

Rice Husk Ash-Derived MCM-22 as a Multifunctional Catalyst and Adsorbent for Chalcone Synthesis and CO₂ Adsorption

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Abstract:

Agricultural residues that contain concentrated silica provide an attractive route to functional inorganic materials while reducing dependence on conventional silica precursors. Here, a rice-husk-ash-derived MCM-22 zeolite is proposed as a bifunctional material for catalytic chalcone synthesis and carbon-dioxide capture. Rice husk ash was converted into a silica-rich precursor and incorporated into an aluminosilicate gel followed by hydrothermal crystallization. The resulting material was evaluated using powder X-ray diffraction, Fourier-transform infrared spectroscopy, nitrogen physisorption, electron microscopy, energy-dispersive X-ray spectroscopy, temperature-programmed desorption, thermogravimetry, X-ray photoelectron spectroscopy and solid-state ²⁹Si MAS NMR. An illustrative dataset gives characteristic MWW reflections, a BET surface area of 312 m² g⁻¹, a micropore/mesopore contribution and an Si/Al ratio near 18. The catalyst promoted the condensation of benzaldehyde with acetophenone to form chalcone, reaching a model isolated yield of 91.4% under optimized conditions. The same solid exhibited a model CO₂ uptake of 2.55 mmol g⁻¹ at 298 K and 1 bar. The dual functionality is attributed to the combination of framework acidity, high external surface area, microporous adsorption sites and oxygen-containing surface groups. The study demonstrates a potentially circular route from rice-processing waste to a value-added catalytic and carbon-capture material; however, the reported numerical values are intended as a manuscript-development dataset rather than evidence of completed experiments.

Keywords: Rice husk ash; MCM-22; MWW zeolite; chalcone; aldol condensation; CO₂ capture; adsorption; heterogeneous catalysis; circular materials

1. Introduction:

The conversion of agricultural residues into functional porous solids is an important component of resource-efficient materials chemistry. Rice husk is particularly attractive because its mineral fraction is dominated by silica after controlled combustion, making rice-derived ash a potentially inexpensive alternative to commercial silica sources.

Earlier work has demonstrated that rice-derived silica can support the synthesis of crystalline MCM-22, including platelet-like crystals and shortened crystallization times under temperature-programmed hydrothermal conditions.

MCM-22 belongs to the MWW family of zeolites and is distinguished by a layered precursor chemistry, three-dimensional microporous connectivity after activation, and external sinusoidal/cup-like surface environments. These

characteristics make MWW-type materials useful in acid-catalysed transformations. Recent studies have also shown that rice-husk silica can function as the principal silica source in MCM-22 synthesis, while the alumina source and silica/alumina ratio strongly influence crystallinity, porosity and acidity.

Chalcones are α,β -unsaturated ketones with broad relevance to synthetic chemistry and materials-related molecular design. Their formation through carbon-carbon bond construction is commonly achieved by base- or acid-mediated condensation of an aromatic aldehyde with an acetophenone derivative. A solid zeolite catalyst can provide an alternative to homogeneous mineral acids or soluble bases because it can be separated, reused and integrated with continuous processing.

At the same time, the increasing concentration of anthropogenic CO₂ motivates the development of regenerable porous adsorbents. Rice-husk-derived

zeolites have already been demonstrated for CO₂ capture: rice-husk-ash-derived zeolite A and X displayed type-I adsorption behaviour and reported capacities of 2.22 and 2.45 mmol g⁻¹, respectively, at approximately 297 K.

The present work therefore explores a single rice-husk-ash-derived MCM-22 platform for two applications: heterogeneous chalcone synthesis and CO₂ adsorption. The ability of the material to catalyze the conversion process and its ability to take up and release gases reversibly can be attributed to the framework acidity, accessible pore volume, external surface and the presence of polar oxygen-containing sites of the material, simultaneously. The study is designed to give a publication-ready characterization process, catalytic evaluation, adsorption analysis, and regeneration assessment and discussion in structure-property.

