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A review of rice husk silica as a heterogeneous catalyst support

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Abstract

The yield of amorphous silica has less residue of mineral content in rice husk (RH) and a high specific surface area through the simple alkaline extraction process at first, then acid precipitation of RH. At this time, the leaching process using alkali and calcination of RH is the best method to acquire amorphous silica with a high surface area. The different temperatures were used for the calcination of RH and continue with sodium hydroxide (NaOH) treatment by using different concentration. The sample titrated using hydrochloric acid (HCl) to extract silica. Pretreatment with acid leaching for the RH was also conducted before the calcination of the RH. Results acquired were analysed and compared.

1. Introduction

RH are attracted as worth supplementary material towards waste utilisation and value reduction in the domestic and industrial processes. India and China contribute about 22% and 33% of rice production globally, which means it is wide obtainable of RH, a by-product of the rice edge. About 90% of silicon oxide contains rice husk ash (RHA) and valuable, economic stuff for silicon oxides and silica assembly. It has distinctive properties that have many purposes and makes it a valued raw material. Besides, another use of silica extracted from RH is, in the process of a soluble silicate, reinforcing filler in natural, silicon-based chemicals, synthetic rubber, and silicones and its alloy [5,24-33].

Even there are many RH users; there is still has a large amount of leftover in the production of the rice industry, which is narrowly commercially utilised and cause to disposal matter of RH. RH consists of cellulose, lignin, silica, and moisture, where about 20% is silica [37]. To obtain the silica, the RH should be burning, and RHA produced. RH is not easily burned or ignited with an open flame, except a path for the air to go through it. The result of burning RH yielded more than 80% of silica, which depends on the treatment process of RH and a small percentage of impurities like K_2O, Na_2O, and Fe_2O_3 [37]. The fabricated silica can be formed in an amorphous or crystalline structure, dependent on how the RH was handled. RH silica were produce as a catalyst support by incorporate with metal or organic material to form a catalyst by a few methods that was found from the previous study which are sol gel method, wet precipitation, ion exchange, impregnation, wet impregnation, and deposition-precipitation method that was explain more in 2.1.

Silica is a common raw material for various other compounds, including sodium silica, silica gel, and silicones. It has become increasingly important in today's environment. Silica is found in many forms across the industry. The variety of uses for silica and items containing silica indicates how common this substance is in people's daily lives. The significance of silica in material science research is that researchers analyse silica to improve its application and make it more environmentally friendly. Silica is an essential component in producing silicon carbide, used in ceramics, glass production, and a semiconductor material. It has the ability to conduct electricity, but not as well as copper or silver. This physical feature, silicon, is a valuable commodity in the various manufacturing industry. Currently, the use of fumed silica and amorphous silica are increasing, especially in biomedical application [42], diagnostic [43], and drug delivery [44]. Materials based on silica have high potential and are extensively used to prepare artificial bone tissue [42]. The silica-based materials are nanospheres, silica sphere, silica aerogel, silica star gel, and mesoporous silica gel. Silica-based bioactive and mesoporous silica material has to lead the evolution of a large scale area of research on new silica-based bioactive materials for biomedical applications. It showed the evolution to wide-area because, since Hence has discovered the silica-based bioactive glass in 1971 and Mobile Corporation and Waseda University ordered the mesoporous silica material in the early 1990s'.

Generally, silicon alkoxide raw material was used to produce amorphous silica such as tetramethyl orthosilicate (TMOS) [3], tetraethyl orthosilicate (TEOS) [12], and poly ethoxy disiloxane (PEDS) [59,61]. The alkoxides are commonly used for the preparation of amorphous silica. Using alkoxides in making amorphous silica is

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quite costly [13], so that another silica precursor is needed to replace alkoxide. Researchers have been found that RH contains 20% [35] of silica which is RHA is an economical source of amorphous silica of natural resources. The RH still can harmlessly be used even though there are a few percentages of metallic impurities since RH is from nature.

Rice production in South and South-East Asia is about 90% of the world's rice production. RH has a high quantity of organic volatile that is 85% to 95% silica, and the remaining is another compound that is not containing carbon, which is inorganic [36]. Besides, it is also known as a source of energy in which RH can generate energy, as an example by the burning process. RHs are the leftover rice grains that produced in large quantities. In some regions, they use RH as fuel, while in other countries, it is also considered waste products that create a problem like pollution and disposal problems. As our concern to the environment, the RH was burned under controlled conditions to conserve energy and resources. Based on the previous study [17], they were analysis the content of raw RH, which consists of silicon dioxide (SiO_2), magnesium oxide (MgO), calcium oxide (CaO), manganese dioxide (MnO), iron(iii) oxide (Fe_2O_3), aluminium oxide (Al_2O_3), organic material and moisture. The highest content in RH is the organic material and moisture, which is about 73.87%, and the percentage of silica is founded at about 22.12% that it is one of the plants that contain high content of silica. While for total of $MgO+CaO+MnO+Fe_2O_3+Al_2O_3$ are about 4% where each value of them are 0.21%, 1.24%, 0.074%, 1.28%, and 1.23%.

It has been reported that many preparation of RH as catalyst support to create a catalyst that has high activity and selectivity. Each characteristic of the catalyst produced plays a crucial role in ensuring that the catalyst produced is of good quality. The catalyst produced wants in the amorphous phase, high surface area and porous structure. This is because amorphous silica used to support the reactivity of supported metal oxide species while high surface area can increase the rate and allow more collision of the reactant and catalyst atom or molecule. The porous structure is important because it is contribute for an ecofriendly disposal, easy to be handle, high activity, catalyst regeneration, selectivity and negligible level of reactor plant corrosion. The material used for mesoporous molecular sieve has been thoroughly studied in detail. As was reported by Grisdanurak *et al.* [10] that cetrimonium bromide (CTAB) has been used as a structure-directing agent (SDA) and also for produced MCM-41 that containing pores which is mesoporous material. In this case, CTAB is a surfactant that makes silica more porous as explained in the figure below how the surfactant works onto silica. As shown in the Figure 1, the silica precursor can be achieved because of the different parameters like temperatures, silica sources, types, and surfactant concentration. At the same time, pH does affect the production of structural material of silica with a desire pore size.

