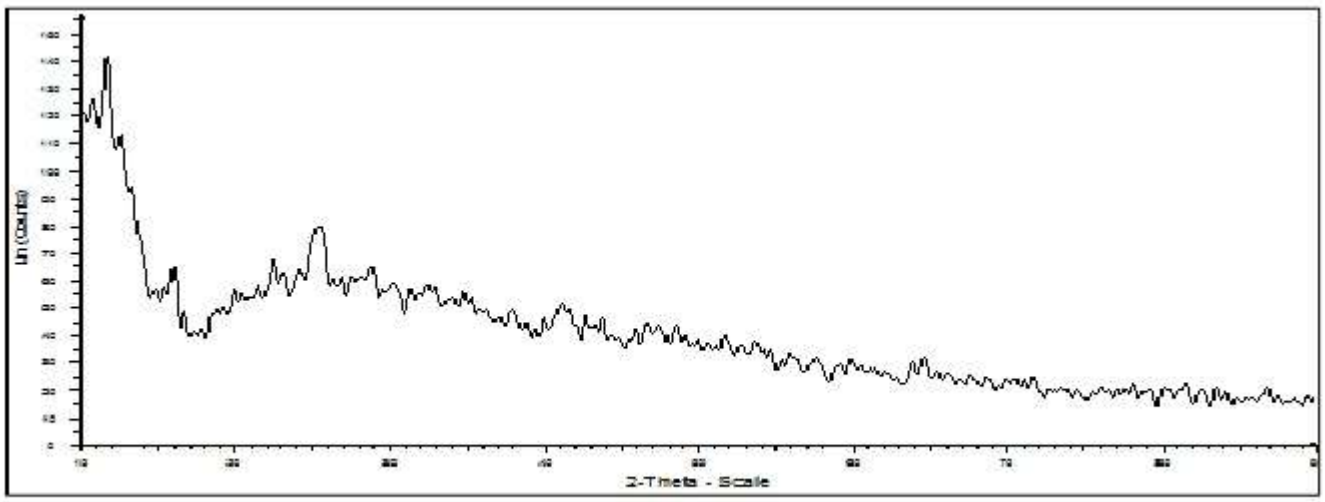


Fig. 3: The X–ray diffraction pattern shows amorphous nature of RHAC-Pd(DTO)$_2$

3.5 Fourier Transformed Infrared spectroscopic analysis (FT-IR)

The FT-IR spectrum of RHAC-Pd(DTO)$_2$ is shown in Fig. 4. The broad band at 3438 cm^{-1} is usually assigned to O-H vibration from Si-OH and H-OH of absorbed. The bands at 3222 and 3066cm^{-1} were due to the stretching vibrations of υNH$_2$ and υNH groups, respectively. The band at 2918 cm^{-1} is assigned to the C-H vibration for CH$_2$ groups, while the bending vibrations of the CH$_2$ groups can be seen at 1461 cm^{-1} [21]. The (-CSN-) stretching frequencies appeared at 1526 and 1384 cm^{-1}, while in the spectrum of [Pd(DTO)$_2$]Cl$_2$ [16] were 1587 and 1429 cm^{-1}. The bands around 584 cm^{-1} and 463 cm^{-1} were assigned to the Pd-N vibrations and Pd-S vibration, respectively [22].

