Egypt. J. Chem. **Vol. 63,** No. 4, pp.1541 -1553 (2020)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

The Influence of PO_4 to Bio-silica Catalyst on Synthesis Benign Additive Fuel

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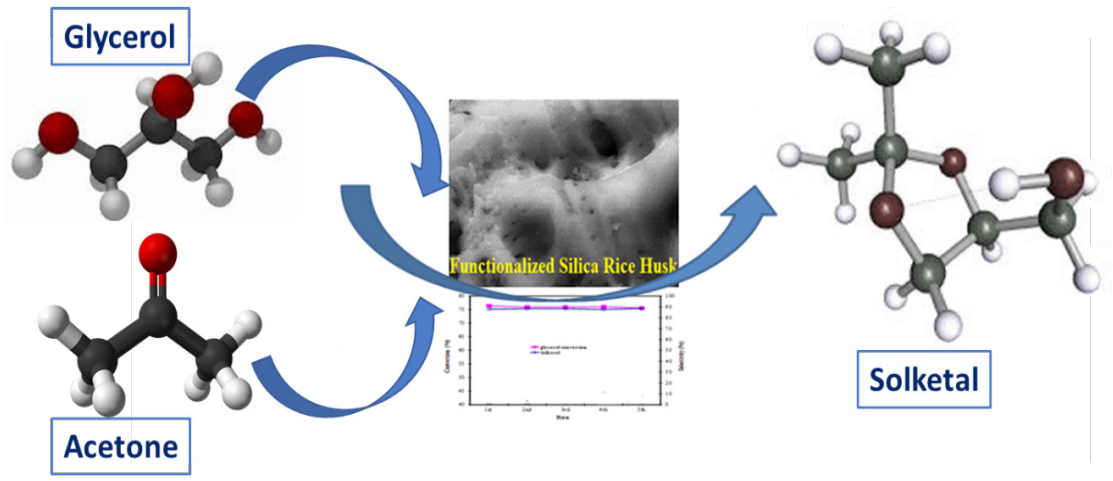
FUEL additive solketal can be produced through acetalization reaction of biodiesel by-product (glycerol) and acetone. This reaction was conducted over acidified silica derived from sustainable bioresource rice husk in a batch reactor under the solvent-free condition. The chemical and structural properties of the prepared catalyst were studied by X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), N_2 adsorption/desorption isotherms, temperature-programmed desorption of ammonia (NH_3-TPD) and scanning electron microscope (SEM). Based on this paper, the optimized conditions using 15% phosphoric acid acid ifiedsilica extracted from rice huskash (10 wt.% PO_4 loaded SiO_2) are 50°C (lower temperature) with the molar ratio of acetone: glycerol = 2. Reusability test used to examine the stability of the catalytic activity was investigated. This effort is a serious step for development and taking apart of solketal as the main product from glycerol and acetone by using waste resources.

Keywords: Silica, Acidic, Solketal, Renewable resources, Rice husk, Glycerol, Acetone.

Graphical Abstract



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Received 11/07/2019; Accepted 20/08/2019

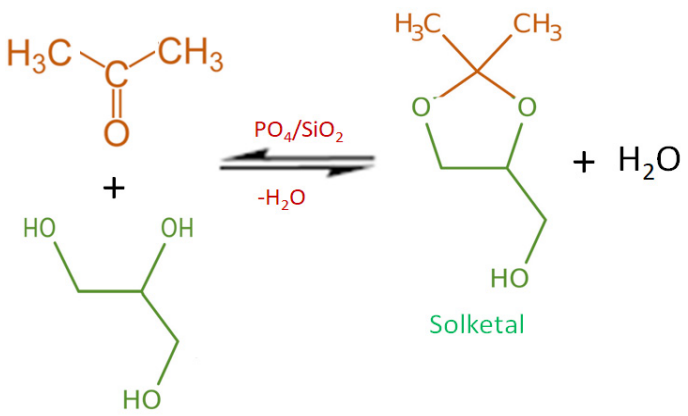
DOI: 10.21608/ejchem.2019.14728.1890

Introduction

As a sustainable bioresource, biomass has concerned attention to preparing of highly developed materials for different applications, attributable to their low value, their abundance particularly in rice-producing countries like Egypt, their speedy regeneration and being friendly in respect to the environment. In the rice milling industry, rice husks are by-products of huge amount in the world (~2.9×10^7 t annually). It mainly consists of organic materials like hemicellulose, cellulose, and lignin (75-90 wt.%). The ash (17–20 wt.%) produce by burning the husk underneath controlled conditions including high pure silicon oxide, that represents 90 wt.% of that ash.Consequently, the husks of rice areconsidered as natural stocks to preparefor silica-based adsorbents or catalyst supports [1- 3]. The biodiesel, the future's fuel, has been considered as a decent alternative forfossil fuels, like diesel.Recently, numerous studies have been given to this renewable fuel [4-6]. However, the low cost of diesel and the expanding cost of the source oils for biodiesel production had been considered as challenges. It is then important to enhance the financial plausibility of biodiesel production by the increase of value-added of by-products such as glycerol, which are formed during the biodiesel production [7]. The glycerol is catalytically converted for produce the intermediates chemicals such as solvents, and additives, like 1,3-propanediol, 1,2-propanediol [8], polyglycerols [9], di- and tri-acetyl glycerol esters [10], 3-hydroxypropionaldehyde [11], acrolein [12], and solketal [13]. The solketal (2,2-dimethyl 1,3-dioxolane-4-methanol), which is the product of the catalytic reaction of glycerol and acetone, has a significant function which used to enhance transportation fuel quality (in the additive form), in the polymer industry (as a plasticizer) also in the pharmaceutical industry (as a solvent) [14].