The previous studies of using RHA have revealed that it can produce high silica content in forming an amorphous or crystalline state according to its usefulness. Silica extracted from RH is a cheap raw material that consists of more than 60%, and Kamath and Proctor [1] and also Chakraverty and Kaleemullah [2] were reported that it was used for producing powders and also silica gels. Various silica production was developed, such as silicon nitride, silica carbide, silica itself in an amorphous state, and elemental silicon, starting material from the RH.

2. Acid pretreatment of RH

RHA usually used in cement [45], refractory industries [46], and steel [47]. Example of the amorphous silica produced are complex organo-silica matrixes, silica nanoparticles, and metal-silica compounds have been extensively analysed and reported in the literature [4-6,35]. The operation of getting rice from the paddy helps obtain around 23% of the husk, which the paddy's initial mass. 95% to 97% of silica were produced from the RHA is known as rich siliceous [1,2]. The research data from journals shows there are various of procedure were exists in reasonable and cheap cost to acquire silica from the RHA. Besides, chemical treatment and thermal treatment is beneficial which increasing the purity of the silica.

Acid pretreatment is critical in synthesising amorphous silica with high activity and specific surface area [62]. Acid pretreatment is a method of removing lignin and hemicellulose from biomass by using acid as a catalyst. Its primary function is to solubilise the hemicellulosic portion of the biomass, allowing enzymes to reach the cellulose more easily. Compared to the original RH, the levels of residual metal impurities all reduce to varying degrees after acid pretreatment [62]. Acid pretreatment can be done in dilute or concentrated acid to convert cellulose to glucose in concentrated acid hydrolysis. The powerful acid can dissolve polysaccharide glycosidic linkages, resulting in monosaccharide components. It also has the ability to extract monomeric carbohydrates [63]. When polysaccharides are transformed into monosaccharides, impurities in the RH are bound in organic matter are easily exposed. They will undergo a chelate reaction with the acids and will be removed by the acid leaching solution. The metal impurities in the RH can be classified into three categories: water-soluble parts, acid–leachable parts, and residual [62]. According to the previous study, potassium and sodium have similar behaviour that is almost water-soluble. At the same time, calcium,

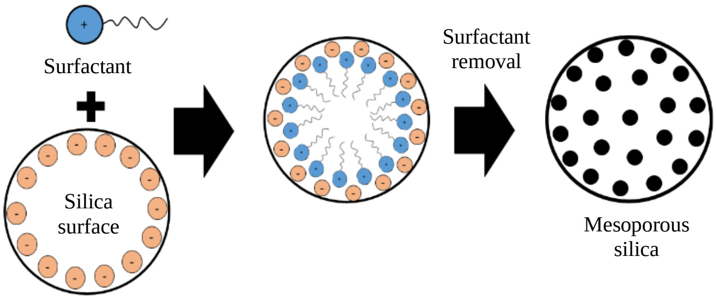

Figure 1. Cationic surfactant onto silica to form a mesoporous silica.

magnesium, and manganese formed as acid-leachable. This proves that the metal contains in the RH have different behaviour. Acid treatment can remove the metal impurities about 70% and above. In this treatment, the acid is promoting the hydrolysis process of organic matter in the RH. It can increase the porosity, and the small mono-saccharide burns more efficiently since the combustion obstacle was eliminated, generating smaller silica particles [62]. Other than improving all properties of the RHA, it also inhibits crystallisation.

A variety of methods are used in obtaining great value or pure or ultrapure silica from the RH or RHA. Acid leaching is the average pre-treatment mostly used, and HCl is the best acid that is often used. In Table 1, there is a record of studies that analyse the acid treatment in lessening the contamination, have better properties of RHA, and extract the pure silica. The acid pretreatment can give high purity of the silica in an amorphous state with a large surface area. Besides, the RH's organic substance can be eliminated by treating the RH via the pyrolysis process [37].

Figure 2. Acid treatment.

Table 1. Studies that investigated acid pretreatment processes used to extract silica from the RH.

Author	Objective	Methods	Results
Sankar *et al.*	To produce nano silicon powder from three kinds of RH.	• Combustion of RH in the open. • Acid leaching • Incineration at 700°C under atmospheric conditions	The RHA silica is spherical, completely amorphous silica particles with a large specific surface area. The specific surface area and their average pore diameter of sticky RH are 7.55 m^{2}·g^{-1} and 37.53 nm, red RH is 201.45 m^{2}·g^{-1} and 5.93 nm, and brown RH is 247.18 m^{2}·g^{-1} and 4.33 nm. Brown RH has the smallest particle size, which is 5 nm to 10 nm.
Bakar *et al.*	To investigate the ideal conditions to obtain high purity silica.	• Washing of RH with water • Acid leaching • Incineration at 500, 600, 700, 800, and 900°C for 2 h under atmospheric condition	All silicas had amorphous particles with uneven and highly roughened, and RH leached with HCl produced the highest silica content, 99.582%, at 600°C. The surface area for RH treated with HCl gives the best result which is 218 m^{2}·g^{-1} compare to treated with sulphuric acid (H_2SO_4) and untreated that are 208 m^{2}·g^{-1} and 116 m^{2}·g^{-1} respectively.
Ma *et al.*	To develop a new, recycling-based technique to produce silica from RHA.	• Acid leaching of RHA • Extraction in a reactor with NH_4F • Acid precipitation of silica	Acid washing able to wash out small percentage of minerals in the RHA and the particle were in spherical shape. Yield of silica reach up to 94.6% with diameter 50 nm to 60 nm.
Liou and Yang	To investigate the effect of experimental conditions on the characteristics of the nanosilica obtained.	• Leaching of RH with water and then acid • Incineration • Extraction with NaOH, forming silicate • Precipitation	They using different acid which are citric, oxalic, hydrochloric, and sulphuric acid. $HCl > H_2SO_4 > C_2H_2O_4 > C_6H_8O_7$ for the surface area while for their sodium content is $C_6H_8O_7 > C_2H_2O_4 > H_2SO_4 > HCl$. The pore volume of the silica decreases due to the high proportion of sodium content that blocks the pore. The silica produce is $C_6H_8O_7 > C_2H_2O_4 > HCl > H_2SO_4$. Best results with pH 3, silicate 0.15 M, the aging time of 12 h at 50°C, with 99.48% purity silica.
Carmona *et al.*	To extract and characterise nanosilica from two types of RH, alguhinha and cetato RH, using a milder acid solution.	• RH + weak acid and sumitted to high pressure at 2 kgf·cm^{-2}, at 150°C for 1 h. • RH treated to dH_2O, summitted to high pressure, and temperatures repeat four times. • RH calcined under 10°C·min^{-1} heat rate up to 650°C and summitted to isotherm for 1 h.	By using acid treatment, it was able to remove the impurities like metal oxide. The average size particle of the RHA are CH_3COOH (294.7 nm) > $C_6H_8O_7$ (250.4 nm) > H_3PO_4 (241.7 nm). RH treated with acid has high activation energy compared to untreated that leach with water about 126.7 kJ·mol^{-1}, untreated 127.0 kJ·mol^{-1}, acetic acid 146.8 kJ·mol^{-1}, citric acid 134.8 kJ·mol^{-1}, and phosphoric acid 146.0 kJ·mol^{-1}. All of silica extraction by weak acid is white and amorphous.