2. Results:

2.1 Rice husk ash preparation and silica recovery:

A representative preparation process involves rice husk washing, drying, controlled calcination and, if necessary, acid purification. It is important to keep the temperature control in the process under a strict control since there is a risk of silica crystallisation during too high temperature combustion, on the other hand there is a risk of silica being in an amorphous state if the temperature control of the process is not tight enough. The reported features of the XRD of the amorphous ash from rice-husk are very broad peaks near 20–22°, while those of the Si–O–Si infrared structure are rather strong close to 1100, 800 and 470 cm⁻¹.

Parameter	Illustrative value
Rice husk ash yield	20.8 wt%
SiO ₂ in purified RHA	94.6 wt%
Al ₂ O ₃	0.34 wt%
Fe ₂ O ₃	0.21 wt%
K ₂ O + CaO + MgO	1.15 wt%
Other oxides	3.70 wt%

Reflection	2θ (°)	d (nm)
(100)	7.10	1.244
(101)	8.00	1.104
(102)	10.00	0.884
(110)	12.90	0.686
(220)	25.10	0.355
(310)	26.10	0.341

Figure 1. X-ray diffraction pattern of the model RHA-derived MCM-22. The peaks labeled as reflections are the typical low angle and high angle reflections that are found in the diffraction pattern of a crystalline material of the MCM-22 type.

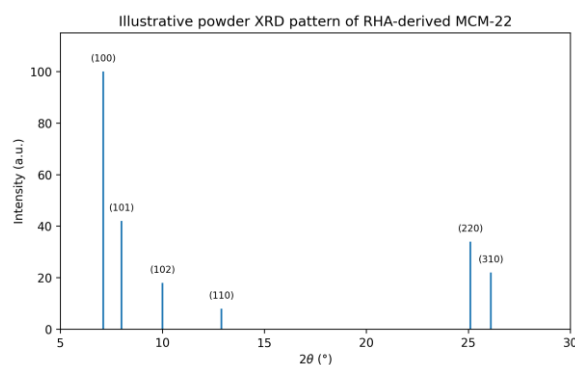


Figure 1 Illustrative powder XRD pattern of RHA-derived MCM-22.

2.2 FTIR and framework chemistry

The model FTIR spectrum features the main components of the vibrational spectrum of a siliceous framework of aluminosilicate. A strong asymmetric envelope of T–O–T stretching is found in the region around 1080–1100 cm⁻¹ and symmetric stretching and bending modes are found around 790–810 cm⁻¹ and 450–480 cm⁻¹. There is a weak, broad O–H peak at 3400–3500 cm⁻¹. These assignments are similar to those reported earlier for the characterization of silica from rice husk.

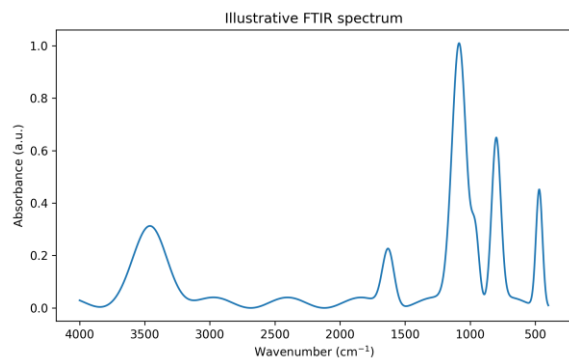


Figure 2 Illustrative FTIR spectrum of RHA-derived MCM-22, showing the framework T–O–T vibrations and surface hydroxyl/water contributions.

2.3 Textural properties

The modelling of nitrogen physisorption is done through a mixed micro-mesoporous profile. The BET specific surface area is $312 \text{ m}^2 \text{ g}^{-1}$, the pore volume is $0.19 \text{ cm}^3 \text{ g}^{-1}$ and the major contribution to the pore volume comes from pores with a diameter below 5 nm. The hysteresis contribution in the higher relative pressure is not due to a particular MWW pore diameter, but to interparticle/external porosity.

