Preparation of Solid Catalyst from Extracted Silica of *Iris persica* L.

Ahmed A. Amin

Department of Chemistry- College of Education- Salahaddin University-Erbil / Erbil-Iraq

Ahmed.dezaye@su.edu.krd

Received: 17 August 2017 **Accepted: 22 August 2017**

Abstract

The present study is the first describe the synthesis of solid catalyst from *Iris persica* Leaves. Solid catalyst was hydrothermally synthesized after determining the ratio of silica from different parts of *Iris persica*. Leaves extract are the best silica sources that can be used in synthesizing solid catalysis, the flowers, bulbs and rhizomes do not content a significant amount of silica. The synthesized solid catalyst was characterized by Fourier Transform Infrared (FTIR) spectroscopy, X-ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). The results obtained by X-ray diffraction (XRD) show moderate average crystal size of 36.30nm. The average pore size, pore volume and surface area were determined by Brunauer-Emmett and Teller (BET) method with values of 18.88nm, 0. 12mL.g-1 and 21.60 mL. g-1 respectively. Finally, Transmission Electron Microscopy (TEM) was used to find the average crystal size and shape of catalyst, showing 21.82 nm of its average crystal size. The results verified that solid catalyst get from the hydrothermal condition, present a good solid catalyst characteristic and then can be suitable for using in adsorption and ion exchange applications.

Keywords: Extraction, Catalyst; *Iris persica* L.; Hydrothermal synthesis.

DIYALA JOURNAL FOR PURE SCIENCES

Preparation of Solid Catalyst from Extracted Silica of *Iris persica* L.

Ahmed A. Amin

تحضير عامل محفز صلب من مستخلص السليكا لنبات *Iris persica L.*

أحمد انور أمين

قسم الكيمياء - كلية التربية - جامعة صلاح الدين - أربيل

الخلاصة

يعتبر هذا البحث اول دراسة لتحضير عامل مخفز صلب من أوراق نبات *Iris persica* . تم تحضير عامل محفز صلب بطريقة هيدروحرارية ، بعد تقدير نسبة السليكا من اجزاء مختلفة من نبات *Iris persica* . كانت الأوراق المصدر الأفضل للسليكا المستخلص والتي يمكن استخدامها في تحضير العامل المحفز الصلب حينما كانت البصيلات والزهور والريزومات غير محتوية على كميات كافية من السليكا. تم دراسة خصائص العامل المحفز الصلب بتقنيات FT-IR, XRF و SEM. النتائج الذي تم الحصول عليها بطريقة XRD أظهرت معدل الحجم البلوري 36.30nm ولهاذا فان معدل كبر المسامات حجم المسامات, المساحة السطحية قدرت بطريقة Brunauer-Emmett و Teller بقيم 18.88nm, 0.12mL.g-1 و 21.60 mL.g-1 على التوالي. اخيراً تم استخدام تقنية TEM لإيجاد حجم البلورة وشكل العامل المحفز مبينا 21.82 nm كمعدل حجم البلورة. برهنت النتائج بان العامل المحفز الصلب المستحصلة من الظروف الهيدروحرارية يعتبر عامل محفز صلب ملائم لإستخدامه في عمليات التبادل الأيوني بعملية الامتزاز وإجراء التطبيقات عليها.

الكلمات المفتاحية : الأستخلاص، العامل المحفز، نبات *Iris persica* L., تحضير الهايدروحرارية.

Introduction

The family Iridaceae contains 92 genera and more than 1800 species [1]. *Iris* is the largest genus of the family Iridaceae with up to 300 species, many of them natural hybrids. Modern classifications, starting with Dykes (1913), have subdivided them [2]; among them, 12 species were found in Iraq (most of them in northern) [3]. Nearly all species are found in temperate Northern hemisphere zones, from Europe to Asia and across North America. Although diverse in ecology, *Iris* is predominantly found in dry, semi-desert, or colder rocky mountainous areas,[2] other habitats include grassy slopes, meadowlands, bogs and riverbanks. *Iris persica* is a medicinal plant belonging to the Iridaceae family and is widely distributed in Kurdistan region-Iraq and used by the local people as a treatment of inflammation and tumor.