Table 1. (continued).

Author	**Objective**	**Methods**	**Results**
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Yalcin and Sevinc.	To achieve completeness of combustion, high purity, and high specific surface area.	• Washed with water • Acid leaching by HCL • Alkaline leaching • Incineration at 500, 600, 700, and 800°C • The sample was calcined under four different atmospheres.	Produce pure and amorphous silica and a tendency to form agglomerates. The surface area for untreated RH is 63 m^2·g^{-1}, RH treated with 3% HCl (post) give the highest, which is 321 m^2·g^{-1}, treated with distilled water (pre) is 194 m^2·g^{-1}, RH treated with 10% H_2SO_4 (pre) is 282 m^2·g^{-1}, and 3% HCl treated the RH before and after calcination is 244 m^2·g^{-1}. The RH treated with acid before and after calcination produces silica > 95.14%. RH average particle size for the untreated is 75 µm, while the RH treated with the 3% HCl (pre) is 0.0030 µm.
Ghorbani *et al.*	To optimise silica extraction procedure and increase its purity and eventually get a high-quality one.	• Washed with tap water • Leaching with HCl, HNO_3, H_2SO_4, NaOH, and NH_4OH, • Two methods, burnt without any treatment and pretreatment by acid leaching and combustion • Silica dispersed in NaOH • Titrated with H_2SO_4	HCl gives the best result because it produces the highest silica in RHA, 95.55%, followed by HNO_3 and H_2SO_4, 94.79% and 92.89, respectively. The morphology of the amorphous silica treated by HCl is non-spherical and irregular fibre-like. Surface area is up to 409 m^2·g^{-1}, average particle size is about 200 nm, average pore size 10.89 nm and 0.95 cm^3·g^{-1} their total pore volume.
Kalapathy *et al.*	to analyse the effectiveness of: 1. washing RHA with acid before alkali extraction 2. washing dried silica gel (xerogel) with water	• Acid washing • Silica extraction – wash with NaOH, titrate with HCl, • Chemical analysis of silica gel	Yield of silica 91%. Using a simple low energy chemical method, acid leaching at pH 1 is more effective in removing Ca, Fe, and Mn from RH. The last washing of the xerogel gave a silica result with less content of Na and K.
Krishnarao *et al.*	to understand the formation of the black particles in silica ash from RH	• Sieved • Acid treatment • Calcination at 400, 500, 600, and 700°C • Treated with HF + H_2SO_4 • Dried and heated at 1000°C for 1 h to remove silica	The black particles of RHA can be reduced if the RH were treated with acid. This is because it does allow the oxidation of carbon while the RH was burning. Acid treated RHs produced bright white silica. Acid treatment, temperature, and heating rate do affect the formation of RHA. The impurity was removed in acid-treated RH, and no carbon appears in the silica ash. The surface area of RH treated with acid is 260 m^2·g^{-1} and surface area of untreated RH is decrease to <1 m^2·g^{-1}
Liou.	to produce valuable silicon nitride and silicon carbide powder	• Wash with dH_2O • Acid leaching the water-rinsed and acidic solution was mixed under stirring • Pulverised, and then ground • RH heat between 300 K and 1000 K temperature	95% of the impurities are extracted after thermal decomposition. Impurity content is reduced by acid-leaching and the thermal decomposition process. The heating rate also play an important role because it may affect the surface area.

Table 2. Comparison between treated and untreated RH after thermal treatment.

Characteristics	**Not leaching RH**	**Rice leaching by hot citric acid**
Carbon content	40%	0.1%
Color of RHA	Light grey	White
Remaining inorganic oxide	High level	Low level
BET surface area (m^2·g^{-1})	313	220
Particle size (µm)	9.2	4.3
Pore volume (cm^3·g^{-1})	0.26	0.38
Pore diameter (nm)	4.8	4.9
Structure phase	Agglomerate	Some part is backbone
Silica produced (wt%)	86	97

Since it was reported in many journals that by using acid as a treatment, it does give the different reading results because it changes the composition of the RH. Olawale *et al*. [51] are researching chemical constituents using raw RH and leached RH. They found that the RH that uses chemical constituents with acid gives the best result compared to the raw one. Besides, the thermos chemical treatment for the RH reported by Alyosef *et al.* [25] also compared the RH treated with hot citric acid and not treated RH that have identified the biogenic silica generated from it. It shows that leaching has given many advantages, especially to the percentage of the silica produced and also their porosity. Their scanning electron microscopy (SEM) result shows the texture of not treated RH with a rough surface and not to clear backbone shape compare to the treated RH. The table below, explain the comparison between treated and not treated RH [25].

