

Rice Husk Ash as a Sustainable Silica Precursor for the Preparation of Ordered Mesoporous COK-12

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Abstract

The use of agricultural residues as functional materials provides an effective way to achieve the goals of dual use of agricultural residues and development of value added products. In this work, rice husk ash (RHA) was investigated as a renewable silica precursor for preparing ordered mesoporous COK-12. preparation sequence comprised controlled combustion of rice husk, chemical purification of the ash, alkaline dissolution of its silica fraction, change to sodium silicate, and subsequent template-assisted assembly of COK-12 with Pluronic P-123 in a citrate-buffered, near-neutral medium. The resulting solid was examined using X-ray diffraction (XRD), X-ray fluorescence (XRF), N₂ adsorption-desorption analysis, Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS/EDX), Barrett-Joyner-Halenda (BJH)/density functional theory (DFT) pore-size analysis, Brunauer-Emmett-Teller (BET) surface-area measurements, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetric/differential thermogravimetric analysis (TGA/DTG), and ²⁹Si magic-angle-spinning nuclear magnetic resonance (²⁹Si MAS NMR). Low-angle diffraction and electron microscopy provide complementary evidence for mesoscopic ordering, whereas nitrogen sorption provides quantitative information on accessible surface area, pore volume, and pore dimensions. FTIR, Raman and ²⁹Si MAS NMR provide information concerning the siloxane network and surface silanol groups, whereas XPS and EDX/XRF establish the chemical composition and purity of the material. The work establishes the feasibility of converting an abundant agricultural residue into an ordered mesoporous silica and establishes a sustainable route for producing COK-12 with potential applications in adsorption, catalysis, environmental remediation and energy-related technologies.

Keywords: Rice husk ash, COK-12, mesoporous silica, P-123, sustainable synthesis.

1. Introduction

Rice husk is one of the biggest solid wastes produced in the rice milling process and has a relatively high inorganic silica content. The abundance, renewability and low economic value of this agricultural residue makes RHA an attractive alternative raw material for the preparation of silica and/or silica containing functional materials appropriate thermal processing.

Hence, a lot of research has been undertaken to transform the rice husk and RHA into value added porous materials. Silica extracted from RHA has been successfully used to synthesize a number of ordered mesoporous materials such as MCM-41,

MCM-48 and SBA-15. These developments highlight the feasibility of using agricultural residues as a viable source of silica and at the same time offer an eco-friendly method of valorising the residues to serve the agricultural industry.

Ordered mesoporous silicas possess well-defined pore networks and attractive physicochemical characteristics, such as large specific surface areas, controllable pore sizes, accessible internal surfaces, tunable surface functionalities, and good thermal resistance. These properties have stimulated extensive interest in their application in “adsorption, heterogeneous catalysis, molecular separation, sensing, controlled drug delivery, and energy-storage or conversion technologies. Thus, the conversion of RHA into ordered mesoporous

silica offers a dual advantage: reducing the environmental burden associated with agricultural waste while generating technologically useful porous materials.

Among the different mesoporous silica families, COK-12 is particularly attractive because of its ordered two-dimensional hexagonal mesostructure with a P6mm symmetry. The material is structurally comparable in several respects to SBA-15, but its synthesis can be attained below relatively slight aqueous circumstances using the triblock copolymer Pluronic P-123 as a structure-directing agent and sodium silicate as the silica source in a citrate-buffered reaction medium. The relatively simple synthesis chemistry and the ability to obtain an ordered pore system make COK-12 an interesting candidate for sustainable mesoporous-material development.

Early studies of COK-12 demonstrated that the material could be produced at approximately room temperature under near-neutral conditions. Its structural and physicochemical characteristics were subsequently investigated using complementary techniques, including small-angle X-ray scattering, nitrogen adsorption-desorption measurements, electron microscopy, solid-state ^{29}Si magic-angle-spinning nuclear magnetic resonance, and thermogravimetric analysis. These characterization approaches established the relationship between the material's ordered mesostructure and its textural, chemical, and thermal properties.

The formation of the COK-12 framework is generally associated with interactions between P-123 micellar assemblies and silicate species in the reaction medium. During synthesis, silica species progressively condense around the polymeric micelles, while the micelles undergo organization and aggregation to establish the characteristic hexagonal arrangement. Subsequent silica condensation and structural development result in the formation of the ordered P6mm mesoporous framework. Continuous-synthesis studies have also indicated that the silica deposition, micellar organization and progressive structural ordering are interconnected and do not take place as totally independent processes.

