

# Sustainable Synthesis of MCM-22 from Rice Husk Ash: Characterization, Catalytic Optimization, and Reusability in Knoevenagel Condensation

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## Abstract:

Agricultural residues provide promising precursors for sustainable catalyst development. In this study, rice husk ash (RHA), a silica-rich biomass waste, was used as the silica source for synthesizing MCM-22 zeolite. The resulting RHA-MCM-22 was modified with nickel by impregnation/ion-exchange to produce Ni/MCM-22 catalysts with tailored physicochemical and catalytic properties. The materials were considered by powder Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy–energy-dispersive spectroscopy (SEM–EDS), nitrogen adsorption–desorption, thermogravimetric analysis (TGA), inductively coupled plasma optical emission spectroscopy (ICP-OES), NH<sub>3</sub>-temperature-programmed desorption (NH<sub>3</sub>-TPD), pyridine-FTIR, H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR), and X-ray photoelectron spectroscopy (XPS). Catalytic activity was assessed using the Knoevenagel condensation of benzaldehyde with malononitrile. The effects of catalyst loading, nickel content, reaction temperature, reaction time, solvent, and reactant ratio were examined to establish suitable conditions. Optimized catalyst was further tested with various substrates, multiple cycles and post-reaction characterization. Nickel incorporation is believed to change the number and/or acid–base character of the sites, but not the MWW framework of the MCM-22. The work shows a practical approach to recycling RHA to become value-added, reusable zeolitic catalysts, which further facilitates waste utilization, while decreasing the reliance on commercial silica and greener carbon–carbon bond formation by improved resource efficiency and less environmental burden in general.

**Keywords:** Rice husk ash; MCM-22; nickel; Ni/MCM-22; zeolite.

## 1. Introduction

Renewable and waste products as raw materials for inexpensive materials are becoming increasingly attractive as a source for heterogeneous catalysts, and this has led to substantial interest in these materials. The agricultural residues are usually rich resources, very cheap, and often have high levels of inorganic materials that can be extracted to provide value added products. One such agricultural residue, which after carefully combustion, has a significant silica content, is rice husk. Rice-husk silica is therefore regarded as a potential silica source for zeolite synthesis, and thus, has received a lot of attention. It was previously shown that MCM-22 could be prepared under hydrothermal conditions using rice husk silica as a

source of silica and K<sub>2</sub>CO<sub>3</sub> as a structure-directing agent with high crystallinity<sup>1</sup>.

MCM-22 belongs to the MWW family of zeolitic materials and has a unique precursor layered structure that transforms to a three-dimensional microporous structure after a proper thermal treatment. It has a high surface area and microporosity, as well as an appropriate distribution of acid sites, which make it very interesting for catalytic use. Typical characterization methods of MCM-22 include XRD, FTIR, electron microscopy, thermal analysis and nitrogen adsorption and acidity measurements.

The catalytic properties of zeolites can be modified by ion exchange, impregnation and dealumination,

metal incorporation and surface functionalization. Nickel is especially interesting because  $\text{Ni}^{2+}$  species can interact with the aluminosilicate framework, and alter the electronic, acidic and adsorption properties of the parent material. The preparation of Ni/MCM-22 catalysts by impregnation and their use in other catalytic reactions have shown the possibility of preparing Ni-containing MCM-22 structure.

The Knoevenagel condensation is an important carbon-carbon bond-forming reaction between aldehydes or ketones and active methylene compounds such as malononitrile, ethyl cyanoacetate or malonic ester. The resulting  $\alpha,\beta$ -unsaturated compounds have applications as intermediates in pharmaceutical, fine-chemical and materials synthesis. Heterogeneous zeolite catalysts are attractive for this reaction because they can provide "acidic, basic or bifunctional catalytic sites and can be separated from the reaction mixture. Previous studies have demonstrated that modified MCM-22 materials can exhibit significant catalytic activity in Knoevenagel condensation, with acid-base synergy playing an important role.

Despite these developments, the combination of an agricultural-waste-derived MCM-22 support with nickel modification for Knoevenagel condensation has received comparatively limited attention. Therefore, the present work aims to develop a sustainable Ni/MCM-22 catalyst using rice husk ash as the silica source and to establish relationships between synthesis conditions, physicochemical properties, nickel dispersion, surface acidity/basicity and catalytic activity.

The specific objectives were:

1. To recover high-purity silica from rice husk ash.
2. To synthesize MCM-22 using RHA-derived silica.
3. To modify the resulting MCM-22 with different nickel loadings.
4. To establish the structural, morphological, textural and acidic properties of the catalysts.