Catalysis is a term coined by Baron J. J. Berzelius at 1835 to describe the characteristic of compounds that facilitate chemical reactions without being consumed in them. A broad definition of catalysis also allows for materials that slow the rate of a reaction. Heterogeneous catalysts (solid catalysts) are distinguished from homogeneous catalysts by the different phases present during the reaction. Homogeneous catalysts are in the same phase as chemical reactants and products, usually liquid, furthermore solid catalysts were in a different phase, usually solid. The advantage of using a solid catalyst was relative ease of catalyst separation from the product stream that aids in the creation of the continuous chemical process. Also, heterogeneous catalysts are typically more tolerant of extreme operating conditions than their homogeneous analogues [4]. Many catalysts of practical importance are highly porous and possess large surface area. Although the catalytic activity may be only indirectly related to the available surface, evaluation of the surface area was considered to be an important requirement in catalyst characterization [5,6]. Also, it is necessary to assess the pore size distribution to study whether the molecular transition and reaction pathways were affected by changes in the pore structure. The aim of the present work is the synthesis of solid catalyst from *Iris persica* Leaves.

Materials and Methods

1. Plant material:

Iris persica (flowers, leaves, rhizomes and bulbs) were collected in April 2016 from Korek Mountain-Kurdistan/Iraq. The plant was identified by Dr. Abdullah Sh. Sardar from Salahaddin University-Erbil/Iraq. A voucher specimen (No. 7229) was deposited at Education Salahaddin University Herbarium (ESUH).

2. Determination of Silica (Analytical method):

A prepared sample (0.100 g) is added to lithium metaborate/lithium tetraborate flux, mixed well and fused in a furnace at 1000°C (industrial Microwave furnace 1700 degree 2.45GHz microwave oven. The resulting melt is then cooled and dissolved in 100 ml of 4% nitric acid 2% hydrochloric acid. This solution is then analyzed by inductively coupled plasma - Atomic emission spectroscopy (ICP-AES) and the results are corrected for spectral inter-element

interferences. Oxide concentration is calculated from the determined elemental concentration and the result is reported in Table 1.

Note: For samples that are high in sulphides, we may substitute a peroxide fusion in order to obtain better results.

3. Silica extraction:

Iris persica (flowers, leaves, bulbs and rhizomes) were extracted with distilled water, dried at 100°C overnight then refluxed in (1M) HCl (100 ml) solution for 6 hours and filtered. The solid product was repeatedly extracted with de-ionized water (D.I water) until the filtrate was neutral and dried at 100°C overnight. Finally, the refluxed *Iris persica* leaves was put in a hot furnace muffle at 600°C for 3 hours to remove the organic contents to obtain the white silica [7].

2.4 Preparation of solid catalyst:

Solid catalyst was prepared from sodium silicate and sodium aluminate solution with a method modified and described by [8]. The sodium silicate solution was prepared by slowly adding extracted silica leaves into 100 mL of 14% wt NaOH solution under stirring until a homogeneous solution was obtained. In the synthetic procedure, sodium aluminate was dissolved in distillated water and added into a solution containing NaOH. The new solution was mixed with sodium silicate solution. The resulting mixture was transferred into a polypropylene bottle, sealed with paraffin film. Aging and crystallization were carried out at 70°C for 3h without stirring, then adjusted to 100°C for 2 hours to complete crystal formation; the sample was cooled down to room temperature and washed with deionized water and dried at 100°C overnight. The obtained product was kept in bottle until characterization [8].