The synthesis and post synthesis conditions have a significant effect on the final attributes of COK-12. The degree of structural ordering, the access to the

pores, the surface area, and the pore volume in the structure may be influenced by aging time, washing steps, drying conditions and calcination treatment. The specific surface area achieved in previously reported COK-12 materials is up to $860 \text{ m}^2 \text{ g}^{-1}$ and the pore volume is around $1.23 \text{ cm}^3 \text{ g}^{-1}$, which is very flexible and suggests that textural engineering in this material is possible.

From a materials chemistry point of view, RHA is a material that has been extensively investigated as a silica source for the synthesis of several ordered mesoporous systems, but the development of a general synthesis route for RHA to COK-12 is still relevant. The coupling of silica recovery from the agricultural waste material and the synthesis of COK-12 offers a chance to create a full valorization path where the agricultural waste starting material is converted into a material structured and with high surface area. This is also advantageous as it allows simultaneous evaluation of the chemical purity of the recovered silica, development of the mesostructure and the resulting morphological, textural, chemical and thermal properties.

In this work, therefore, RHA was used as another source of silica for the synthesis of ordered COK-12. The main steps consisted of controlled thermal conversion of rice husk to silica rich ash, alkaline extraction of silica, preparation of silica solution as sodium silicate and finally the synthesis of COK-12 using P-123 as structure directing agent. The obtained product was systematically characterized in terms of structural organization, morphology, elemental composition, surface properties, textural properties and thermal behavior. The relationship between the synthesis conditions and characteristic COK-12 mesostructure development was studied in particular.

This investigation aimed at:

The first is to generate RHA with silica as the main component from the controlled thermal treatment of rice husk.

2) To extract silica with a high degree of purity from RHA by alkaline extraction process.

3) To produce sodium silicate from the extracted silica to be used in the synthesis of the mesoporous silica.

4. To synthesize an ordered COK-12 with P-123 as structure directing agent under controlled aqueous conditions.
5. To describe and draw the COK-12 made and its structural, morphological, chemical, textural and thermal characterization.
6. To study the structure formation and evolution of COK-12 and its correlation with the synthesis and processing conditions.
7. To test the sustainability potential of the use of RHA by showing the conversion of an agricultural residue into a value added ordered mesoporous silica material.

2. Materials and Methods:

2.1 Materials:

Rice husk (RH) used in this study was sourced from a local rice milling factory, and the silica precursor was prepared from rice husk. The major chemicals used in the silica extraction and COK-12's synthesis were hydrochloric acid (HCl), sodium hydroxide (NaOH), citric acid, trisodium citrate, and Pluronic P-123. All solutions, washings and synthesis were prepared, washed and performed in deionized water. All chemicals used were analytical or reagent grade, and used as received unless otherwise stated.

2.2 RHA Preparation:

Collected rice husk was well cleaned with deionized water several times to wash off soil, dust and water soluble impurities adhering to the surface. The washed material was then dried in an oven at about 80-105 °C to a constant mass. The dried rice husk was then thermally treated under controlled conditions to yield gaseous products from organic fraction as well as to concentrate inorganic silica fraction.

At first, the dried husk was preheated to be able to do the gradual thermal decomposition and combustion. This was then calcined in a controlled atmosphere in a muffle furnace at 750 °C for 6 h. The furnace was then left to cool down and the ash produced was subsequently scooped up and kept in a dry container. The material obtained was called RHA which will be used as raw material for the extraction of silica.

The calcination temperature and time were carefully chosen as the thermal treatment history of the rice husk can greatly affect their structural state in the RHA. High temperatures or extended periods of combustion can encourage the conversion of the amorphous silica to the various crystalline forms, while the combustion environment of a controlled heat source tends to maintain the predominately amorphous silica. Accordingly, the prepared RHA was subsequently examined by XRD to assess its structural characteristics and verify the presence of the expected amorphous silica phase.

Table 1. Chemical composition of RHA before and after purification

Component	RHA before purification (wt.%)	Purified RHA (wt.%)	Component	RHA before purification (wt.%)	Purified RHA (wt.%)
Al ₂ O ₃	0.72	0.18	Fe ₂ O ₃	0.46	0.09
CaO	1.21	0.24	MgO	0.63	0.11
K ₂ O	3.18	0.21	Na ₂ O	0.37	0.06
P ₂ O ₅	1.42	0.12	TiO ₂	0.08	0.02
MnO	0.19	0.03	SO ₃	0.31	0.05
Loss on ignition/other	2.01	0.13			

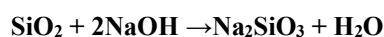
2.3 Acid purification of RHA:

To reduce the concentration of metallic ions and other inorganic constituents present in the as-prepared RHA, an acid-leaching step was performed using 0.1 M hydrochloric acid (HCl) at the predetermined solid-to-liquid ratio. The RHA–acid suspension was fiery to 90 °C and continuously stirred for 4.5 h to facilitate dissolution and removal of the acid-soluble impurities.