To date, there are a few studies that have investigate the best leaching agent to extract silica by using different acid. Ghorbani *et al.* [40] studied the properties of extracted silica by using the different leaching agent types for the acid treatment method. HCl, H_2SO_4, and HNO_3 were used as leaching agent. These acids were mixed with the RH to analyse the outcome from the different types of acid used for the pretreatment of the sample. The silica extraction process has been carried out under a controlled condition of the calcination process in a muffle furnace at 600°C. The treatment method that produced high ash product is leaching by HNO_3, which 30.92% and followed by RH treated by HCl, H_2SO_4, and no leaching that is 24.58%, 22.93% and 16.60%, respectively. This report shows that H_2SO_4 gives the highest BET surface area, which is 299.04 $m^2 \cdot g^{-1}$, compared to other acids and the RH that was not treated only has 19.57 $m^2 \cdot g^{-1}$ of BET surface area. Therefore, the different leaching agent used does affect the end product of silica extracted from the RH. Other than that, how the experiment conduct also can affect their end product, as compared in Table 1. As Ghorbani *et al.* [40] proved, the acid treatment method effectively removed some portion of alkali metal oxides in the ash sedge. The RH change from the golden colour rice husk turns to grey powder ash when the non-treated RH calcination at 600°C and the treated RH in 1N of hydrochloric acid calcinated at 600°C turn to white powder ash. Based on the characterisation result of X-ray diffractometer (XRD) and X-ray fluorescence (XRF) [40], the pretreatment using HCl gives the best result compared to HNO_3 and H_2SO_4. The main impurities in RH after the treatment and silica are K_2O, CaO, and phosphorus pentoxide (P_2O_5), which was reduced after acid leaching treatment.

The untreated RH gives the possibility to form dark colour particle with an increase in temperature of burning and heating rate. This is because untreated RH commonly generates ash with a large percentage of unburned carbon due to incomplete combustion and the melting of alkaline minerals in the ash, which entrap and complicate the fixed carbon's continued oxidation. Besides, using high temperature also can cause the formation of potassium melt which can also traps the carbon and volatile matter present in the residues from escaping during burning [71]. There are a lot of researchers studied on how to remove the black particle which Krishnarao *et al.* [36] were reported, that the consumption of HCl in acid treatment of RH can lessen the oxidation of carbon at a lower temperature which is at 400ºC and the treated RH is sluggish. Besides, there is no effect reported so far for using organic acid in treating RH and acid treatment and not affect the form of silica in the amorphous state [35]. The environment needs to be our priority since RH can prevent the open burning of RH activity that affects our environment's condition.

Acid treatment proved an important literary genre to produce the high quality of amorphous silica according to the suitability of the application to be used. Before calcination at low concentration of acid used in the acid treatment, it gives the best result with a high surface area and high silica produce. The acid-treated RH also allows the oxidation of carbon in calcination to reduce the black particle of RHA as long as the oxidation of carbon occurs with slowly heated. The carbon content of RH treated with acid is reduced when it was burned. This is because the oxidation of carbon can occur easily when the temperature increase. Oxidation of carbon happens during the combustion process, where the lignin, cellulose and other organic matter will decompose into carbon that was heated at room temperature. As the temperature rise, the oxidation of carbon will occur, and the RHA will obtain in white colour. Besides, acid leaching at the lower energy chemical is remarkably effective in efficiently removing and reducing mineral, alkali metal oxide, and impurities in RH.

Few researchers studied the pretreatment for the RH that can produce a high percentage of silica extraction and were eco-friendly to the environment. Xu *et al.* [52] have reported that using boiling water as a leaching agent for RH extraction is more economical and eco-friendly. They compared the RH pretreatment with acid leaching (HCl) and boiling water leaching to remove the alkali metal impurities in the RHA silica. The silica content is 96.41%, and the surface area is 248.21 $m^2 \cdot g^{-1}$ for acid leaching pretreatment, while boiling water leaching gives 94.03% of silica content and a surface area of 130.82 $m^2 \cdot g^{-1}$. Even the percentage for boiling water pretreatment is smaller than acid pretreatment, but the boiling water-leaching pretreatment technique is more economical and environmental than acid leaching pretreatment.

Other than that, pH for the acid leaching also does affect the result where Kalapathy *et al.* [6] has reported that the mineral content of acid-soluble from RHA was checked by using different pH from acidic to natural at 1, 3, 5, and 7. The mineral content in RH that can be removed by acid leaching is Na, K, Ca, Mg, Fe and Mn. It was reported that pH at 1 gives the best results and the most effective to remove the mineral content in RH and produced a high percentage of silica extracted from RH. Silica has a high solubility at a pH above 10, and silica cannot be dissolved at pH below 10.

Moreover, it produces amorphous silica with high surface area and nano-sized spherical particles, leading to a highly porous structure with a homogeneous particle distribution that is suitable for a catalyst. Carmona *et al.* prove that acid-treated RH can increase the activation energy and lower thermal degradation. This characteristic is needed for a catalyst to produce an effective catalyst and save energy while preparing it. The performance of silica obtained, treated by HCl, is the most effective compared with untreated RH, RH treated with HNO_3, H_2SO_4, $C_2H_2O_2$, and $C_6H_8O_7$, which make the amorphous silica has the highest purity, highest surface area and remove the impurities like metal oxide exclude silica. Various acid treatments will produce various sizes of sodium salts during precipitation. Sodium citrate has bigger salts that can become stuck in the gel matrix and hence aren't wash out from the matric and lead to reduce the sample's surface area because the leftover metal is blocking the pore. HCl has produced lower sodium content due to the size of sodium chloride being smaller and easily eliminated by water. Besides, even the same acid treatment used for the different types of RH gives different results of the silica produced, which the type of RH used can become one of the factors that contribute to their surface area.

2.1 Technique incorporated of catalyst support with metal or organic compound.

Silica is usually can be found in the form of gel, amorphous and crystal. The base of the tetrahedral (SiO_4) structure is silica (SiO_2). Every silicon atom is attached to 4 oxygen atom which each of them was bound to 2 atoms of silicon. Two categories of silica functional groups consist of the surface of silica known as siloxane (Si-O-Si) and silanol (Si-O-H). The properties of silanol are extra adsorptive, and it is the reactive one. The production of silica has many processes and also required high pressure and temperature. Among of all materials, silica is a very good catalyst support material due to its excellent physical and chemical properties.