5. Characterization:

Characterization of the synthesized catalyst was carried out by X-Ray Diffractometer type PANalytical (XRD) with Bragg-Brentano geometry and Ni-filtered Cu Kα radiation (λ=0.154° nm) at 20kv and current 15mA. The solid catalyst was quantity on holder catalyst followed by scanned from 2θ to range 5-50° degree with the step size of 0.01° in order to

confirm the formation of catalyst phase [9]. The presence of catalyst formation was determined using (FTIR), type Shimadzu 8400s [10]. The spectrum was elucidated for catalyst at wave numbers between 400 and 4000 cm^{-1}. The method of (BET) was used to find surface area, total pore volume, and average pore size of catalyst [9]. The surface areas of catalyst was counted from the adsorption desorption isotherm using the equation of BET [11]. Pore size distribution was discovered by using the Barrett-Joyner-Halenda (BJH) method. The surface area of the samples was conducted by Micromeritics (3FLEX Surface characterization) analyzer. An amount of 0.1g of the sample was weighed and heated at 300°C, ramp rate 20°C/min for 260 min to dehydrate the sample catalyst. The morphology of the solid catalyst was found by using SEM. Samples were coated with gold powder at 5.0kv with 100.000 magnified [12]. TEM picture was taken on a JEM-2100 Electron Microscope JEOL with accelerating voltage of 250kv to study the fine structure, morphology and particle size. XRF type Oxford Instrument X-Supreme 8000.

Results and Discussions

In this work, the synthesis of solid catalyst from different fractions (flowers, leaves, bulbs and rhizomes) of *Iris persica* which was collected in Kurdistan region/Iraq by using different techniques was evaluated. Solid catalyst was hydrothermally synthesized after determined the ratio of silica from different parts of *Iris persica*. The content of silica of four different parts (flowers, leaves, bulbs and rhizomes) has been determined as shown in Table 1. The chemical composition of catalyst synthesized by utilization of silica extracted from the selected raw materials was summarized in Table 2. The surface area, pore volume and average pore size were attributed to the presence of the porous structures in the synthesized solid catalyst summarized in Table 3.

1. FTIR Spectrophotometer:

In (Figure 1), the band at 456cm^{-1} is related to the Si–O–Al bending of vibration mode (T=Si or Al), [13]. The bands around 663cm^{-1} and 714cm^{-1} stretching modes involving motions primarily associated with the T-atoms. The bands around 1031cm^{-1} are due to the Si-O-Si asymmetric stretching vibration and asymmetric stretching of SiO_4 tetrahedra. While the

bands around 1503cm^{-1} -1661cm^{-1} resulted due to bending vibration of H-OH. This band was present even in sintered samples because water molecules were unable to escape from the silica matrix. The band is around 3488cm^{-1} are due to the stretching vibration of the O-H bond from the (Si-OH) groups and is due to the adsorbed water molecules on the silica surface in the catalyst surface [14].

Analysis XRD: (Figure 2), illustrates the XRD patterns of the synthesized solid catalyst, from *Iris persica* leaves, XRD phase of solid catalyst is found to match with the show peaks at 2θ =27.05, 31.42, 37.00, 39.92, 41.58 and 50.60 . These peaks are characteristic for solid catalyst, that the synthesized sample showed the formation of solid catalyst phase [15]. The average crystal size was measured using Scherrer's equation [16].

$$d=G\lambda/\beta\cos\theta \quad \text{.....(1)}$$

Where d is average crystal size (nm), G is the Scherrer's constant (0.9), λ is the wavelength (nm), and θ is the value of the Bragg angle (i.e. the angle of the peak maximum). β is the full width at half-maximum (FWHM) of the broad peak after correction for intrinsic instrumental line broadening and must be in radians.

2. SEM Analysis:

SEM images in (Figure 3), for synthesized catalyst shows that the most crystals formed as spheres. Flat crystals observed due to the high concentration of silica, the solid product contained a mixture of spherules crystal with an ice hockey shape with different particle diameter along with round amorphous particles [17]. The SEM technique only shows the particulate structure of the catalyst in to confirm the presence of the nanometer spherical coagulation seen with the SEM technique.

3. Pore Distribution Analysis and Surface Area:

Catalyst was characterized using N2 sorption to find their pore structure and surface area [18]. Depending on the structure of solid, the adsorption of gasses and vapors gives rise to I-VI types of the isotherm. (Figure 4), shows the isotherm, pore distribution and total pore volume for synthesized catalyst. It was found to BET surface area of solid catalyst have a Type IV isotherm it can be seen from Fig. 4 at a relative pressure range of 0.55-1.0. According to the

IUPAC classification [19]. This kind of behavior is associated with nano porous structure. Additionally, hysteresis loops are characteristics in nano porous material, related to capillarity condensation. The loops showed that the shape is classified as type H3 and this could be related to cylindrical pore channels [18].