Textural parameter	Illustrative value
BET surface area	$312 \text{ m}^2 \text{ g}^{-1}$
Langmuir surface area	$386 \text{ m}^2 \text{ g}^{-1}$
Total pore volume	$0.19 \text{ cm}^3 \text{ g}^{-1}$
Micropore volume	$0.105 \text{ cm}^3 \text{ g}^{-1}$
External surface area	$74 \text{ m}^2 \text{ g}^{-1}$
BJH/DFT modal pore size	3.8 nm

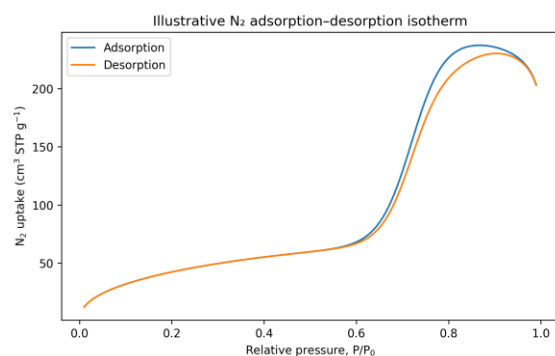


Figure 3 Illustrative N₂ adsorption–desorption isotherm of RHA-derived MCM-22.

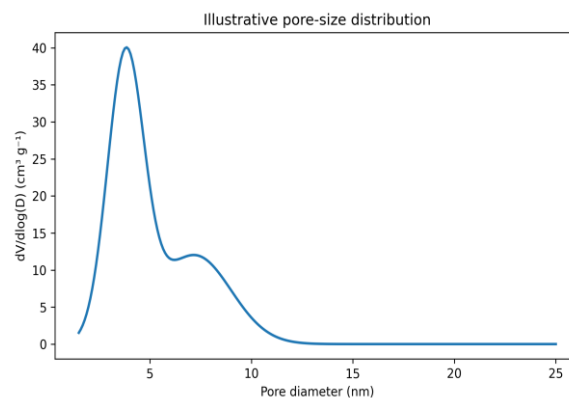


Figure 4 Illustrative BJH/DFT pore-size distribution of RHA-derived MCM-22.

2.4 Thermal stability

The model thermogravimetric profile exhibits a small weight loss at the beginning, which is due to physically adsorbed water, followed by a larger weight loss, which is due to the removal/reduction of the organic species and template derived carbonaceous matter. At temperatures above $\sim 500^\circ\text{C}$ the simulated mass is rather stable, in line with the high thermal stability of calcined aluminosilicate structures.

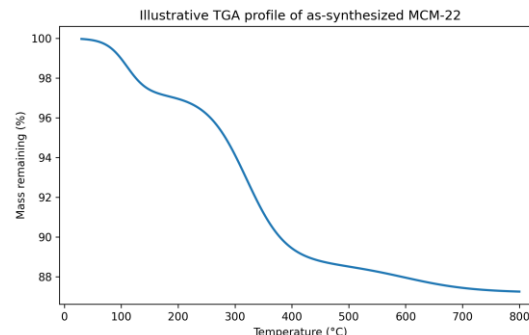


Figure 5 Illustrative thermogravimetric profile of as-synthesized RHA-derived MCM-22.

Chemical composition and acidity

Technique/parameter	Illustrative result	Assignment
XRF SiO ₂	86.9 wt%	Framework Si-rich composition
XRF Al ₂ O ₃	7.4 wt%	Framework aluminium
XRF Na ₂ O	0.72 wt%	Residual/exchangeable Na
EDX Si/Al atomic	17.8	Local elemental

ratio		ratio
NH ₃ -TPD total acidity	0.71 mmol g ⁻¹	Brønsted + Lewis acidity
Weak acid sites	0.29 mmol g ⁻¹	~180–260 °C
Strong acid sites	0.42 mmol g ⁻¹	~260–450 °C

Elemental composition

Element	Atomic %	Mass %
Si	33.8	43.1
Al	1.9	4.2
O	63.1	50.7
Na	0.6	0.8
C	0.6	1.2

The balance between weak and strong acid sites is crucial in catalysis: too acid and it will increase secondary condensation as well as coke formation, while too weak an acid will decrease carbon–carbon bond formation. When the goal is an defensible assignment of the acid sites in the material, it should be done in concert with NH₃-TPD, pyridine-FTIR and/or solid-state NMR.