There is a copious way for silica extracted from the RH to attach with organic or inorganic material to form a catalyst. The technique that were used are ion exchange, simple impregnation, simple precipitation, sol-gel, deposition-precipitation, and wetness impregnation method. Every technique gives different properties to the catalyst produced such as the active and adsorption sites and also the surface area.

Sol-gel is a process that involves numerous steps in the following order: hydrolysis and polycondensation, gelation, ageing, drying, densification, and crystallisation as explain in the Figure 3. It is also known as chemical solution deposition. Sol-gel is used to produce thin-film, monoliths, prepare fibre, microspheres and fine powders, which catalyst is an application using the sol-gel method. This method has more advantages than disadvantages, which is the process can produce high-quality materials with homogeneity and low temperature. It also creates a fine powder and can produce compositions impossible by solid-state fusion. This process is taking a long time that has become a disadvantage for this process. Adam *et al.* [14] have studied the production of catalysts by using industrial waste, which is rice hull by sol-gel technique. The uniform aggregate spherical particle is obtaining with range of diameter, 15 nm and 91 nm. This kind of particle structure can avoid the gelation and agglomeration of silica particle because particle aggregate of silica form negatively charge colloidal particle that lead to strong electrostatic repulsion energy. The table below, show the result of silica nanoparticle by using sol gel method studied by Adam *et al.* [14].

Next, the ion exchange is the chemical reaction between two substances consisting of positive and negative charges known as an ion. This process involves exchanging ionic components that release ions of a different kind with the same polarity, transforming ions in solution into a solid. This indicates that various ions originally contained in the solid replace the ions in solutions. There are a few types of ion exchange which is cation exchangers and anion exchangers. Chang *et al.* [9] reported that the RHA supported the characterisation of copper catalyst through ion exchange. They are comparing the incorporation of copper and RH by using ion exchange and incipient impregnation methods. The copper catalyst supported by RHA using the ion-exchange method is more stable and active for the dehydrogenation of ethanol to produce acetaldehyde. The ion exchange process has metal crystallites that are equally distributed. As widely speculated, the higher surface area of catalyst can have higher active sites, leading to higher activity. However, the catalyst Cu/SiO_2 with a surface area of 329 $m^2·g^{-1}$ has lower activity than Cu/RHA with 186 $m^2·g^{-1}$. The higher activity of the Cu/RHA (547.3 wt%) is because they have a higher copper surface area compare to Cu/SiO_2 (510.0 wt%). The rate of reaction increased as the exposed copper surface area is higher. In terms of deactivation, it has become the advantage for ion exchange technique that has reduced significantly compared to the conventional method. From this paper journal, the catalyst is stable and active for up to 2 h by ion-exchange Cu/RHA, while the catalyst produces by the impregnation method is deactivated due to less active. The table below, is showing the comparison between catalysts prepared by ion exchange and incipient wetness impregnation method by Chang *et al.* [9].

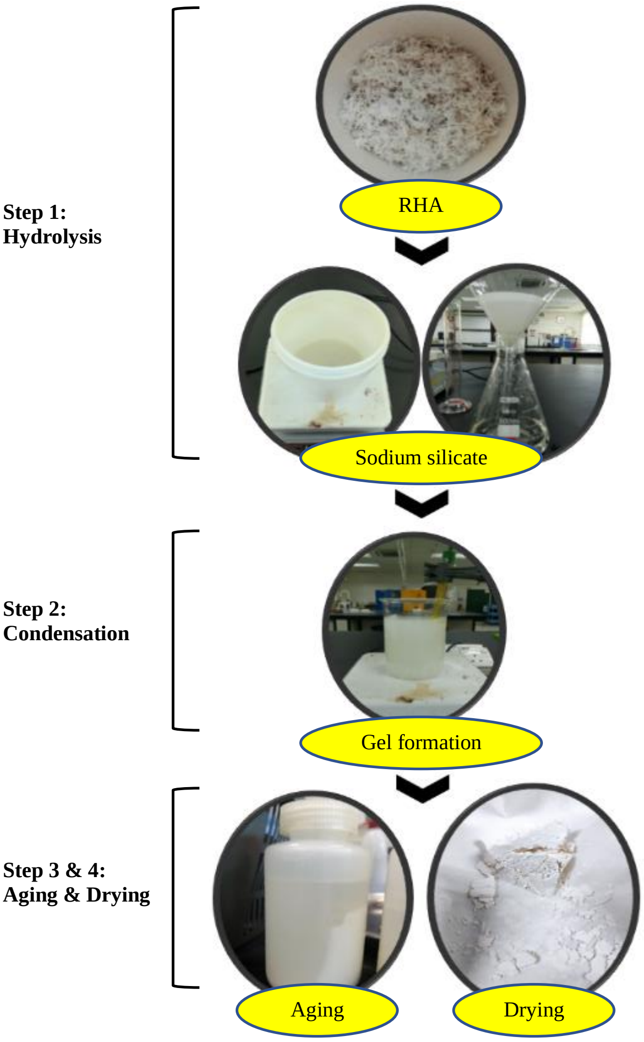

Figure 3. Sol-gel process.

Table 3. Silica nanoparticle results using sol-gel method.

Characteristic	Result
Surface area	245 $m^2·g^{-1}$
Pore volume	0.78 $cm^3·g^{-1}$
Pore distribution centered	7.9 nm
Structure	porous
Carbon content	low

Table 4. Properties of catalysts prepared by ion exchange and incipient wetness impregnation method.