4. SEM Analysis:

Transmission Electron Microscopy is important technique Provides information about catalyst shape and size of crystal [20]. (Figure 5), TEM picture shows the surface of synthesized solid catalyst, taken at 0.5µm magnified also confirm the nature of the support, solid catalyst, the TEM picture of the channel that observed by an arrow was not clearly seen due to the strong agglomeration of the catalyst. This results in agreements with the SEM picture. The same information was found in literature [21].

Table 1: Analysis of Silica extracted from different parts of *Iris postii* by ICP-AES

Plant Parts	Silica Content %
Flowers	6.09
Leaves	2.11
Bulbs	0.65
Rhizomes	3.43

Table 2: XRF data showing the chemical composition of the synthesized solid catalyst.

Sample	Oxides (weight %)						
	Na_2O	Al_2O_3	SiO_2	P_2O_5	SO_3	MnO	Fe_2O_3
Catalyst	0.039	12.346	86.192	0. 152	0.332	0.022	0.412

Table 3: N_2 adsorption-desorption for synthesized solid catalyst

Catalyst	BET surface area (m^2 g^{-1})	Pv^b(mLg^{-1})	Average crystal size (nm)- from TEM	Average crystal size (nm)- from XRD	Average pore size (nm)
Solid	21.60	0.12	21.82	21.30	18.88

Preparation of Solid Catalyst from Extracted Silica of *Iris persica* L.