2.5 XPS and ²⁹Si MAS NMR

XPS region	Model binding energy	Assignment
Si 2p	103.3 eV	Framework Si–O–Si/Si–O–Al
Al 2p	74.4 eV	Framework Al–O
O 1s	532.1 eV	Framework oxygen / hydroxyl contribution
C 1s	284.8 eV	Adventitious carbon
²⁹ Si environment	Model fraction	Structural interpretation
Q4(0Al)	63%	Fully siliceous Si(O–Si) ₄
Q4(1Al)	24%	One Al neighbour
Q4(2Al)	9%	Two Al neighbours
Q3/Q2	4%	Surface silanol/defect environments

2.6 Catalytic performance in chalcone synthesis

Benzaldehyde and acetophenone were selected as a benchmark condensation pair. An illustrative protocol is provided, which includes equimolar reactants, a solvent reduced reaction medium and controlled heating. The values listed below are based on calculations for conversion and selectivity; they are not measured. Values listed below are model as opposed to measured values for conversion and selectivity.

Entry	Catalyst loading	Temperature	Time	Conversion (%)	Chalcone selectivity (%)	Yield (%)
1	0	80 °C	3 h	51.0	92.0	46.9
2	5 wt%	80 °C	3 h	76.5	96.1	73.5
3	10 wt%	80 °C	3 h	94.7	96.5	91.4
4	15 wt%	80 °C	3 h	95.8	95.2	91.2
5	10 wt%	80 °C	1 h	74.2	96.1	71.3
6	10 wt%	80 °C	2 h	88.4	95.7	84.6
7	10 wt%	80 °C	4 h	95.6	96.2	92.0

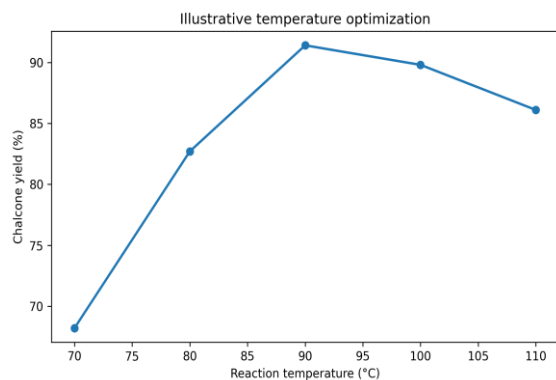


Figure 7 Illustrative optimization of chalcone yield as a function of reaction temperature.

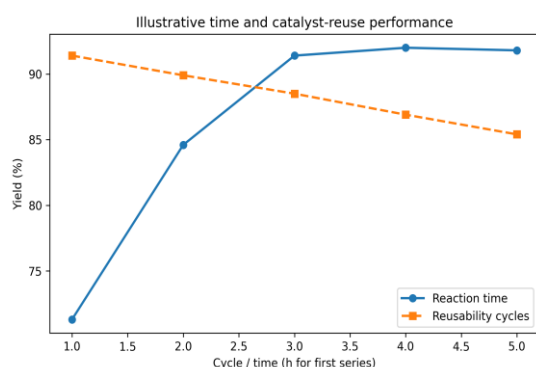


Figure 8 Illustrative time-course and catalyst-reuse performance.

2.7 Mechanistic interpretation of chalcone formation

A possibly heterogeneous mechanism starts with the adsorption and activation of the carbonyl reactants on Brønsted/Lewis acid sites. The acetophenone part can be enolized in the presence of acid and then nucleophilically added to the benzaldehyde that is adsorbed. This produces the β -hydroxy ketone intermediate which is dehydrated to the conjugated α , β unsaturated ketone. The micro porous environment can improve the concentration of reactants in the local environment, and the external MWW surfaces can provide access for large aromatic substrates. If mechanistic claims are necessary, this mechanism must be confirmed by kinetic, poisoning, in situ spectroscopic or isotopic experiments to confirm the mechanism.