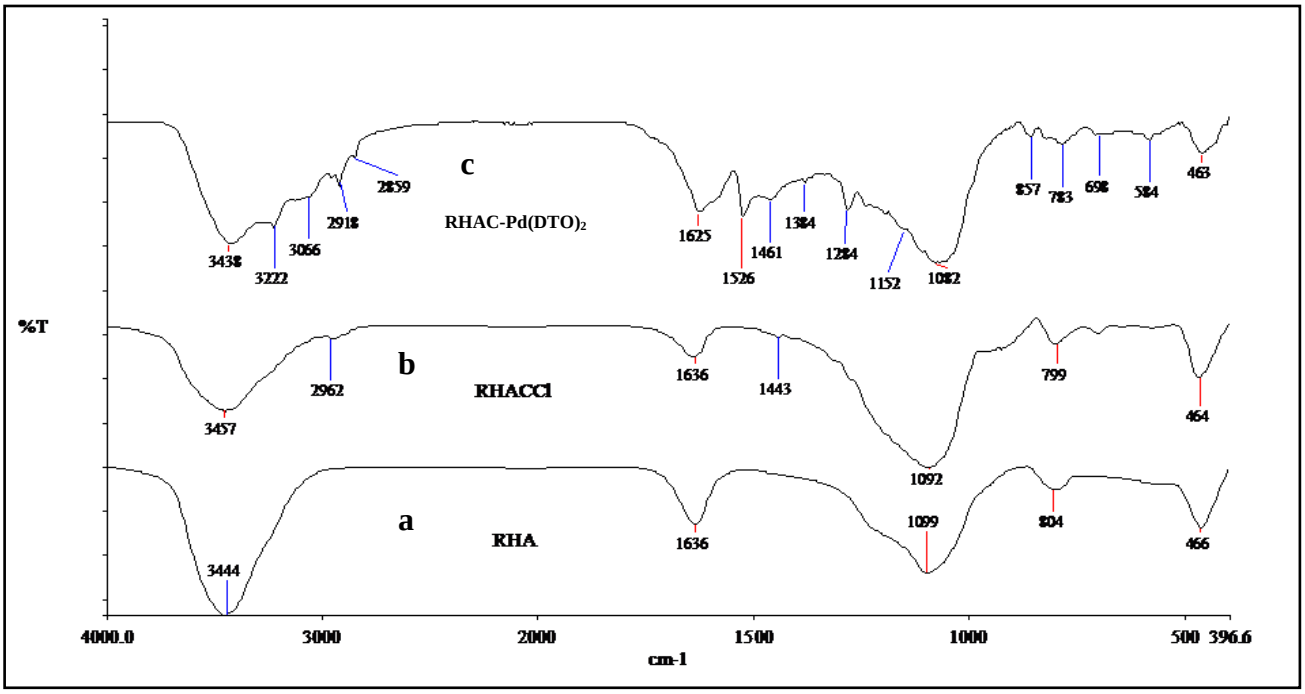


Fig.4: The FT-IR spectra of **a** RHA, **b** RHACCl and **c** RHAC-Pd(DTO)$_2$

3.6 Transmission electron microscopy (TEM) and Scanning electron microscopy–energy dispersive X–ray (SEM/EDX)

The morphology of the RHAC-Pd(DTO)$_2$ particles was studied by TEM and SEM as shown in Fig. 5 (a) and (b). Dark particles were observed which may believed to the Pd nanoparticles as can be seen in Fig. 5 (a). The SEM Fig. 5 (b) showed a small degree of pore arrangement.

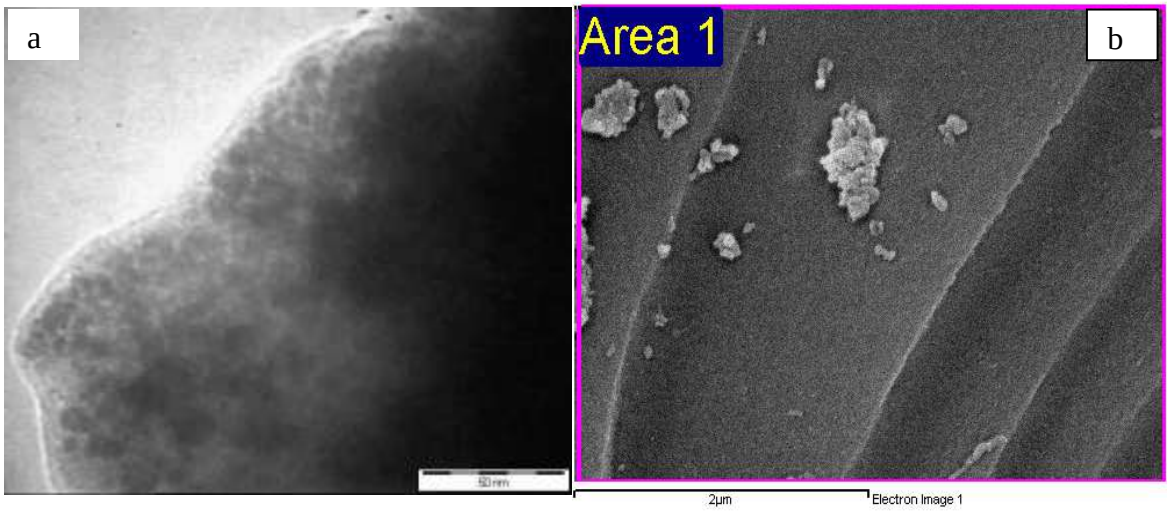


Fig. 5: (a) The TEM image of RHAC-Pd(DTO)$_2$ at ca. 50 nm, showing the irregular pore arrangements. (b) The SEM image, showing a small degree of pore arrangement.