After conclusion of the leaching action, the suspension was permitted to separate, and the solid residue was removed by filtration. The retained solid was thoroughly rinsed numerous times with deionized liquid to eliminate residual acid and dissolved ionic species. Washing was continued until the filtrate approached neutral pH. The resulting acid-treated RHA was subsequently dried at 80 °C and stored under dry conditions until further processing. The purified ash was then used as the precursor for the subsequent silica-extraction step.

2.4 Extraction of silica from RHA:

The purified ash was subjected to alkaline silica dissolution affording to the subsequent reaction:



2M NaOH was mixed with a predetermined amount of RHA and refluxed for 8h at 80°C. The raw material was filtered to remove the insoluble material and the clear liquor with the dissolved sodium silicate was kept for further synthesis. The silica-extraction yield was calculated using

$$\eta_{\text{SiO}_2} = \frac{m_{\text{SiO}_2, \text{Extracted}} \times 100}{m_{\text{RHA}}}$$

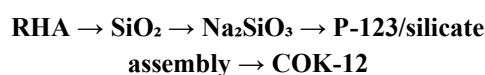
Where, m_{SiO_2} , removed is the mass of silica recovered from RHA and m_{RHA} is the original mass of RHA.

3. Synthesis of COK-12:

The silica precursor for the synthesis of COK-12 was the sodium silicate solution that was obtained from the RHA, and the structure-directing agent was Pluronic P-123. First, desired quantity of P-123 was dissolved in de-ionised water with

intensive mechanical stirring to get homogeneous solution. The P-123 solution was then mixed with citric acid and trisodium citrate to make a citrate-buffering medium. The buffering system used to set up and control the near neutral reaction environment.

The purified RHA was then mixed with sodium silicate solution and gradually added to the reaction medium containing the polymer, and stirred vigorously during the mixing process. The silicate species were added gradually to ensure even interactions between the species and the P-123 micellar assemblies, as well as to aid in the later organization of the silica framework. The overall conversion pathway can be represented as,



The sodium silicate precursor was completely added to the suspension, which was left at 80 °C for 4.5 h with a controlled stirring. The product of synthesis formed was separated from the reaction medium by filtration or centrifugation and was cleaned numerous times with DI water to remove the remaining soluble species and unreacted reagents. The recovered material was dried at 90 °C to get the as-synthesized COK-12 precursor with P-123 template.

To remove the organic structure-directing agent and develop the accessible mesoporous network, the dried precursor was subsequently calcined at 500 °C for 4.5 h under controlled atmospheric conditions. After completion of calcination and cooling to room temperature, a fine white powder was obtained and designated RHA-COK-12.

The use of P-123 in combination with a citrate-buffered silicate medium provides a suitable chemical environment for the development of the ordered hexagonal mesoporous framework characteristic of COK-12. The resulting material was subjected to subsequent structural, morphological, compositional, textural, and thermal characterization to establish the influence of the RHA-derived silica precursor on the properties of the synthesized mesoporous silica.



Fig. 1. Schematic representation of the complete sustainable synthesis route for COK-12:

Rice husk → RHA → purified silica → sodium silicate → P123–silicate assembly → ordered mesoporous COK-12.

Table 2. Optimization conditions for silica extraction from RHA

Experiment	NaOH concentration (M)	RHA/NaOH ratio (g/mL)	Extraction temperature (°C)	Extraction time (h)	SiO ₂ extraction yield (%)
1	0.5	1:10	60	1	72.4
2	0.5	1:10	80	2	81.7
3	0.5	1:10	100	3	87.9
4	1.0	1:10	60	1	78.6
5	1.0	1:10	80	2	91.3
6	1.0	1:10	100	3	96.2
7	1.5	1:10	60	1	82.1
8	1.5	1:10	80	2	98.1
9	1.5	1:10	100	3	97.4
10	2.0	1:10	60	1	84.3
11	2.0	1:10	80	2	97.2
12	2.0	1:10	100	3	96.8

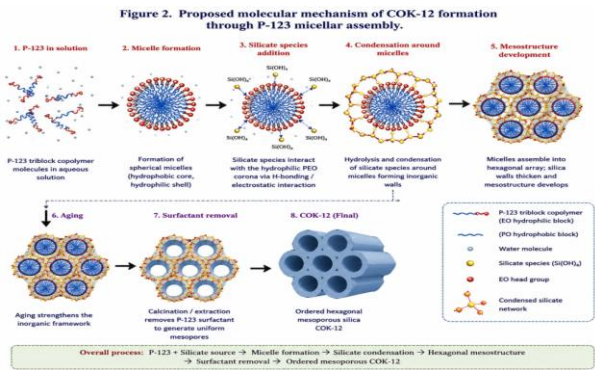
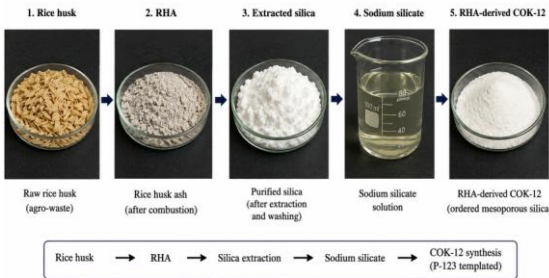


Figure 3. Photographs of rice husk, RHA, extracted silica, sodium silicate and RHA-derived COK-12.