Catalyst properties	Ion exchange	Incipient wetness impregnation
Surface area ($m^2\cdot g^{-1}$)	86-86	126
Average pore diameter (nm)	8.7-5.3	6.6
Copper loading (wt%)	2.23-5.75	5.00
Coper surface area ($m^2\cdot g^{-1}$)	443.7-547.3	2.3
Average copper particle size (nm)	1.52-1.24	14.6

While Adam *et al.* [58] used RHA as an inert material, the metal is chemically mixed and spread to every component of samples at room temperature and calcined at 700°C that were prepared by simple precipitation technique. Precipitation is a technique for separating a mixture based on its components' solubility. The ionic strength, pH, and temperature of a solution determine a compound's solubility. Manipulation of these parameters can cause a chemical to solidify and fall out of the solution. This process transforms a solution into a solid by turning the substance into an insoluble or saturated solution. A freshly produced residue is left in the solution from which it precipitates during precipitation, usually at a higher temperature. As a result, the recrystallised particles are purer and larger. They were using ruthenium to make ruthenium catalysts and denoted as RHA-Ru and RHA-RU700. Ruthenium catalysts are sufficiently selective to keep away from the oxidation of aldehyde going overboard to the acid. The presence of a functional group in the molecule of alcohol is tolerant. Their research results for the specific surface area of RHA-Ru is 65.10 $m^2\cdot g^{-1}$, and RHA-Ru700 is 10.38 $m^2\cdot g^{-1}$ which is less than RHA-Ru. The specific surface is decreased because when the temperature is more than 700°C, the condensation between the particle of the hydroxyl group freely occurs. They are getting together by changing the position of the silica globules in making their configuration steadier. XRD and SEM indicate that RHA-Ru is at an amorphous state since the SEM image shows the short-range order and random arrangement of their atomic and for XRD, it shows there is no sharp peak in the graph. On the other hand, the SEM image for RHA-Ru700 reveals some fine needles and some sharp peak in the XRD result, which means there is a crystalline phase. The crystalline phase in the matrix present in the RHA-Ru700 is because of using the high temperature during calcination on the sample.

It has been reported about the metal incorporation with silica extracted from RH by some researchers. To get Ni/RHA–Al_2O_3, Tsay and Chang [7] use nickel nitrate, aluminium sulfate and aqueous ammonia through the ion exchange technique and simple impregnation methods.

The preparation of supported metal (oxide) catalysts can be done in a variety of ways. Deposition precipitation is a general process for depositing metal oxides, metal sulphides, or metal hydroxides as small particles onto a support material. The preparation of copper impregnated was reported by Chen *et al.* [8]. They use the deposition-precipitation technique and then burn the sample at 673 K. Chen *et al.* [8] uses copper nitrate trihydrate as the source of copper to obtain copper incorporation with silica. They get this through an incipient wetness impregnation method. The preparation of copper solution by dissolving in urea. Cu/RHA catalysts obtain a high copper surface area when copper loading is 10.2%, which is 46.0 $m^2\cdot g^{-1}$, and their average particle size is about 1.5 nm. 10.2% copper loading is the most effective catalyst with the highest catalytic activity and selectivity due to its high copper surface area and copper dispersion (66.4%). 5.6% copper loading has the highest copper dispersion (67.8%), but it had the lowest activity due to its low copper surface area (25.6 $m^2\cdot g^{-1}$). The surface area of copper reduced as copper loading increased.

The incipient wetness technique was used to expand the metal support catalysts extracted from RH, reported by Chang *et al.* [11]. Using the metal oxide and metal impregnation methods to silica matrixes can develop the high surface of the silica solids in particulate form. Impregnation is the process of contacting the support material with a solution of a suitable metal salt, such as nitrate, over a period of time under regulated conditions to allow the catalyst precursor salt to adsorb from the solution. The impregnation technique is usually used for the catalyst preparation, which is the efficient way for occluding active metal in the pore of support. There is a simple impregnation method and incipient impregnation (IWI) method. IWI is the method that is always used for the heterogeneous catalyst. This method becomes attractive due to its low costs, limited waste, and technical simplicity. The technical simplicity is by the impregnated of support with precursor solution and then dried. Compared with simple impregnation, this method will produce a large cluster of metallic with low metal dispersion. Nowadays, binary oxides are currently used as catalyst supports that are different from the composite oxides formed. The characteristic of composite oxides is easily spread on the support matrix while also getting better catalytic effects. So, the interrelationship between chemical and physical properties can be understood. The RH extracted will produce silica at an amorphous state by a treatment that uses the acid as an acid leaching agent, calcination at a high temperature that the carbon elimination has been used as catalyst supports. The extraction method will produce the high porous content of silica and a high surface area that is saturated with copper-metal by ion-exchange mechanism and was used in the dehydrogenation of ethanol. Table below are showing the advantages and disadvantages of the technique used for catalyst preparation which every method got their pros and cons.

Many research papers are still in progress: a study about the catalyst that is not harmful to the environment. A lot of research papers or journals have been proved the effect of organic catalysts that are eco-friendly, which increases the production of the heterogeneous catalyst. As we already know, the use of silica gels and powders have primarily produced that function as an absorbent, insulator, release agent, pozzolan, repellents, soil ameliorant, water purifier [53], catalyst, catalytic support [54], chromatographic agents [55], and also fillers [56]. The determination of raw material and specific mechanisms in the making of catalysts was selected based on their reusability, which is easy to use.

Table 5. Advantages and disadvantages of technique for catalyst preparation.

Technique	Advantages	Disadvantages	Reference
Sol-gel	a simple process, inexpensive method for prepare metal oxides that allows for control over the doping process or the addition of transition metals, small particle size, high yield, and low operation temperature	it has a long processing time, chance formation of agglomerates, and large shrinkage during process.	[64,65,70]
Ion-exchange	the ability to use them indefinitely or repeatedly without having to renew them	its low thermal stability, low surface area, the conversion rate is low, expensive cost of preparation,	[66,67,70]
Precipitation	Small particle size, high dispertion rate, high activity in oxidation	Choice of precipitating agent, high impurities	[68,70]
Impregnation	Simple preparation technique	Low activity, high rate of impurity, weak support interaction, large particle size	[69,70]
Deposition-precipitation	high metal loadings can be combined with small particles and narrow particle-size distributions	Choice of precipitating agent	[70]

Supports are giving mechanical stability to catalyst nanoparticles or powders that immobilise the particle by reducing mobility and favouring chemical stabilisation. The solid support of the catalyst is solid with a large surface area to which the catalyst is bound. The activity of the heterogeneous catalyst is promoted mainly by the atoms present on the accessible surface of the material. The support can be inert or participate in a catalytic reaction. Typical supports include various kinds of carbon, alumina, and silica. The role of the solid support is to give mechanical stability to the catalyst, which also supports immobilising the particle, reducing its mobility and favouring chemical stabilisation, which can be considered solid capping agents. It also allows the nanoparticles to be easily recycled. Silica is the name given to a group of minerals composed of silicon and oxygen. Silica is found commonly in the crystalline state and rarely in an amorphous state. It is composed of one atom of silicon and two oxygen atoms, resulting in the chemical formula SiO_2. Silica is crucial because it has widespread industrial applications in food additive, bioanalysis, biochip, biosensor, glass making, ceramic, foundry, raw material for silicon chips, and many others. Silica can be synthesised by various preparation techniques to prepare NPs, transparent films, or solid flat materials. There are several advantages of using silica as a catalyst. These include high thermal stability, large pore size, high surface area for catalyst impregnation, irreducible and inert properties that can support catalyst and minimise leaching of the catalyst.