The addition of the solketal to diesel fuel motors reduces the carbon monoxide, hydrocarbons and unregulated aldehydes emissions. Also, it used as cold flow improver for biodiesel fuel. Blending the solketal with standard gasoline fuel (1-5 vol. %) reduces the gum formation and consequently improves the octane number [15]. From environmental sight, it is less toxicity fuel additive than the traditional one, Methyl tert-butyl ether (MTBE) [16]. Regarding the conventional catalytic production of solketal, inorganic acids such as H_2SO_4, H_3PO_4 or HCl are usually used. This, in turn, can lead to cause environmental problems because of using toxic materials, elimination of the effluents and serious erosion of devices. In the industrial procedures in last year's, heterogeneous solid acid catalysts, including Amberlyst resins [17], mixed oxides [18], niobia [19], zirconia [20] and functionalized activated carbons [21,22], have the perspective to use rather than this dangerous catalyst (liquid acid). Also, solid catalysts can reuse for several runs after easy separation methods like filtration or centrifugation [23-25].

During this work, the catalytic acetalization of the glycerol with acetone (Scheme 1) was investigatedusing phosphate silica derived from sustainable bioresourcerice husk under the solvent-free condition. The catalyst was characterized by different physicochemical characterizations techniques for verifying the catalyst properties. Also, the effective acetalization variables such as different reaction temperatures,acetone: glycerol molar ratios, and weight of catalyst used during the reaction are studied in detail.



Scheme 1. Acetalization of glycerol with acetone .

Experimental

Extracted silica from the rice husk

Dry the raw rice husk obtained from Egyptian agricultural field (Kafr El-Shaikh) was sieved to a grain diameter of less than 0.5 mm. The raw husk was carefully rinsed with distilled water, filtered and then dried in the oven at 110°C. The dried rice husk (100 g) placed in a ceramic tube and introduced into a muffle furnace where the pyrolysis step was performed under nitrogen flow (10 ml/min). The temperature was raised with ramping with 5°C/min till 700° C. The samples were held at this pyrolysis temperature for 4 h.

Preparation of phosphate silica

Acidified silica by phosphoric acid (10 wt.% PO_4 loaded SiO_2) prepared byacidification silica using H_3PO_4 solution (15 wt%). Thattreated silica dried at 120º C up to 12 h and subsequently was heated in purified nitrogen with the flow (10 ml/min) at 530 ºC for 3 h.

Characterization of the materials

X-ray powder diffraction Analysis (XRD) performed out using Shimadzu XD-1 diffractometer in 2θ =20-80°. The spectra of Fourier Transform Infrared Spectroscopy (FTIR) were verified by a Nicolet 740 FTIR spectrometer under ambient conditions by using KBr disks for averaging 100 spectra with a nominal resolution of 4 cm^{-1}. Surface properties of the prepared materials were characterized by Quantachrome NOVA2000 at low temperature (-196°C) through N_2 adsorption-desorption isotherms and measuring the pore size distribution. Before adsorption measurements, the samples were evacuated at 350 ºC for over night. Temperature programmed desorption of ammonia (NH_3-TPD) was carried out in automatic equipment (Chem BET 3000, Quantachrome). The microscopic characteristic by scanning electron microscope (SEM) of silica ex rice husk ash and phosphoric acidification silica texture are examined using a JEOL JSM-5300 scanning electron microscope.

Catalytic reaction

Glycerol catalytic acetalization was performed in a batch reactor containing a round bottom flask with a reflux condenser at temperatures ranging from 50, 70 and 100 ºC and an acetone/glycerol ratio of 2, 4 and 6 mol/mol. Typical acetalization reactions were performed by the magnetically stirring of 100-700 mg for one hour. Also, the stability of the catalysts for6 hours was studied. The solvent used to wash catalyst every run is acetone. After the certain reaction time, a segment of the reaction mixture was taken apart by centrifugation, which was analyzed by a GC equipped with a wax capillary column called a BP-20 and analyzing using a flame ionization detector (FID). The catalyst recyclability was studied via reused spend catalyst five times. After each run, the catalyst powder was separated from the reaction mixture by centrifuge, rinsed thoroughly and dried, before reusing. The conversion of glycerol and the selectivity to solketal were estimated using these following equations:

$$Conversion\% = \frac{G_i - G_f}{G_i} \times 100$$

$$Selectivity\% = \frac{S_p}{G_i - G_f} \times 100$$

Where as, Gi, G_f and S_p were the initial and final moles value of glycerol and produced solketal in the reaction medium, respectively.