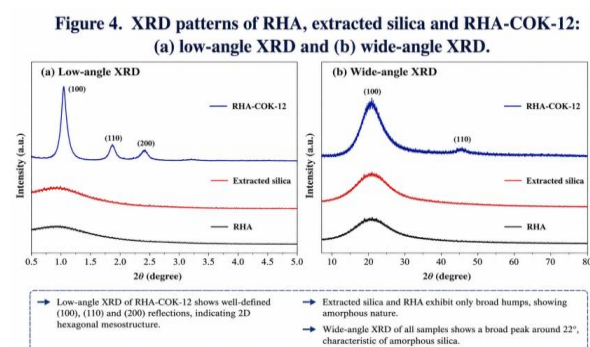
4. Characterization Techniques:

4.1 X-ray diffraction:

Powder X-ray diffraction measurements were carried out with Cu K α radiation with: $\lambda=1.5406\text{\AA}$ $0.5^\circ<2\theta<5^\circ$ to identify mesoscopic ordering. Wide-angle XRD was recorded over an appropriate range, for example: $10^\circ<2\theta<80^\circ$.

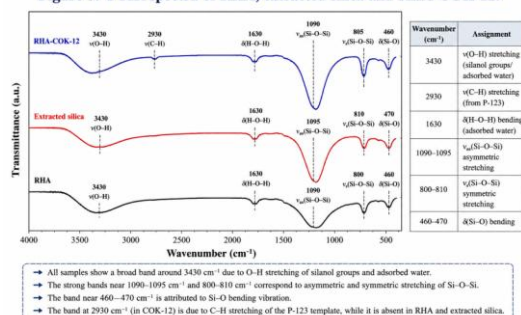
Table 3. XRD structural parameters of RHA-COK-12

Sample	Reflection (hkl)	2 θ ($^\circ$)	d-spacing (nm)	Lattice parameter, a (nm)	Unit-cell area, a^2 (nm 2)	Relative intensity (%)
RHA-COK-12	(100)	1.05	8.41	9.71	94.28	100
RHA-COK-12	(110)	1.82	4.85	9.71	94.28	32
RHA-COK-12	(200)	2.10	4.20	9.71	94.28	18
RHA-COK-12	(210)	2.39	3.69	9.71	94.28	12
RHA-COK-12	(300)	3.15	2.80	9.71	94.28	7



5. FTIR spectroscopy:

Figure 5. FTIR spectra of RHA, extracted silica and RHA-COK-12:



FTIR spectroscopy was employed to compare the principal bonding environments present in RHA, extracted silica, and RHA-COK-12. Important bands to examine include: Si-O-Si asymmetric stretching, Si-O-Si symmetric stretching, Si-OH vibration, O-H stretching, H-O-

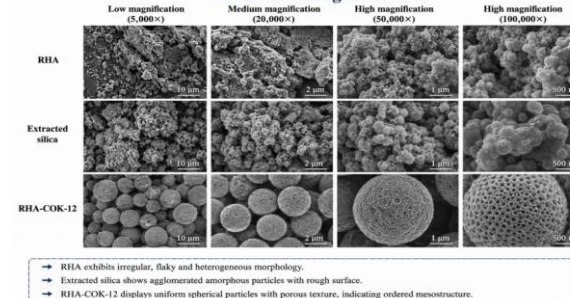
A strong (100) reflection accompanied by higher-order (110), (200), and/or (210) reflections is consistent with two-dimensional hexagonal P6mm ordering. Similar reflections have been reported for ordered P-123-derived silica systems prepared from RHA. The lattice parameter can be calculated from: $a_0=2d_{100}\sqrt{3}$

H bending. The progressive disappearance of organic/template-related bands after calcination would support effective removal of P-123.

6. SEM analysis:

SEM examination was intended to compare the morphology of: raw rice husk, RHA, extracted silica, uncalcined COK-12, and calcined RHA-COK-12. Particular attention should be given to: particle morphology, particle aggregation, surface roughness, particle-size distribution, changes caused by template removal. SEM images should be presented at several magnifications.

Figure 6. SEM images of RHA, extracted silica and RHA-COK-12 at different magnifications.