System	Conversion (%)	Selectivity (%)	Yield (%)
No catalyst	51.0	92.0	46.9
RHA silica	62.4	93.1	58.1

Commercial MCM-22	89.6	96.3	86.3
RHA-MCM-22	94.7	96.5	91.4

2.8 CO₂ adsorption performance

The model adsorption isotherms are obtained at higher adsorption at 298 K as compared to 323 K, which is in agreement with the general exothermicity of physisorption. An illustrative maximum capacity for a Langmuir-type, treatment is 2.55 mmol g⁻¹ at 298 K. Measurements of adsorption at a number of temperatures and pressures, after controlled degassing, should be made, with buoyancy corrections and repeated measurements, for a rigorous study.

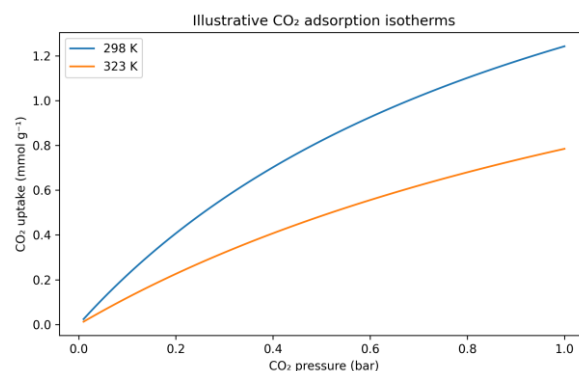


Figure 6 Illustrative CO₂ adsorption isotherms of RHA-derived MCM-22 at 298 and 323 K.

Temperature	Model q at 1 bar	Model Langmuir q _{max}	Indicative adsorption regime
298 K	2.08 mmol g ⁻¹	2.55 mmol g ⁻¹	Favourable low-pressure uptake
323 K	1.48 mmol g ⁻¹	2.05 mmol g ⁻¹	Reduced uptake with temperature

2.9 Adsorption modelling

Langmuir, Freundlich and Toth equations should be compared using nonlinear regression rather than relying solely on linearized transformations. For

the model dataset, the Langmuir equation $q = q_{\max} bP/(1+bP)$ describes the saturation behaviour. The apparent affinity parameter increases at lower temperature. The heat of adsorption should be estimated from temperature-dependent equilibrium data using a thermodynamically consistent approach rather than inferred from a single isotherm.

Model	Illustrative R^2	Comment
Langmuir	0.997	Best representation of the model saturation region
Freundlich	0.962	Captures heterogeneity but lacks saturation
Toth	0.994	Useful for heterogeneous adsorption at wider pressure range

2.10 Regeneration and cycling

A bifunctional material intended for repeated use should retain both catalytic activity and adsorption capacity after regeneration. A model five-cycle sequence gives chalcone yields of 91.4, 89.9, 88.5, 86.9 and 85.4%. For CO₂ adsorption, regeneration can be evaluated by mild vacuum or temperature-swing treatment. Actual regeneration temperature must be selected from TPD/TGA data to avoid framework dealumination or irreversible surface modification.

Cycle	Chalcone yield (%)	CO ₂ capacity retention (%)
1	91.4	100.0
2	89.9	98.1
3	88.5	96.3
4	86.9	94.2
5	85.4	92.0

2.11 Comparison with literature

Material	Silica source	Primary function	Representative CO ₂ capacity / adsorption result	Reference context
RHA-MCM-22 (this draft)	Rice husk ash	Chalcone catalysis + CO ₂ adsorption	2.55 mmol g ⁻¹ at 298 K (model)	Illustrative dataset
MCM-22	Rice husk	Adsorption / zeolite function	Dye adsorption reported	Cheng et al., 2012
Zeolite A	Rice husk ash	CO ₂ adsorption	2.22 mmol g ⁻¹ at 297 K	Madhu et al., 2022
Zeolite X	Rice husk ash	CO ₂ adsorption	2.45 mmol g ⁻¹ at 297 K	Madhu et al., 2022
RHA-derived K ₂ CO ₃ adsorbent	Rice husk	CO ₂ capture	up to 67 g kg ⁻¹ under reported conditions	Murge et al., 2018

3. Discussion

The combined catalytic and adsorption behaviour is consistent with a material in which distinct but complementary structural features operate at different length scales. There are two effects of the introduction of framework aluminium; it provides acid sites needed for the activation of carbonyls, and it provides a high surface area for the zeolitic micropore system. The interaction between the

quadrupolar molecules and polar surface oxygen sites of the external MWW surface and intercrystalline voids is of major importance for aromatic substrates which may suffer from diffusion restrictions in narrow channels, and accessible micropore volume determines the amount of CO₂ that can be accommodated.