Results and Discussion

The XRD patterns of extracted silica from rice husk and acidified one are shown in Fig. 1. The patterns of both samples are similar. As detected the very broad peaks at 2θ = 22o are a characteristic peak of silica which authenticated its nature amorphous [1]. This elucidates that crystallization of silica did not format that pyrolysis temperature (700ºC for 4h), Acidified silica with phosphoric acid, which was heated at 530 ºC demonstrated an exceedingly broad peak in the 2θ range from 15º to 30º, which representative for amorphous silica phase, and no detectable peak for PO_4/SiO_2 in the pattern. That is meaning well dispersion of phosphoric acid over silica surface which may cause some deformation of silica phase to create catalytic active sites.[26].

The FTIR spectrums of the obtained parent silica and phosphate silica are given in (Fig. 2 a and b). The characteristic bands of the asymmetric and symmetric stretching vibrations of the Si–O–Si at 1055 and 800 cm^1, successively. The bending vibrations of the adsorbed and coordinately bound water appeared at 1635 and 3450 cm^{-1}, respectively [27]. On the other hand, the FTIR spectrum of the phosphate silica (PO_4/SiO_2) showed a shoulder of frequencies around 1030 cm^{-1}, which featured to the stretching mode of PO_4^{-3} vibration indicating the formation of acidified silica PO_4/SiO_2[8, 28].

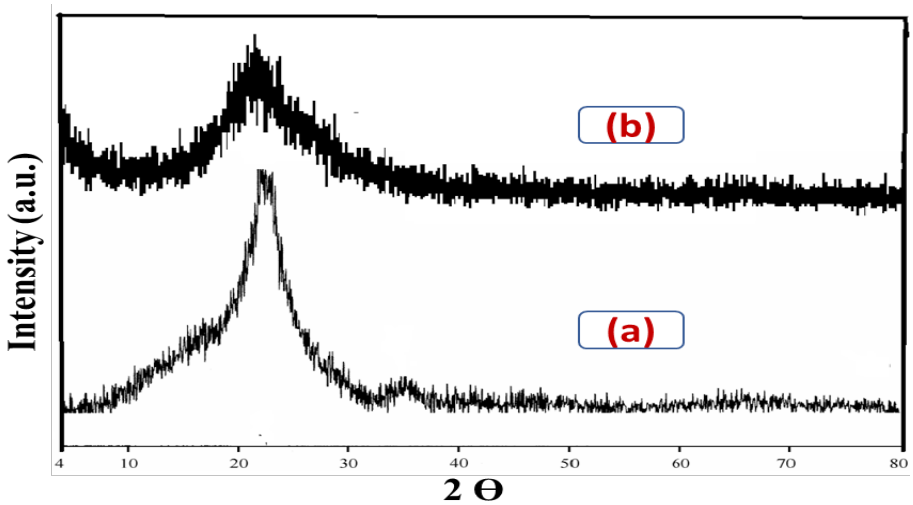


Fig. 1. X-ray diffraction patterns for (a) parent silica and (b) PO_4/SiO_2.