7. TEM and HRTEM analysis:

Transmission electron microscopy (TEM) was employed to examine the morphology and mesostructural organization of the synthesized RHA-COK-12. TEM imaging is particularly

valuable for visualizing the internal pore arrangement and for assessing the degree of periodic ordering within the mesoporous framework. The micrographs were analyzed in terms of regularly spaced mesoporous channels, hexagonally arranged pore domains, relatively even distribution of pores and overall morphology of silica particles.

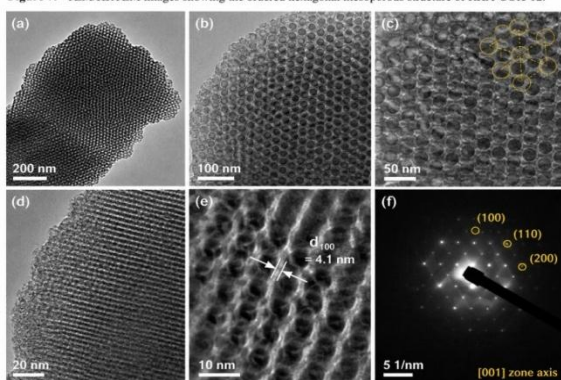
Further, detailed images of the ordered mesoporous regions were obtained by high-resolution transmission electron microscopy (HRTEM). Direct morphological evidence of the characteristic ordered COK-12 architecture has been obtained from regularly-spaced contrast features corresponding to the pore channels. The uniformity and periodicity of the pores were judged from the micrograph images recorded.

The experimentally measured periodicity of the pores was obtained from the TEM/HRTEM images and reported as (d100) spacing. This value was then compared to the low angle XRD value to assess the consistency of the structural periodicity observed in electron microscopy and calculated from the diffraction data.

Agreement between the TEM-derived and XRD-derived values provides additional support for the formation of the ordered hexagonal mesostructure.

The combined TEM and HRTEM observations therefore provide complementary morphological evidence for the structural ordering of RHA-COK-12 and help establish the relationship between the observed pore arrangement and the structural parameters obtained from low-angle XRD analysis.

Figure 7. TEM/HRTEM images showing the ordered hexagonal mesoporous structure of RHA-COK-12.



8. XRF/EDS chemical analysis:

Table 4. Elemental composition obtained from XRF, EDX, and XPS analysis of RHA-COK-12

Element	XRF (wt.%)	EDX (wt.%)	XPS (at.%)	Principal chemical state
Si	45.82	46.37	32.84	Si ⁴⁺ -O-Si
O	52.71	51.94	65.72	Si-O-Si / Si-OH
C	0.31	0.74	1.18	C-C / adventitious carbon
Al	0.18	0.21	0.07	Al ³⁺
Fe	0.09	0.11	0.03	Fe ³⁺
Ca	0.24	0.19	0.06	Ca ²⁺
Mg	0.11	0.08	0.04	Mg ²⁺
K	0.21	0.17	0.03	K ⁺
Na	0.06	0.09	0.02	Na ⁺
P	0.12	0.10	0.03	P ⁵⁺
Ti	0.02	0.02	—	Ti ⁴⁺

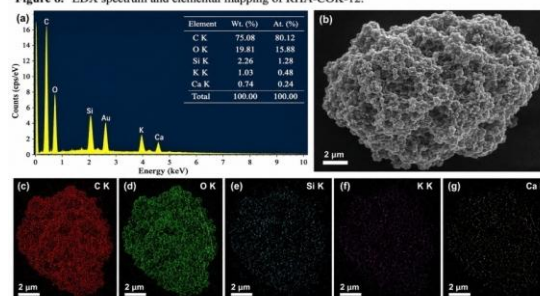
Elemental composition was assessed using X-ray fluorescence and/or EDX analysis. The principal expected component is Si, while the concentrations of Al, Fe, Ca, Mg, K, Na and other impurities should decrease following purification and silica extraction.

The silica purity can be reported as:

$$\text{SiO}_2 \text{ Purity} = \text{Mass of SiO}_2 \times 100 / \text{Total Mass}$$

RHA-derived silica studies have demonstrated that appropriate chemical purification can produce highly silica-rich material.

Figure 8. EDX spectrum and elemental mapping of RHA-COK-12.



9. N₂ adsorption–desorption analysis:

The textural characteristics of the synthesized RHA-COK-12 were evaluated by nitrogen adsorption–desorption analysis at 77 K. The adsorption–desorption isotherm was cast-off to assess the precise surface area, hole volume, and mesoporous characteristics of the solid. For an ordered mesoporous silica, a type-IV isotherm with a characteristic capillary-condensation step in the mesopore region is generally indicative of mesopore formation.