Fig. 6 shows the EDX analysis. The spectrum showed the presence of Palladium and other elements in the complex, from which it can be further conclude that the [Pd(DTO)$_2$]Cl$_2$ was incorporated on the RHACCl. The average values of the chemical composition obtained from the EDX analysis are shown in Table 2.

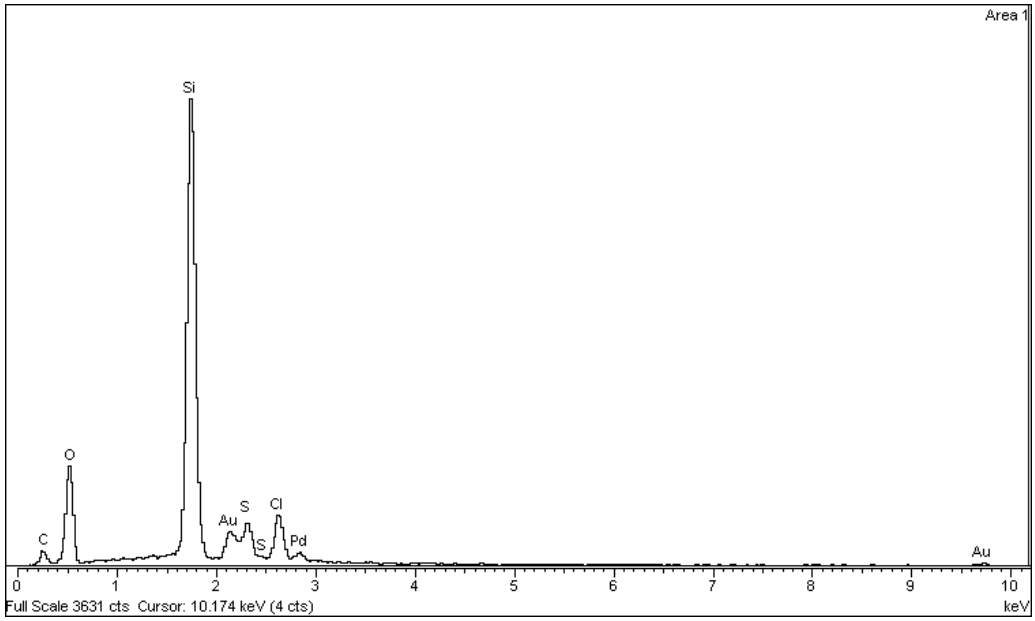


Fig. 6: The EDX analysis of RHAC-Pd(DTO)$_2$

Table 2. The average values obtained from EDX analysis for RHAC-Pd(DTO)$_2$.

Element	Average mass (%)
C	24.05
O	30.32
Si	33.38
S	4.19
Cl	6.27
Pd	1.80

4. Conclusion

In this work, rice husk ash (RHA) which is an agriculture waste was used to prepare silica immobilized with [Pd(DTO)$_2$]Cl$_2$ complex. Palladium complex was successfully incorporated onto the RHACCl via nucleophilic substitution reaction to form RHAC-Pd(DTO)$_2$. The physical properties of prepared material were investigated by means of several spectroscopic techniques. A comparison of the FT-IR spectra of [Pd(DTO)$_2$]Cl$_2$ complex and RHAC-Pd(DTO)$_2$ exhibit presence of NH stretching frequency at 3066 cm^{-1} in the former complex. The specific surface area measurements confirmed the immobilization of a large molecule of the [Pd(DTO)$_2$]Cl$_2$ on the silica surface leading to a considerable decrease in the pore diameter and average pore volume. The powder x-ray diffraction showed that the RHAC-Pd(DTO)$_2$ have amorphous characteristic feature. The transmission electron microscopy (TEM) and scanning electron microscopy–energy dispersive X–ray (SEM/EDX) techniques prove the amorphous highly nanoporous characteristics of the prepared compound, hence it is regarded as a benefit to use as catalyst.