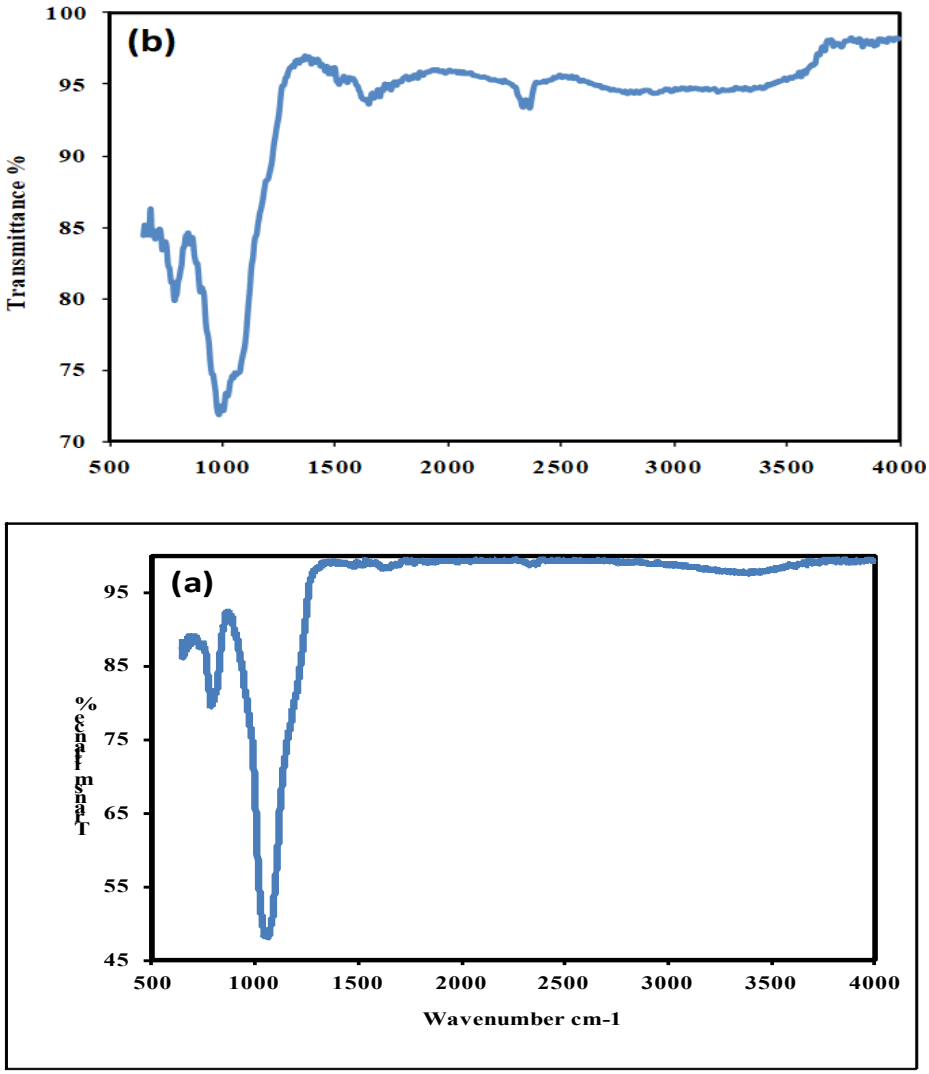


Fig. 2. Infrared spectra of (a) parent silica and (b) PO_4/SiO_2.

The nitrogen adsorption isotherm of as-prepared silica and phosphoric acidified silica (Fig. 3) is related to the type IV isotherm according to the IUPAC classification [29], which reveals the existence of the micropores and the macropores in the surface texture. The isotherms are exhibiting H3 hysteresis loop that ended at P/Po= 0.25, which usually associated with the swelling of the non-rigid pores [30]. The BET surface areas of silica and acidified silica samples are 161.9 and 120.5 m^2/g, respectively (Table 1). The porosity of ex silica created from the pore opening, which takes place during the burning of the rice husk in the air causing the condensation of silanol groups to siloxane bridges. Which is confirms the porosity nature of obtained silica from rice husk [31].

The pore radius distribution (Fig. 4) shows that the silica contains micropores, which has maxima at about 1.8 nm and narrow mesopores between 2.4 and 4.2 nm. Pores with the large range may be created during silica extraction or due to the presence of enduring voids of tiny particles. While the small ranges were formed during the oxidation process inside the particles [32]. The phosphorous acidified silica exhibits only microspores at about 2.4 nm. Table 1 showed that the surface area decreases from 161.91 to 120.5 m^2/g, average pore radius from 20 to 13 Å and pore volume from 0.06 to 0.04 cm^3/g, for parent silica and the acidified silica, respectively. These results attributed to the acidification process and consequently the blocking of the pores by the PO_4 groups. Acetalization of glycerol with a ketone (acetone) is evaluated by the surface acidity of the prepared catalyst since this reaction is keeping on by the presence of acidic nature catalyst.

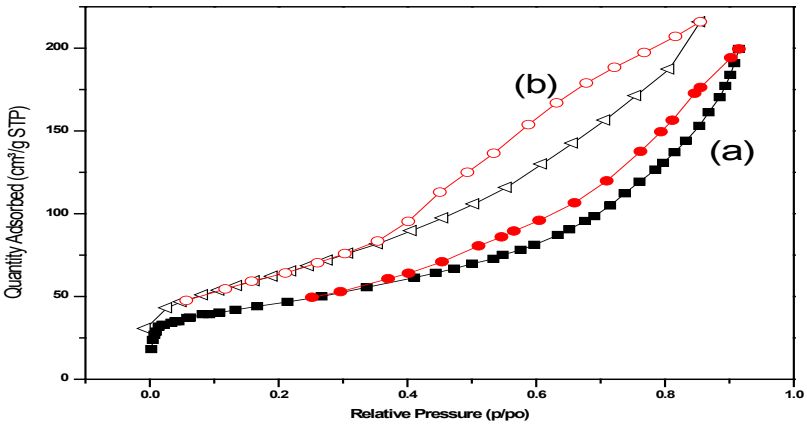


Fig. 3. N_2adsorption-desorption isotherms of (a) parent silica and (b) PO_4/SiO_2.

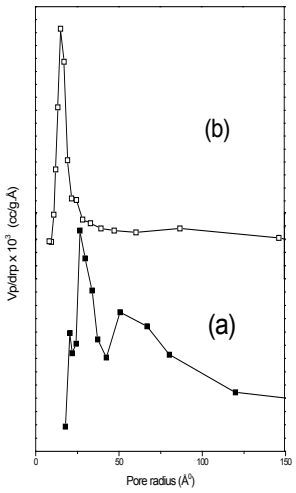


Fig. 4. Pore radius distribution of (a) parent silica and (b) PO_4/SiO_2.

The profile of NH_3-TPD over the surface of the parent silica sample (Fig. 5.a) showed a little apex around 400ºC, which may be attributed to the existence of acid sites having moderate strength (i.e. silanol groups) [33]. While the phosphate silica showed significant amounts of weak, moderate and strong acid sites that represented by apexes at 150, 400 and 550 ºC, respectively [8]. The total amount of the desorbed ammonia was calculated by integrating the areas under the curves and it was found to be 50 and 117 µmol NH_3 g^{-1} for parent silica and phosphate silica, respectively, which already confirmed by FTIR analysis.

The SEM images of extracted SiO_2 and PO_4/SiO_2 affirmed its porous structure. The SiO_2 image keeps the outer alleviation of raw RH owing to the layer of surface protective having the regular distribution of SiO_2. The walls of the cells located around and between the pores were destroyed, resulting in the formation of relatively small pores on the heterogeneous surface. During the acidification process (PO_4/SiO_2 formation) the well-arranged backbones of rice husk hulls ruined by liberating silica content [31-33]. The smoother surface of the extracted SiO_2 (Fig. 6a) and porous structure of PO_4/SiO_2 (Fig. 6b) affirmed the formation of new fine pores in the later.