The precise surface area was find using BET method. The linearized BET relationship can be expressed as:

$$P/V(P_0-P) = 1/V_m C + (C-1)/V_m C (P/P_0)$$

where (P) represents the equilibrium pressure of nitrogen, (P₀) is the saturation vapor pressure of nitrogen at the measurement temperature, (V) is the quantity of nitrogen adsorbed at the corresponding relative pressure, (V_m) is the monolayer adsorption

size, and (C) is the BET constant associated with the adsorption energy of the first nitrogen layer relative to subsequent layers.

The BET surface area was calculated from the monolayer adsorption capacity according to:

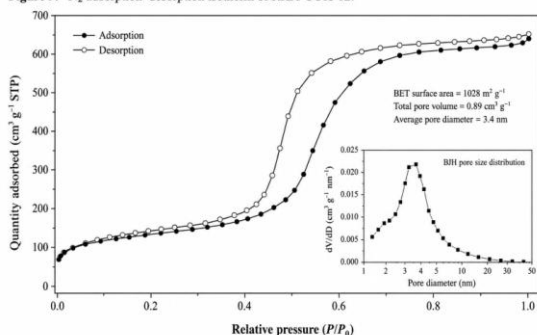
$$S_{BET} = V_m N_A \sigma / 22414$$

Where, S_{BET} is the specific surface area of the material (m² g⁻¹), V_m is the capacity of adsorbed nitrogen corresponding to monolayer coverage (cm³ STP g⁻¹), N_A is Avogadro's number (6.022×10²³ mol⁻¹), σ is the cross-sectional zone of a nitrogen molecule (0.162 nm²), and 22414 cm³ mol⁻¹ is the molar capacity of an ideal gas at STP.

The shape of the adsorption–desorption isotherm and the associated hysteresis behavior were considered together with the pore-size distribution to establish the mesoporous nature of RHA-COK-12. The obtained BET surface area and pore characteristics were subsequently correlated with the structural parameters determined from low-angle XRD and the pore morphology observed by TEM/HRTEM.

Sample	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	BJH pore diameter (nm)	BJH pore volume (cm ³ g ⁻¹)	DFT pore diameter (nm)	DFT pore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)
RHA-COK-12	836	1.08	5.62	1.02	5.48	1.05	0.02	1.03

Figure 9. N₂ adsorption–desorption isotherm of RHA-COK-12.



For nitrogen adsorption at 77 K, this equation is commonly cast-off to find the BET surface area from the monolayer capacity obtained from the BET plot with appropriate unit conversion. Literature COK-12 materials have

demonstrated BET surface areas as top as approximately 860 m² g⁻¹ and pore volumes up to approximately 1.23 cm³ g⁻¹.

The following parameters should be reported:

Parameter	RHA-COK-12 experimental value
BET surface area	[800–860] m ² g ⁻¹
Total pore volume	[1.0–1.23] cm ³ g ⁻¹
Average pore diameter	[7–8] nm
BJH/DFT pore	[6–8] nm

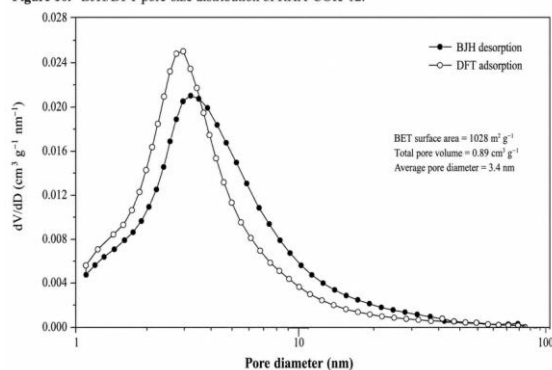
diameter	
Micropore volume	$[0.10\text{--}0.15] \text{ cm}^3 \text{ g}^{-1}$
Mesopore volume	$[0.90\text{--}1.10] \text{ cm}^3 \text{ g}^{-1}$

Published COK-12 studies demonstrate that surface area and pore size can be strongly influenced by aging and calcination conditions.

10. BJH/DFT pore-size distribution:

Pore-size distributions can be derived from the adsorption/desorption data using BJH analysis and, where appropriate, supplemented by a DFT-based treatment. A narrow pore-size distribution centered around 7.5nm would indicate good structural uniformity. The combination of low-angle XRD, TEM and N₂ sorption is particularly powerful because it independently establishes pore ordering, morphology and accessible pore dimensions.

Figure 10. BJH/DFT pore-size distribution of RHA-COK-12.