The properties of the metal with RH or RHA by incipient wetness technique has been studied by the researchers. Still, most of the catalysts produced were disposed of metal leaching due to reaction from the observation. Incipient impregnation is the most used route among the industry's preparation because it is a simple and easy method. Even its advantages are still minimal by poor metal spreading. The metal spreads were increased when inert stuff was present to prepare metal particle separation from touching with one another to reduce the mixing of metal particles. A textural promoter helps reduce the size of particles than those of the active metal species and gives a relatively high melting point. Chromium (Cr_2O_3) is an excellent textural promoter since its melting point is about 2708 K and owing fine particle size [19]. To investigate the result of chromium content for the catalytic activity and surface properties in ethanol dehydrogenation, they were tested with two types of samples for comparison: RHA and commercial silica were supported by chromium-promoted copper catalysts [20]. Adam and Thankappan [21] have used the technique of template-assisted sol-gel precipitation in producing high surface area Cu-Ce incorporated RH silica catalysts. H_2O_2 is used as an oxidant in acetonitrile, and it also has been used for one-step oxidation of using benzene. The existence of Ce and Cu has been studied in the mechanism and silica matrix, which is increasing the catalytic activity. The sol-gel technique was used to chemically incorporate the aluminium ion with silica matrix taken out from the RH, and the fatty acid adsorption also was studied [22]. Adam *et al.* [23] have reported that at the aqueous phase of H_2O_2, the acetophenone has been oxidised under a mild state using the vanadium incorporated RH, which leads to savings and is environmentally friendly.

Researchers are using various techniques and chemicals to extract silica from the RH and incorporated it with metal or organic compound as a catalyst to obtain the best morphology of substance and high surface area. Morphology and surface area play an essential role because the active sites are often created on the catalyst's surface. Therefore if the material has more porosity, it has more surface area to form the active sites, which will produce higher activities.

2.2 Amorphous silica from RH as catalyst support and synthesis methodologies

The standard method for silica extraction is using alkali, then forming the gel with mineral acid. The gel then was aged and filtered, and after that, it was dried. At the same time, during the extraction process, the size of the ultimate particle was controlled by the addition of the structural directing agent (SDA) to the silica gel. The added SDA onto silica gel can be eliminated by pyrolysis up to a suitable temperature that can decompose the SDA. By burning RH with a high temperature in the range of 500°C to 800°C for about 5 h to 6 h in a muffle furnace, it will turn the RH into RHA that contains high silica. The methods were adjust based on the need for catalyst required. Figure 4 is showing the simple standard method for silica of RH catalyst. Chang *et al.* [11] have set a muffle furnace for calcination of the RH at the temperature 900°C for about 1 h to develop a black crude product with N_2 flow in the muffle furnace. White ash was produce by burning the sample at a suitable temperature in atmospheric conditions. Based on Chandrasekhar *et al.* [4], their studies prove that the sample's surface area is very affected by these three factors: calcination of the temperature, acid treatment, and heating rate of the sample.

Calcination is the thermal treatment process that plays a crucial role in forming silica particles of RH to get silica with a high surface area and amorphous. The temperature below 800°C, will form amorphous silica, while the higher temperatures will change the silica's structure to crystalline-like cristobalite, quartz, and tridymite will form [35]. Bhupinder Singh [57] has reported that the calcination condition affected the properties of the sample. The RH properties affected are their crystallinity and the surface area of the RHA. At the temperature between 500°C to 600°C, the duration is about 15 min to 120 min under moderately oxidising condition, making the RHA stay in an amorphous state with a high surface area (97 $m^2 \cdot g^{-1}$ to 122 $m^2 \cdot g^{-1}$). While for the ash that are using temperature at 700°C to 800°C and the duration time is more than 1 h with a highly oxidising condition, its gives partially crystalline to the sample, and low surface area about 6 $m^2 \cdot g^{-1}$ to 10 $m^2 \cdot g^{-1}$ and if using the temperature more than 800ºC and long time for the calcination process, it does turn the sample completely crystalline, and the surface area is less than 5 $m^2 \cdot g^{-1}$

Table 6. Calcination condition.

Citation	Calcination	Result
Change *et al.*	900°C 1 h	White ash produced
Bhupinder Singh	500°C to 600°C 15 min to 120 min Moderately oxidising condition	97 $m^2 \cdot g^{-1}$ to 122 $m^2 \cdot g^{-1}$ surface area Amorphous state
	700°C to 800°C more than 1 h Highly oxygen	6 $m^2 \cdot g^{-1}$ to 10 $m^2 \cdot g^{-1}$ surface area Partially crystalline
	> 800°C Long time	< 5 $m^2 \cdot g^{-1}$ Completely crystaline