Catalytic activity

As a reference, a blank reaction had been achieved without catalyst at the optimum conditions, giving negligible results. Moreover, the low acidity of the parent silica (Fig. 5 and Table 1) caused very low conversion of glycerol (< 1%) at the optimum conditions of the reaction, so no more discussion about silica catalytic activity in this paper.

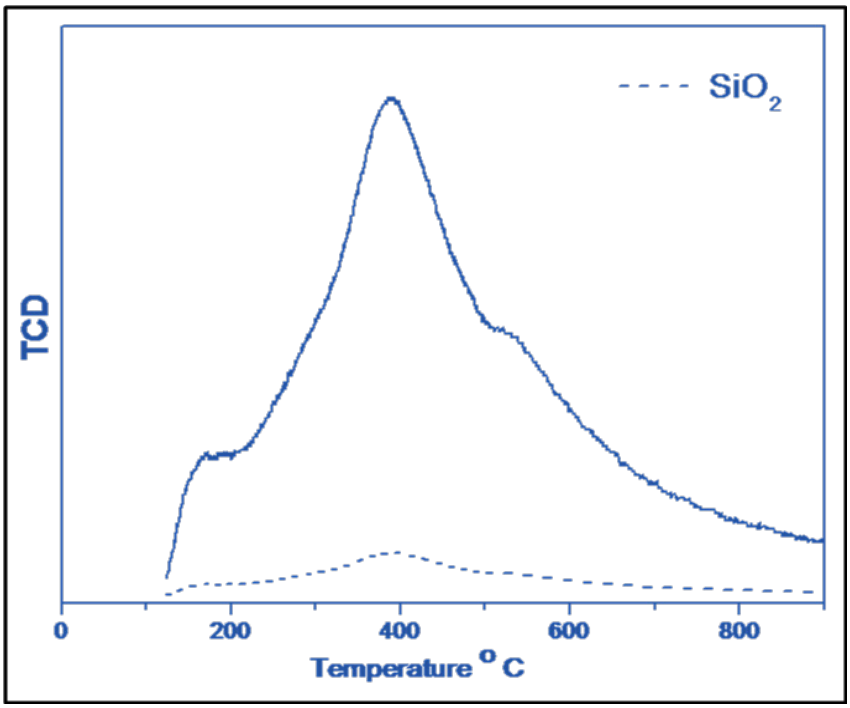


Fig. 5. NH_3-TPD profiles of parent silica and PO_4/SiO_2.

TABLE 1. Texture properties of the prepared catalysts.

Sample	S_{BET} m^2/g	Average pore radius (Å)	Pore volume cm^3/g	NH_3-TPD µmol NH_3 g^{-1}	Intrinsic µmol NH_3/m^2
SiO_2	161.91	20	0.04	50	0.3
PO_4/SiO_2	120.5	13	0.06	117	0.98

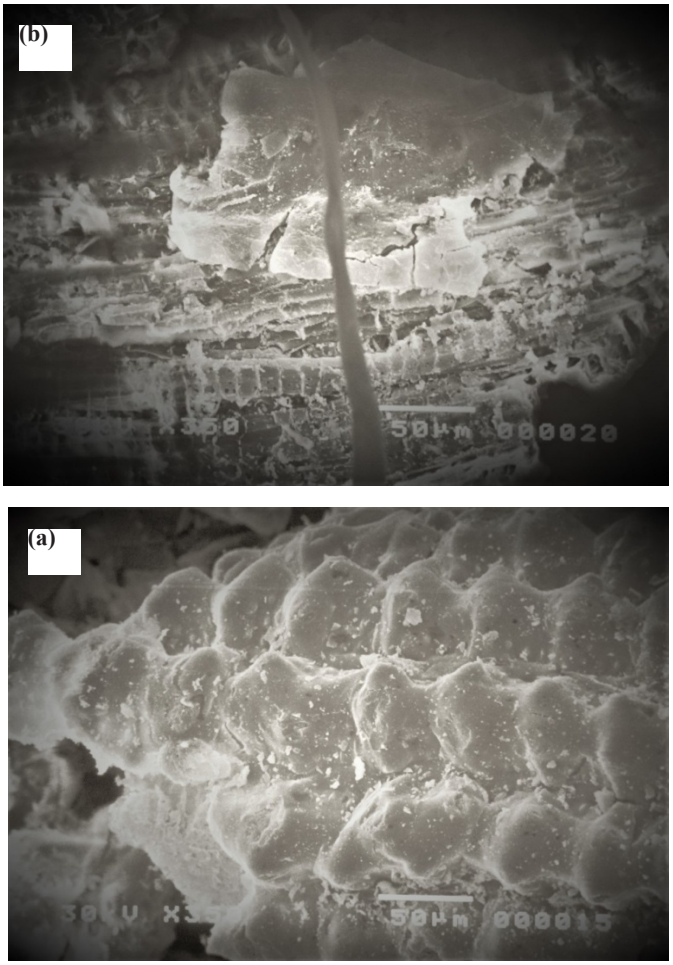


Fig. 6. SEM images of (a) parent silica and (b) PO_4/SiO_2.