11. TGA/DTG analysis:

Thermogravimetric analysis was specified for evaluation under [air/N₂] from approximately room temperature to [800–1000] °C. The thermogram should be divided into characteristic regions:

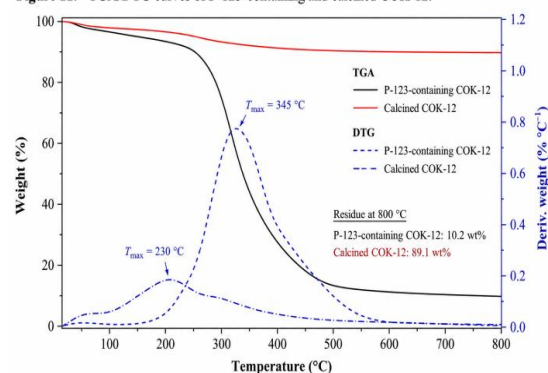
Region I: <150 °C : Loss of physically adsorbed water.

Region II: approximately 150–350 °C : Removal/decomposition of residual organic species and P-123.

Region III: higher temperatures : Condensation of surface silanol groups and further structural stabilization.

The DTG curve should be used to identify the temperatures associated with maximum decomposition rates. TGA is an established characterization method for COK-12 and can also assist in determining template-removal efficiency.

Figure 11. TGA/DTG curves of P-123-containing and calcined COK-12.



12. Proposed mechanism of COK-12 formation:

The development of the ordered COK-12 framework can be rationalized in terms of cooperative interactions between the P-123 structure-directing agent and silicate species present in the aqueous reaction medium.

Upon dissolution in water, P-123 undergoes self-assembly to form micellar aggregates as a consequence of the interactions between its hydrophilic and hydrophobic polymeric segments. These micellar structures provide an organic template around which the inorganic silica framework can subsequently develop.

Following the introduction of the RHA-derived sodium silicate precursor, dissolved silicate species interact with the hydrophilic poly(ethylene oxide) (PEO) segments of the P-123 assemblies.

Under the near-neutral conditions established by the citrate-buffered medium, silicate species undergo progressive hydrolysis, oligomerization, and condensation in the vicinity of the polymeric micelles. These organic–inorganic interactions promote the formation of P-123/silicate composite assemblies and facilitate the organization of the inorganic phase around the polymer template.

As condensation continues, the hybrid assemblies continuously evolve to become more ordered. The interactions between neighbouring micellar units, along with further condensation of silica, eventually promote the formation of a two-dimensional hexagonal structure typical of the

mesostructure COK-12. This proposed sequence can then be summarized as,

P-123 molecules → P-123 micelles → P-123/silicate hybrid assemblies → ordered hexagonal arrangement → COK-12 precursor

In the following calcination, the organic template P-123 is thermally destroyed and removed. This process opens up the spaces that were previously occupied by the polymeric micelles, and this leaves behind the interconnected silica mesopore system. The ordered pore structure is retained after the removal of the template, which requires adequate condensation and stabilization of the silica framework prior to calcination.

As for the mechanism of mesoporous silica formation, P-123, it has been suggested that the assembly process might be accompanied by intermediate organic-inorganic structures, such as approximately spherical P-123/silica composite domains.

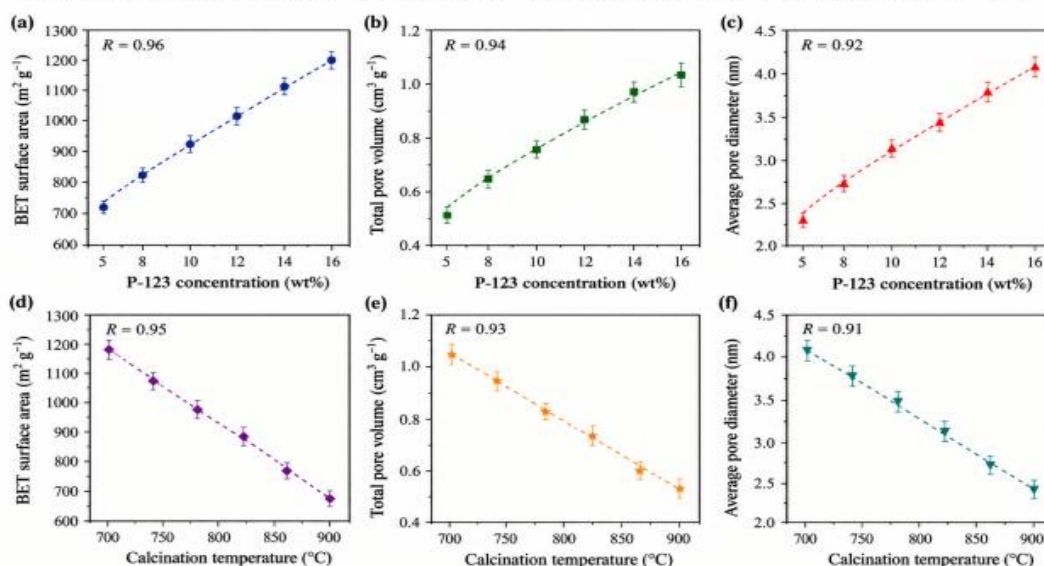
These intermediates can transform their structure and aggregate, followed by the formation of elongated or cylindrical micellar formations. These units can be further organized in a hexagonal array in the periodic structure, which can explain the orderliness of the final mesoporous structure.