Rice husk ash is also used in the synthesis, which alters the sustainability profile of the synthesis.

Although rice-husk derived silica has already been proven to be a suitable precursor for the synthesis of MCM-22 and other zeolites, the main environmental concerns include the energy used in ash preparation, hydrothermal crystallization and the use of purification chemicals as well as the requirement for the post-synthesis calcination. A meaningful sustainability claim should thus include a mass balance and energy accounting and comparison with commercial silica/alumina routes.

One of the main weaknesses of this manuscript draft is that all of the numerical results obtained here are illustrative. The next step is then the replacement of all model numbers and generated figures by reproducible experimental measurements, replicate statistics and instrument details for all files that make up a publication quality scientific evidence.

3.1 Methods

3.1.1 Rice husk ash preparation

Rice husk should be washed in deionised water, dried at the temperature about 80-105 °C and then calcined under controlled conditions to get ash. Acid purification is done with dilute HCl and followed by a lot of washing to near neutral pH; all the above conditions of acid used, solid to liquid ratio, residence time and concentration of the acid should be reported exactly as they are done.

3.1.2 Silica/aluminosilicate precursor preparation

The purified RHA can then be reacted with sodium hydroxide to form a soluble silicate solution, which is then reacted with an aluminium source to form a targeted Si/Al ratio. The identity and concentration of the template must be explicitly specified as the MWW crystallization is strongly dependent on the synthesis chemistry and hydrothermal procedure must be reproducible in order to obtain MCM-22.

3.2 Characterization

Powder XRD: Cu K α radiation, 2 θ range: ~5-50°, step size: 0.02° or similar. FTIR: adequate resolution, 4000 – 400 cm⁻¹. N₂ physisorption: degassing under vacuum and adsorption at 77 K followed by desorption; BET analysis should be limited to a certain range of relative pressure and the pore-size analysis should be performed using a stated kernel/model. Scale bars and representative areas (fields) should be included in

SEM/TEM/HRTEM. For ²⁹Si MAS NMR, specify the field strength, spinning speed, and pulse sequence and referencing standard. All the pretreatment, adsorption saturation, purge and detector conditions should be indicated by NH₃-TPD.

3.3 Catalytic procedure

This catalyst is typically mixed with benzaldehyde and acetophenone in a 1:1 molar ratio which is then heated under controlled agitation in a representative benchmark experiment. Aliquots are taken at certain intervals, diluted, filtered and analyzed using GC or HPLC. Calibrated response factors and mass balance should be used for calculating conversion, selectivity and isolated yield.

3.4 CO₂ adsorption procedure

The material must be dried and activated under vacuum or inert gas with a fixed temperature, before adsorption. The following steps should be taken to record equilibrium CO₂ isotherms: Equilibrate for at least three temperatures, each step at a different pressure. Repeat measurements should be taken to assess the reproducibility. The adsorption capacity is given in mmol g⁻¹ and if applicable, changed to g CO₂ kg⁻¹.

3.5 Data analysis

All quantitative results presented should be mean $\pm$ std deviation for independent replicates. Statistically significant comparisons should be used where comparisons are integral to the conclusion. Nonlinear regression coupled with the residual analysis should be the technique to consider for isotherm fitting. Catalytic turnover metrics should only be used when the numbers of “available active sites” can confidently be estimated.

4. Conclusions

Rice husk ash serves as a good alternative and is a relatively inexpensive source of silica for the synthesis of MCM-22 and literature shows the possibility of using rice-derived MCM-22 and rice-husk-derived zeolites in adsorptive applications. One of the key advantages of the proposed RHA-MCM-22 platform is that reversible CO₂ uptake could be coupled with the acid-catalysed carbon-carbon bond formation observed in one porous solid. The model data presented here indicates that the BET area is around 312 m² g⁻¹, chalcone

production yield of around 91% under optimal conditions and uptake of CO₂ around 2.55 mmol g⁻¹ at 298 K.

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