Effect of different molar ratio of acetone to glycerol at low temperatures (50ºC) was investigated (Fig. 7) in which the total conversion of the reactants decreased from 57.98% to 43.59% by the molar ratio of acetone to glycerol increased from 1:2 to 1:6, while the creation of the solketal (five-membered ring ketal) decreased from 87.95% to 51.32%. On the other hand, the conversion towards the undesired by-products such as six-membered ring acetal, diethyl ether and acetaldehyde increased upon increasing the molar ratio of glycerol: acetone. The previously mentioned selectivity behaviors towards solketal andacetal synthesis associated with decreasing the numbers of reacted moles of glycerol can result from the influence of steric factor [11]. Also, the increasing of the concentration of acetone in the reaction medium may enhance the polarity and consequently directed the conversion towards the six-membered ring acetal [12]. The formation of diethyl ether and acetaldehyde may result from the catalytic cleavage fracture of C-C bond and rearrangement of the hemiketal intermediate [27].

By increasing the reaction temperature from 50 to 100º C the selectivity of PO_4/SiO_2 towards solketal decreased gradually from 87.95% to 73.68% at a lowmolar ratio of glycerol: acetone= 1:2 (best ratio) indicated the exothermicity of the reaction (Fig. 8) [37]. This catalytic behavior may attribute to the raising of the polarity of the reaction medium due to the removal of the by-product water via vaporization at high temperatures [11]. Also, the variation of the selectivity of the catalyst towards the producing of the different cetals could be explained according to the energy of formation (ΔH_f) of these compounds [11]. The obvious increment in the conversion percentage as the reaction temperature increased may be attributed to increasing the percentages of the undesired by-products diethyl ether and acetaldehyde (Fig. 8). Accordingly, the selected optimum conditions were glycerol to acetone molar ratio = 1:2 and the reaction temperature at 50ºC.

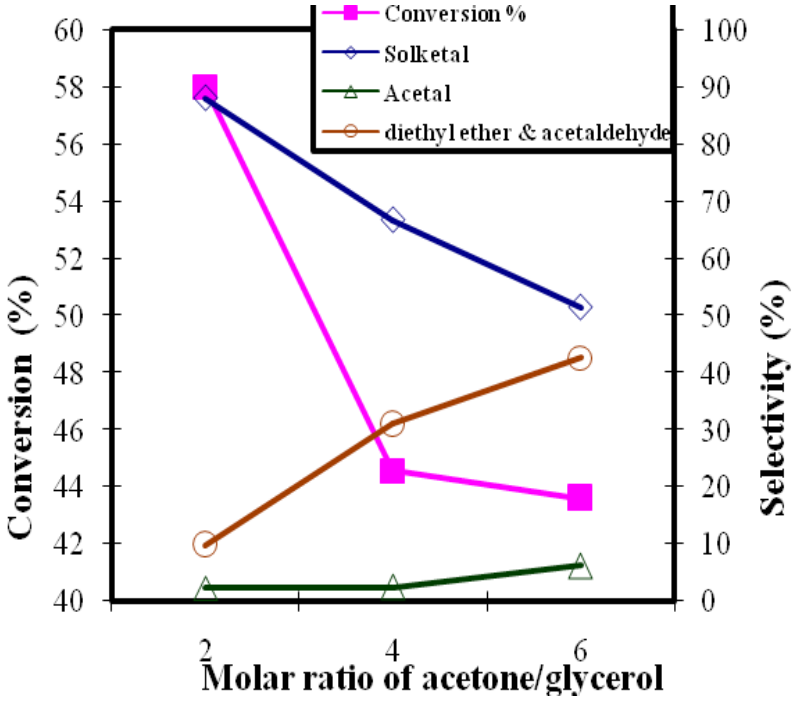


Fig. 7. Effect of acetone to glycerol molar ratio on PO_4/SiO_2 catalytic activity. Reaction conditions: catalyst weight: 0.5 g; reaction temperature: 50ºC; reaction time: 1 h.

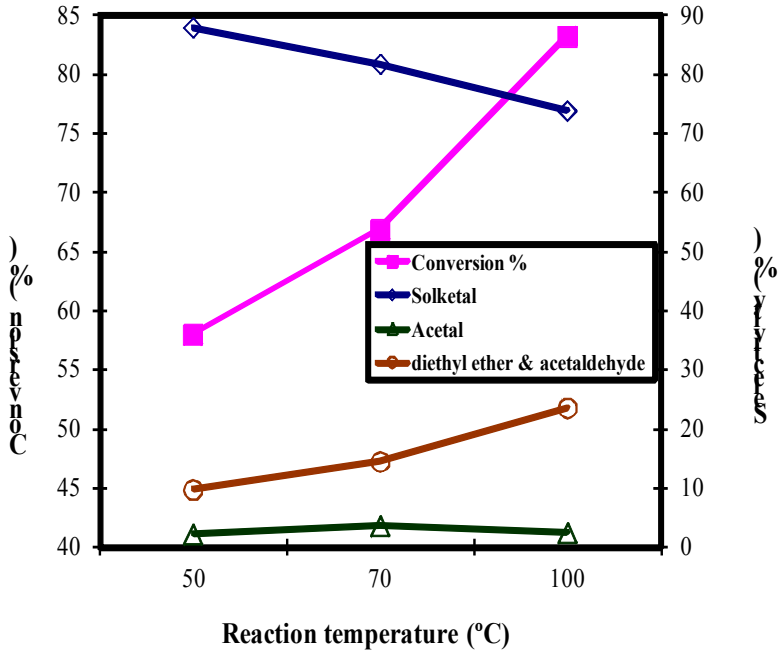


Fig. 8. Effect of reaction temperature on PO_4/SiO_2 catalytic activity. Reaction conditions: catalyst weight: 0.5 g; acetone to glycerol molar ratio= 2; reaction time: 1 h.