Ahmed A. Amin

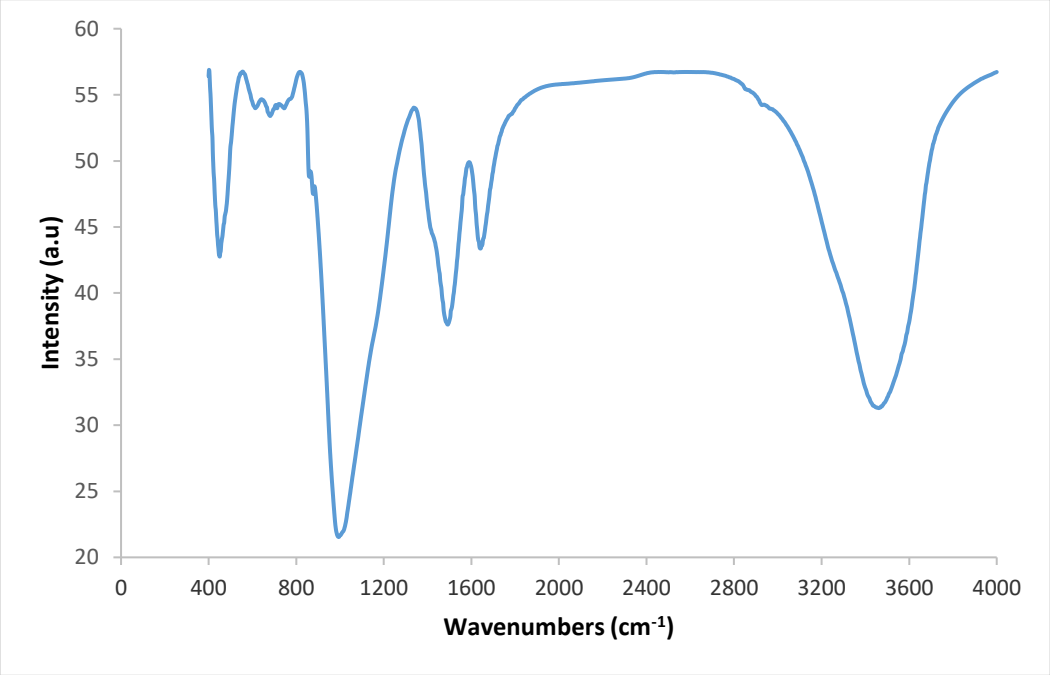

Figure 1: FTIR Spectrum of synthesized solid catalyst

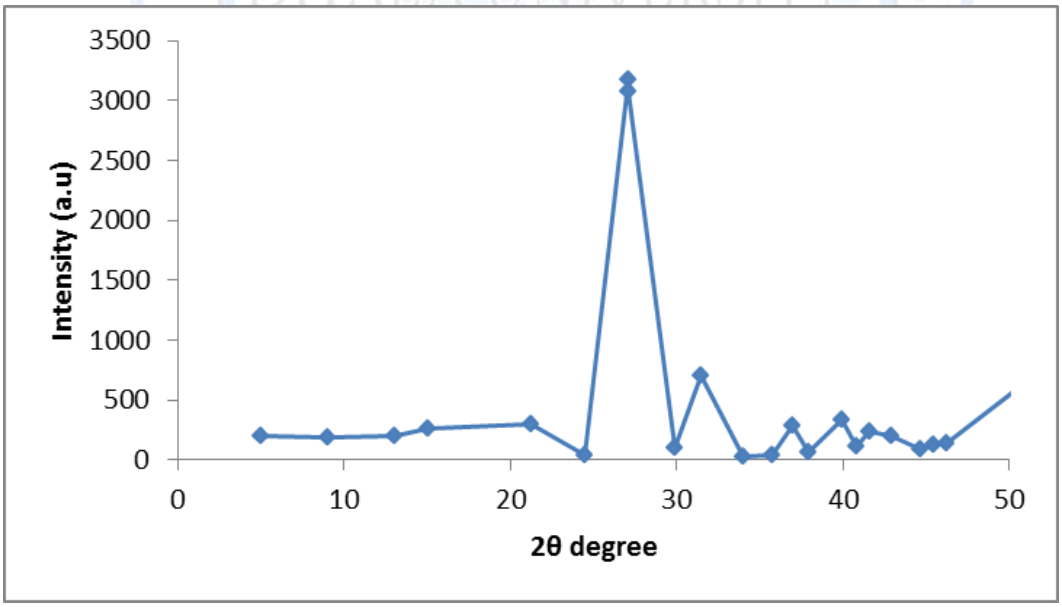

Figure 2: XRD Spectrum of synthesized solid catalyst

Preparation of Solid Catalyst from Extracted Silica of *Iris persica* L.