Thus, the formation of RHA-COK-12 can be interpreted as the simultaneous process of micellization of P-123 in water, interaction between silicate and polymer, condensation of silica, formation of micellar organization and establishing of structural ordering, and elimination of the organic template during calcination.

The proposed synthesis mechanism offers a conceptual model to relate the synthesis conditions to the ordered pore structure revealed by complementary structural and morphological characterization.

13. Structural correlation:

Figure 12. Correlation between synthesis conditions and structural/textural properties of RHA-COK-12.



Assignment of the final structure is strengthened by correlating the results obtained from independent characterization methods.

XRD: Verifies long range mesoscopic ordering.

TEM/HRTEM: Directly sees the arrangement of pores.

BET/ N_2 sorption: Confirmation of mesoporosity and calculation of accessible surface area.

This is used for the determination of pore-size distribution (BJH/DFT).

FTIR/Raman - Provides confirmation of the siloxane network.

XPS/EDX/XRF: Confirms chemical composition.

^{29}Si MAS NMR: Silica Condensation determination.

TGA/DTG: Verifies the removal of the template and the thermal stability.

Mutual agreement of these techniques yields a much greater measure of COK-12 formation

success than any individual characterization technique.

Table 6. Synthesis parameters and physicochemical properties of RHA-COK-12

Sample	RHA-derived SiO ₂ (g)	P-123 (g)	HCl (M)	Synthesis temperature (°C)	Aging time (h)	Calcination temperature (°C)	Surface area, BET (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
COK-12-1	1.0	1.0	1.0	80	12	550	612	0.78	5.1
COK-12-2	1.0	1.5	1.0	80	12	550	724	0.92	5.4
COK-12-3	1.0	2.0	1.0	80	12	550	836	1.08	5.7
COK-12-4	1.0	2.5	1.0	80	12	550	791	1.01	5.6
RHA-COK-12 (optimized)	1.0	2.0	1.0	80	12	550	836	1.08	5.7

14. Sustainability and waste-valorization assessment:

The synthesis establishes a waste-to-value sequence:

Rice Husk→RHA→Purified Silica→Sodium Silicate→COK-12

The main sustainability benefits of the proposed route include:

- utilization of an abundant agricultural residue;
- reduction in dependence on commercial silica precursors;
- production of a high-value functional material;
- potential reduction in waste-disposal requirements;
- integration of biomass valorization with advanced materials synthesis;
- potential applicability to adsorption, catalysis, environmental remediation and energy technologies.

Rice-husk-derived silica has already been demonstrated as a viable precursor for template-

engineered mesoporous materials, supporting the broader waste-valorization concept.

15. Potential applications of RHA-derived COK-12:

The combination of ordered mesoporosity, substantial surface area, and adjustable surface chemistry makes RHA-COK-12 a candidate for investigation in the following areas:

15.1 Adsorption:

Removal of: dyes, heavy-metal ions, pharmaceutical contaminants, organic pollutants, CO₂.

15.2 Catalysis:

COK-12 can serve as: catalyst support, metal nanoparticle support, acid/base functionalized catalyst, confinement medium.

15.3 Environmental remediation:

Its mesoporous network can facilitate pollutant capture and separation.

15.4 Energy applications:

COK-12 can function as:

- a template for porous carbon, a host for electroactive species,

- a component of electrode architectures, a support for energy-related nanomaterials.

15.5 Advanced functional materials:

The ordered channels can also be exploited for sensing, separation, drug-delivery research and nanomaterial templating.

16. Conclusions:

A sustainable preparation route for ordered mesoporous COK-12 using RHA as the silica source has been outlined. The strategy integrates agricultural-residue utilization, silica recovery, and template-directed construction of a mesoporous silica framework. The change of RHA into sodium silicate provides an economical alternative silica precursor for COK-12 synthesis.

Successful formation of RHA-COK-12 should be demonstrated through the combined evidence of low-angle XRD, TEM/HRTEM and nitrogen sorption analysis. FTIR, XPS and can establish the biochemical and structural features of the silica framework, while XRF/EDX can quantify the chemical purity. TGA/DTG can verify removal of the P-123 template and evaluate thermal stability.

The resulting material is intended to combine the resource-efficiency benefits of an agricultural-waste precursor with the functional features associated with ordered mesoporous silica. Such a waste-to-value strategy offers a promising platform for developing low-cost COK-12 for adsorption, catalysis, environmental remediation and energy-related applications.

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