Figure (9) Showed a gradual increase in the conversion of glycerol upon increasing the quantity of the used catalyst from 100 to 700 mg. Such enhancing in the value of conversion may be owing to the increment of the accessible active spots in the surface of the catalysts as the catalyst amount charged to the reactor increased. These acid sites are responsible for the configuration of the intermediate protonated hemiketal, which transformed into solketal or acetal after dehydration step [11, 14].

The non-significant influence of the amount of the catalyst on its selectivity towards the formation of solketal was previously detected [13]. The selectivity towards solketal slightly decreased as the of the amount of used catalyst reached 700 mg, that may refer to the increase of the available polar acidic sites and consequently the stabilization of the protonated intermediate, which is favored conditions for the terminal hydroxyl group nucleophilic attack leading to produce acetal [11].

Figure 10 demonstrated the effect of time on the catalyst performance since it displayed a conversion of glycerol ~76.42% after 1h, and ~90.36% after four hours of reaction time. Afterward, there was no considerable change in the glycerol conversion after 6h (~90.67%). No indications for a deactivation process were observed during experimental tests for up to six hours, which eliminate the possibility of coke deposit formation [28]. In a good agreement with previous reports [11,13], the selectivity of the catalyst towards solketal slightly decreased as the reaction time increased and the selectivity towards acetal increased, which may be attributed to the solketal hydrolysis in presence of the remained by-product water molecules [39].

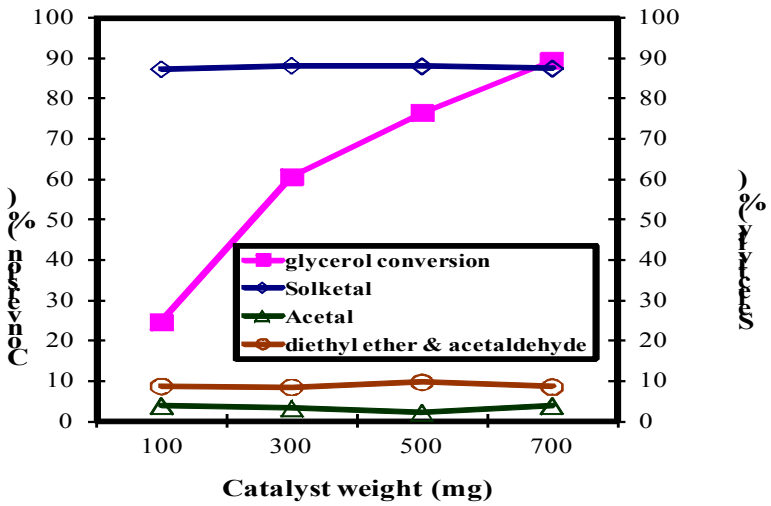


Fig. 9. Effect of catalyst weight on thecatalytic activity. Reaction conditions: acetone to glycerol molar ratio= 2; reaction temperature: 50ºC; reaction time: 1 h.

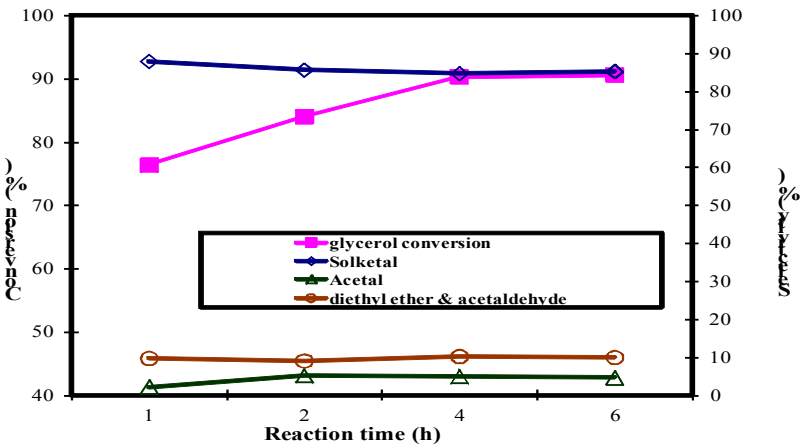


Fig. 10. Effect of reaction time on PO_4/SiO_2 catalytic activity. Reaction conditions: catalyst weight: 0.5 g; reaction temperature: 50ºC; acetone to glycerol molar ratio=2.

In order to study the stability of the catalyst, the reusability test was studied in five subsequent reactions (Fig. 11). As clear, no remarkable change on the conversion and selectivity, this indicates the high stability of the PO_4/SiO_2 catalyst.

Table (2) shows the comparison of solketal selectivity towards the acetalization reaction over different catalysts.