Ahmed A. Amin

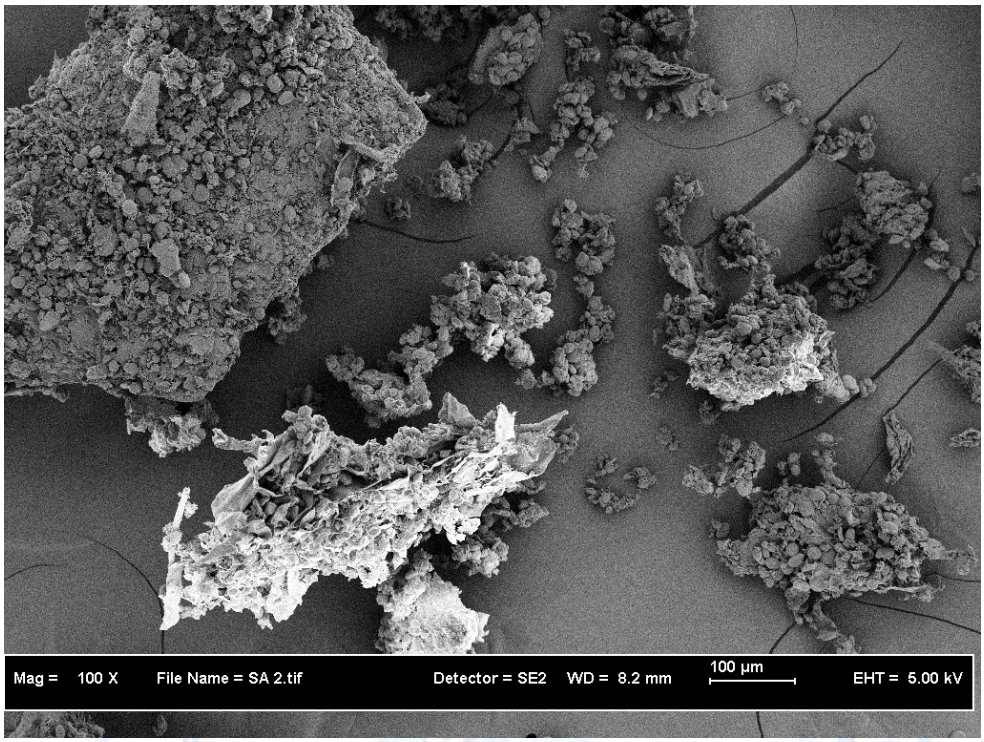

Figure 3: SEM image of synthesized solid catalyst

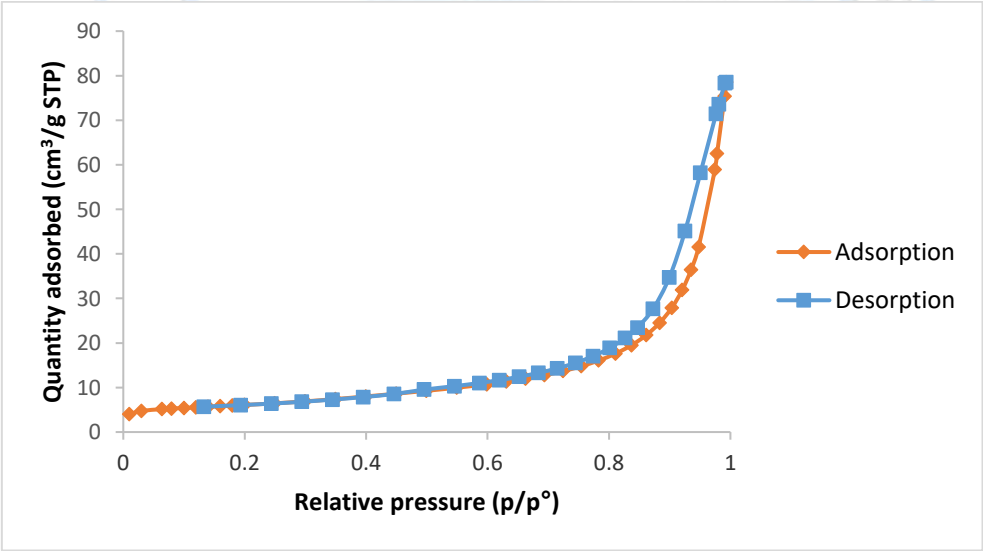

Figure 4: N_2 sorption for synthesized solid catalyst

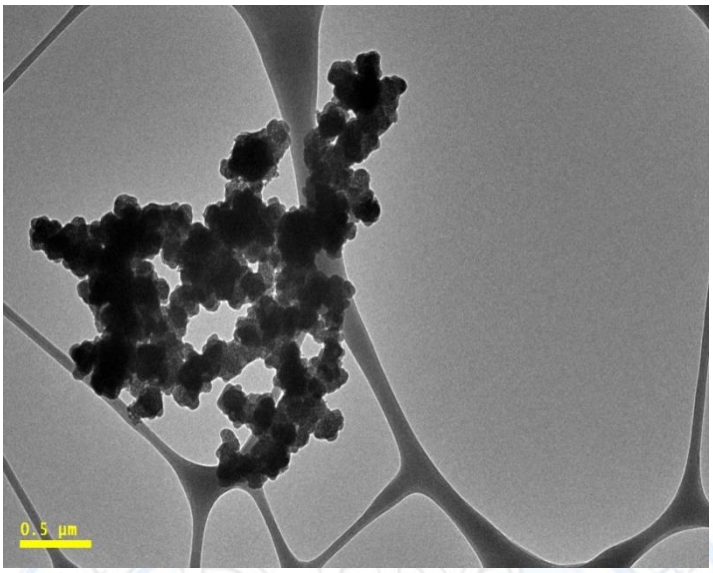

Figure 5: TEM image of synthesized solid catalyst

Conclusions

In conclusion, it can be note that the solid catalyst is able to be synthesized by using *Iris persica* leaves. Other fractions such as (flowers, bulbs and rhizomes) that were used in this method do not contain excess amount of silica. Catalyst gives a big contribution to the world of chemistry by having wide applications especially as the adsorption, ion exchange and for reactions. In many catalytic applications, in the systems molecular size ranging from 0.1 to 1.5 nm which is a small size. It makes big molecules do not react effectively over these micro porous structures because of the limitation of their small pore sizes. Therefore, to overcome this detection of catalyst, the idea of having large pores structure identification is desirable in order to improve the detection of catalyst so that it can be used in wider applications by allowing large molecules react catalyst. The results for Nitrogen adsorption analysis revealed that the synthesized solid catalyst has the type IV isotherm and H3 hysteresis with an average pore size of 18.88nm and BET surface area. The properties of catalyst formed are strongly depended upon the composition and the type of the fraction structure used. Implementation of the found method allows extending the raw materials base, simplifying the synthesis and reducing the cost of powdery mordenite type catalyst and it's available from Erbil-Iraq.

Acknowledgements

The Author acknowledges to ALS laboratory in Spain, University of Pavia/Italy and many thanks to Dr. Abdullah Sh. Sardar for the plant identification.

References