5. References

[1] FAO Statistical Database. (2002). http://apps.fao.org.

[2] Arvind K. and Michiko K., (2016). Developing and Disseminating Water-Saving Rice Technologies in Asia, *Adb Briefs*, No. 60 June.

[3] De Souza, M.F., Magalhães, W.L.E., Persegil, M.C., (2002). Silica derived from burned rice hulls, *Materials research*, 5, 467-474.

[4] Della, V.P., Kühn, I., and Hotza, D., (2002). Rice husk ash as an alternate source for active silica production, *Mater. Lett*, 57, 818–821.

[5] Lanning, F. C., (1963). Silicon in rice, *J. Sic. Food. Agri.*, 11, 435–437.

[6] Sharma, N. K., Williams, W. S. and Zangvil, A., (1984). Formation and structure of silicon carbide whiskers from rice hulls, *J. Am. Ceram. Soc*. 67, 715–720.

[7] Martin, J.I., (1938). The desilification of rice hulls and a study of the products obtained, M.Sc. Thesis. Lousiana State University.

[8] Bae, S.J., Kim, S.W., Hyeon, T., , Kim, M., (2000). New chiral heterogenous catalysts based on mesoporous silica: asymmetric diethylzinc addition to benzaldehde, *Chem. Commun*., 31–32.

[9] Paul, H., Bhaduri, S., Lahiri, G.K., (2004). Platinum carbonyl derived catalysts on inorganic supports: a comparative study, J. Org. Chem., 689, 309–316.

[10] Soundiressane T., Selvakumar S., Ménage S., Hamelin O., Fontecave M., Singh A.P., (2007). Ru– and Fe–based N,N′–bis(2–pyridylmethyl) –N–methyl– (1S,2S) –1,2–cyclohexanediamine complexes immobilized on mesoporous MCM– 41: Synthesis, characterization and catalytic applications, *J. Mol. Catal. A Chem.*, 270, 132–143.

[11] Adam, F., Osman, H., and Hello, K. M., (2009). The immobilization of 3-(chloropropyl)triethoxysilane onto silica by a simple one-pot synthesis, *J. Colloid Interface Sci.*, 331 , 143–147.

[12] Adam, F., Hello, K.M., Osman, H., (2009). Esterification via saccharine mediated silica solid catalyst, *Appl. Catal., A,* 365, 165-172.

[13] Adam, F., Hello, K.M., Osman, H., (2010). The heterogenation of melamine and its catalytic activity, *Appl. Catal., A*, 382, 115-121.

[14] Adam, F., Hello, K.M, Ben Aisha, M.R., (2011). The synthesis of heterogeneous 7-amino-1-naphthalene sulfonic acid immobilized silica nano particles and its catalytic activity, *J. Taiwan Inst. Chem. Eng*., 42, 843-851.

[15] Thana J. Al-Hasani ,Hayder H. M. and Kasim M. H, (2013). Conversion of Rice Husk To A Nanoporous Material Via A Simple One - Pot Synthesis, *Al- Mustansiriyah J. Sci. 8*,61-70

[16] AL-Kaissy, M.H., (2001). Ph.D. Thesis, Al-Nhreen University. Baghdad, Iraq.

[17] Adam F. and Chua J.-H., (2004). The adsorption of palmytic acid on rice husk ash chemically modified with Al(III) ion using the sol-gel technique, *Journal of Colloid and Interface Science*, 1, 55–61.

[18] Ahmed A. E. and Adam F.,(2007). Indium incorporated silica from rice husk and its catalytic activity,"*Microporous andMesoporous Materials*, 1–3, 284–295 .

[19] Adamson, A.W., and Gast, A.P., (1997). "Physical chemistry of surfaces", 6th ed. , John Wiley and Sons , Inc., pp.665.

[20] Hello, K. M., (2010). The heterogenation of saccharin,melamine and sulfonic acid onto rice husk ash silica and their catalytic activity in esterification reaction, Ph.D. Thesis, University of Sains Malaysia, Malaysia.

[21] Silverstein, R.M., Bassler, G.C. and Marrill, T.C., (1981). "Spectrometric identification of organic chemistry", John wiley and Sons., pp.72-108.

[22] Nakamoto, K., (1978). "Infrared and raman spectra of inorganic and coordination compounds", John Wiley and Sons, Inc., pp. 222-300.