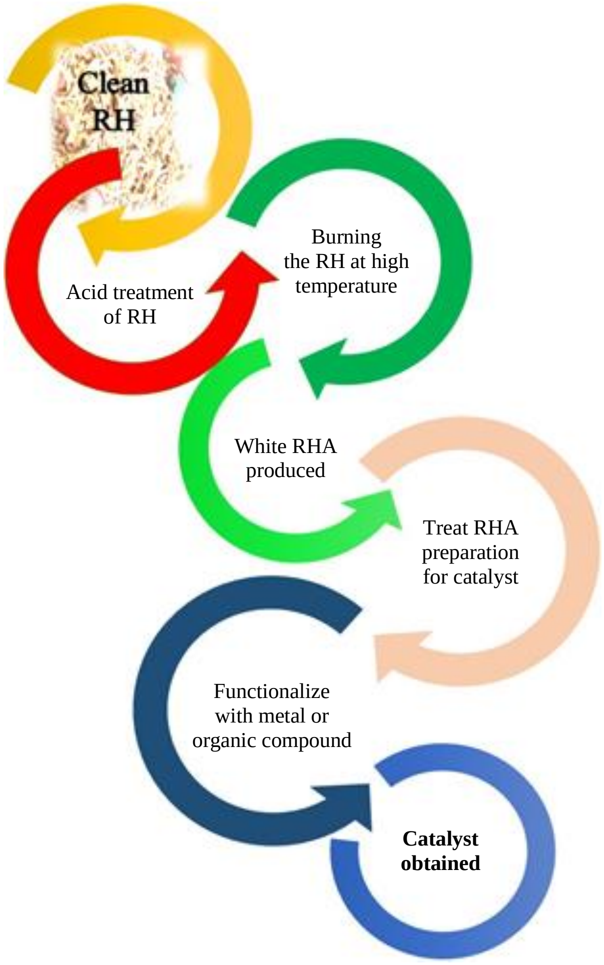

Figure 4. Method for silica extraction from RH to form a catalyst.

Besides, high alkaline conditions also required to get the best result or effective extraction of silica from RH [6]. The chemical concentration used can also disturb the result and the purity of silica. Ahmed and Adam [34] studied the ideal concentration of alkali by testing with values of concentration above 1.0 M in silica preparation. The process of silica preparation is by mixing the RHA obtained with different concentrations of NaOH to produce sodium silicate solution to get the high surface area and the best were incorporated with the indium to form a catalyst. They applied 1 M, 3 M, and 5 M of NaOH in the process of silica preparation that affecting the formation of pore and porosity of the prepared silica. The increase in the NaOH concentration causes the result to reduce pore volume and specific surface area of the sample. The sample with a different concentration of NaOH gives different value on their surface area, pore volume, and average pore diameter [34]. 1.0 M concentration is the best because the surface area and pore volume give the highest value (347 $m^2 \cdot g^{-1}$, 0.8772 $cm^3 \cdot g^{-1}$) compared with 3 M and 5 M that 153 $m^2 \cdot g^{-1}$, 0.589 $cm^3 \cdot g^{-1}$ and 123 $m^2 \cdot g^{-1}$, 0.19 $cm^3 \cdot g^{-1}$. While the average pore diameter of the sample that 1 M concentration is 10.4 nm is a small value compared to 3 M and 5 M. In the extraction process of silica, NaOH was added and turn the RHA into sodium silicate. Kalapathy *et al.* [6] also studied using different concentrations of NaOH with the value of concentration is below 1.0 N, which are 0.10, 0.25, 0.50, and 1.0 N. As reported, it is proved that 1.0 N of NaOH give the highest percentage of silica extracted, which is 91%. The concentration of 0.1 N of NaOH does not extract the silica; 0.25 N only produced a 17% yield of silica, and 0.5 N about 35% of silica extracted. Kalapathy *et al.* and Adli Elhag Ahmad and Farook Adam's [34] journals have proved that 1.0 M of NaOH is the suitable and optimum alkali concentration for RH extraction.

Many studies have researched silica extracted from RH and were incorporated with any metal or organic compound to form a catalyst to be used in various ways. For example, silica was modified by tungsten to form a catalyst that helps in oxidising styrene to the liquid phase. Adam and Iqbal [15] have reported that H_2O_2 can be used as a green oxidant to produce benzaldehyde. They have also studied other material like Cr-MCM-41, Fe-MCM-41, Mo-MCM-41, and V-MCM-41. Adam and Iqbal [15] studied the oxidation of styrene by apply H_2O_2 as an oxidant where the silica extracted by RH incorporated with chromium were produced with different pH.

Cyclohexanol and cyclohexanone are needed in the manufacture of nylon-6 and nylon-66. They were obtained from the transformation of cyclohexene with mesoporous silica were supported by chromium as were investigated. They are using cyclohexane, and the product is cyclohexanone and cyclohexanol. A conversion of cyclohexane is ca. 95% over Ce-MCM-41 at 100°C over 12 h, giving 82% selectivity to cyclohexanol, was reported by Yao *et al.* [18]. 100% transformation of cyclohexane in a short time was reported by Adam *et al.* [24], wheres the catalyst used is from the incorporation of silica RH, and 4-(methylamino)benzoic acid (MBA) then noted as a silica-chromium catalyst and Adam and Farook [24] also researched on the incorporation of chromium and RH where's they are using the RH directly which not ash. H_2O_2 decomposes by Mn–MCM-41 very speedily, letting conversion of styrene to very low, reported by Zhang *et al.* [16].

3. Conclusions

This study discloses the silica's technique and process extracted from the RH and in an undefined shape or form known as an amorphous state. The silica component can be produced in a high amount by eliminating organic and mineral components from the RH. There were many processes for silica production from the RH that usually operated around 1500°C temperature. This study has upgraded the methods to make possible the temperature of burning at the range of 550°C to 750°C. This study has proved the most useful and highly efficient method to solve the waste disposal problem and its utilisation. While the cases applied for the even pyrolysis, the temperature used is less than the conventional technique.

Acid leaching pretreatment for the RH before calcination has proved to upgrade the quality of silica extracted by removing the other inorganic and organic element in the RH. This silica obtained can be used as a catalyst substance that can also be impregnated with organic or any metal and become a catalyst. The surface area and adsorption isotherms can be calculated, and proper catalysts can be obtained from it. The surface area was found to contain pores with small diameters less than 2 mm and a high surface area and can be used as one of the medium that can soak up liquid easily or as a catalyst substance. The silica's high surface area provided the active site of the reaction, and it also does charge transfer to facilitate high rates of reactions. The development of the catalyst was able to be studied, and the oxidation reaction of the sample can be handled

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