1. Muhammad, A.; Zaheer-ud-din, K.; Muhammad, A.; Sabahat Z. Biolo. 2013, 59(2), 345-348.
2. Sabrin, R.; Gamal, A.; Nawal, M. Molec. 2012, 17, 2587-2598.
3. Townsend, C.; Guest, E. Flora of Iraq; 8th Eds.; Ministry of Agriculture & Agrarian Reform; Baghdad: Iraq, 1985.
4. Anderson, I. R.; Boudart, M. Catalysis: Science and Technology: Eds.; Springer-Verlag: Berlin, 1983, p. 245.
5. Haber, J. 1991. Pure App. Chem. 1991, 63 (9), 1227.
6. Lowell, J.; Shields, M. A.; Thomas, M. Sprin.-Verlag. 2014, 167-173.
7. Pongtanawat, K.; Sanchai, P.; Jatuporn, W. Sura. J. of Scie. & Tech. 2007, 14, 367-379.
8. Kühl, G. Else. Scie. B.V.: Amterdam; 2011, pp. 153-154.
9. Harding, G. App. Radi. and Isot. 2009, 67(2), 287-295.
10. Ladavos, A.K.; Katsoulidis, A.; Iosifidis, A.; Triantafyllidis, K.; Pinnavaia, T.; Pomonis, P. Micro. and Mesop. Mate. 2012, 151, 126-133.
11. Kimura, R.; Nghia, D.; Wakabayashi, J.; Elangovan, S.; Ogura, M.; Okubo, T. Bulle. of the Chem. Soci. of Japan, 2012, 85(4), 527-532.
12. EnterrÍía, M.; Suárez-García, F; Martínez-Alonso, A; Tascón, J.M.D. J. of Alloys and Comp. 2014, 583, 60-69.
13. Seyed, N.A., Ahmad, R. and Amir, J. Mate. Rese. Bull. 2013, 48(5), 1753-1759.
14. Atsuo, Y.; Sayaka, Y.; Jun, S. J. of Molec. 2015, 20(2), 2349-2363.
15. Treacy, M.M.J.; Higgins, J.B. Elsevier: Amsterdam; 4th Eds.; 2001, p. 243.
16. Treacy, M.M.J.; Higgins, J.B.; Ballmoos, R.V. Elsevier: New York; 3rd Eds.; 2006, pp. 134-139.
17. Kim, G.J.; Ahn, W. 1991. Zeol. 1991, 11(7), 745-750.

18. Baerlocher, C.; McCusker, L.B.; Olson, D.H. Elsevier: Oxford OX2 8DP: UK; 6th Eds.; 2007, pp. 147-153.

19. Sing, K.S.W. 1985. The use of physisorption for the characterization of microporous carbons, Elsevier, 27(1), pp. 5-11.

20. Cejka, J. App. Catal. 2003, 254, 327-338.

21. Hussein, A.; Jean-Pierre, G.; Richard, R.; Philippe, B.; Jean-Michel, G.; Valentin, V.; Svetlana, M. Nat. Mater. 2015, 14, 447-451.