Conclusion

Based on the activity data, pure silica catalyst shows very low activity (less than 1% glycerol conversion) in acetalization reaction due to the very poor acidic properties as indicated by TPD data. While, in the case of PO_4/SiO_2 catalyst, the glycerol conversion reached ~90.8%. Two ketals including solketal with a 5-membered ring (selectivity = 85.24%) and acetal with a 6-membered ring (selectivity = 4.72%) are formed, this reliesessentially on the acetalization position contained by the glycerol molecule. The 5-membered ring ketal exhibits lower thermodynamic stability than one with the 6-membered ring. It means that the formation of 5-membered ring ketal ismainly kinetically controlled [7]. This data confirmed that, the catalyst type acting amain role in this reaction, which counts on the strength and type of acid sites [48-51], which are essentially for activation of the carbonyl group of acetone and forming a carbonation that was attacked by the hydroxyl group of glycerol to build up an intermediate which then goes through cyclization bywater removing to ketals formation [52]. Moreover, the textural properties of the catalyst (surface area

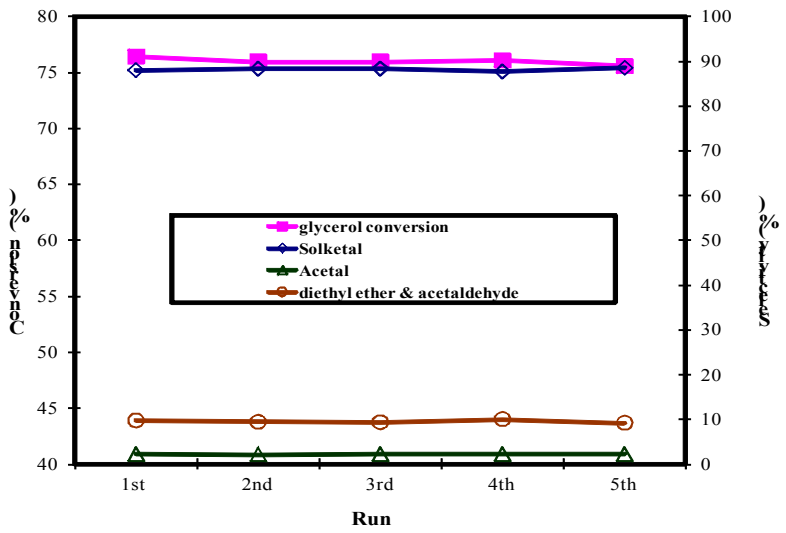


Fig. 11. Reusability of PO4/SiO2. Reaction conditions: catalyst weight: 0.5 g; acetone to glycerol molar ratio= 2; reaction temperature: 50ºC; reaction time: 1 h.

TABLE 2. Comparison of solketal selectivity by the acetalization reaction over different catalysts.

Catalyst	Solketal Selectivity %	Reference
α-zirconium phosphate	98.6	[40]
Acidic carbon-based catalysts	95	[41]
Algerian acid activated clays	95	[42]
p-Toluenesulfonic acid	98	[43]
silica-included heteropolyacids	98	[44]
Amberlyst – 36 (Wet)	94	[17]
M-$AlPO_4$/x$AlPO_4$ (x = Zn, Cu, Ni, or Co)	75	[18]
MoPO/SBA-15	97	[45]
mesoporous Ni–Zr/AC	75	[46]
(NH_4- [$NbO(C_2O_4)_2(H_2O)$](H_2O)n	65	[47]
Co[II](Co[III]$_x$Al$_{2-x}$)O	98	[48]
Ex- rice husk silica phosphate	**90.8**	**This work**

and porosity) are also significant because it assists in the elimination of the diffusion limitation for reactants and products [52]. The optimized conditions of this reaction over 10% PO_4/SiO_2 to give maximum solketal selectivity are 50◦C (lower temperature) and acetone to glycerol molar ratio 2 using a 0.5g catalyst. The catalyst was found to be stable up to more than five cycles.

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تأثير أيون الفوسفات على محفز السيليكا الحيوي على التركيب الوقود النظيف

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يمكن إنتاج solketal المضاف للوقود من خلال تفاعل استسقاء منتج ثانوي للديزل الحيوي (الجلسرين) والأسيتون. أجري هذا التفاعل على السيليكا المحمضة المشتقة من قشر الأرز المستدام كمصدر طبيعى بيئى في مفاعل بدون مذيب. و تمت دراسة الخواص الكيميائية والهيكلية للمحفز المحضر بواسطة حيود الأشعة السينية ، يحول فورييه مطيافية الأشعة تحت الحمراء والأيزوثيرم الامتزاز / الامتزاز ،درجة الحرارة المبرمجة الامتزاز من الأمونيا ومسح المجهر الإلكتروني استنادا إلى هذه الورقة ، فإن الظروف الأمثل باستخدام حمض الفوسفوريك حمض 15 ٪ المستخرجة من قشر الأرزهي 50 درجة مئوية (انخفاض درجة الحرارة) مع النسبة المولية للأسيتون: الجلسرين = 2. يستخدم اختبار قابلية إعادة الاستخدام لفحص ثبات تم التحقيق في النشاط الحفاز. هذا الجهد هو خطوة خطيرة للتنمية والتفكك من solketal كمنتج رئيسي من الجلسرين والأسيتون باستخدام موارد النفايات.