5. To optimize the Knoevenagel condensation reaction using benzaldehyde and malononitrile.

6. To investigate the influence of Ni loading on catalytic activity.

7. To determine the reaction kinetics and apparent activation energy.

8. To explore the scope of the substrate and recyclability of the catalyst.

9. To test structural stability of the recovered catalyst.

## 2. Materials and methods

### 2.1. Materials

Rice husk was collected from a local rice-processing facility in [location]. Sodium hydroxide, hydrochloric acid, sodium aluminate, hexamethyleneimine (HMI), nickel(II) nitrate hexahydrate  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , benzaldehyde, malononitrile and organic solvents were obtained from [supplier]. All chemicals were analytical grade and used without further purification unless otherwise stated. Deionized water was used throughout the synthesis.

### 2.2. Preparation of rice husk ash

The collected rice husk was initially washed several times with tap water followed by deionized water to remove soil, dust and soluble impurities. The washed material was dried at 105 °C for 12 h.

The dried rice husk was combusted under controlled conditions in a muffle furnace at [500–700] °C for [3–6] h. The resulting ash was ground and sieved to get a unchanging particle size.

The ash yield was calculated according to:  $\text{Ash yield (\%)} = m_{\text{RHA}} \times 100 / m_{\text{RH}}$  where  $m_{\text{RHA}}$  is the mass of rice husk ash and  $m_{\text{RH}}$  is the initial dry mass of rice husk. The chemical composition of RHA was resolute by XRF and/or ICP-OES.

### 2.3. Extraction of silica from rice husk ash

Silica in rice husk ash was converted into soluble sodium silicate by treating with aqueous NaOH. A representative method used was the dispersion of RHA in NaOH solution with the ratio of solid-to-

liquid [1:x] g mL<sup>-1</sup>. The suspension was then stirred at [80-100] °C for [1-4] h during the suspension. It was filtered to ensure that the insoluble residues were removed. Slowly added HCl acidified the solution to a pH of around 7-8, which resulted in hydrated silica being formed<sup>2-3</sup>. The precipitated silica was aged for [12-24] h, washed repeatedly with deionized water and dried at 100-110 °C. The extracted rice husk silica was designated RHS. Silica recovery was calculated using: Silica recovery (%) =  $m_{\text{RHS}} \times 100 / m_{\text{SiO}_2, \text{RHA}}$

### 3. Synthesis of RHA-derived MCM-22

MCM-22 was synthesized by a hydrothermal route using RHS as the principal silica source. The synthesis gel was prepared using RHS, sodium hydroxide, sodium aluminate, HMI and deionized water. The final gel composition should be reported in molar ratios:

$$\text{SiO}_2/\text{Al}_2\text{O}_3 = [\text{X1}], \text{H}_2\text{O}/\text{SiO}_2 = [\text{X2}]$$

$$\text{Na}_2\text{O}/\text{SiO}_2 = [\text{X3}], \text{HMI}/\text{SiO}_2 = [\text{X4}]$$

The synthesis mixture was stirred until a homogeneous gel was obtained and subsequently aged for [n] h. The hydrothermal crystallization was conducted in a Teflon-lined stainless-steel autoclave under autogenous pressure. A temperature-programmed route may be employed:

Stage I: 50 °C for 24 h

Stage II: 100 °C for 24 h

Stage III: 150 °C for 24 h

This approach is supported by previous work demonstrating that varying-temperature hydrothermal treatment can substantially reduce the crystallization period of RHA-derived MCM-22. After crystallization, the hard product was recovered by centrifugation or filtration, methodically washed with deionized water until neutral pH and dried at 100-110 °C. The dried product was calcined in air using a controlled heating rate of [1-5] °C min<sup>-1</sup> to [500-600] °C for [4-8] h to remove the organic structure-directing agent<sup>4-5</sup>. The calcined material was designated RHA-MCM-22.

### 4. Nickel modification of RHA-MCM-22

Nickel was introduced onto RHA-MCM-22 by incipient-wetness saturation. Appropriate amounts of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in deionized water to obtain nominal Ni loadings of:

1 wt%, 3 wt%, 5 wt%, 7 wt%, 10 wt%

The required nickel precursor solution was slowly added to the calcined MCM-22 under continuous stirring to achieve incipient wetness. The resulting material was aged for [12] h and dried at 110 °C instant. The dried samples were calcined in air at [450-550] °C for [4-6] h.

The catalysts were designated:

**Ni<sub>1</sub>/MCM-22, Ni<sub>3</sub>/MCM-22, Ni<sub>5</sub>/MCM-22,  
Ni<sub>7</sub>/MCM-22 and Ni<sub>10</sub>/MCM-22**

The optimum catalyst identified from the screening experiments was designated Ni<sub>x</sub>/RHA-MCM-22. For comparison, unmodified RHA-MCM-22 was used as the parent catalyst.

## 5. Catalyst characterization

### 5.1. X-ray diffraction

Powder XRD patterns were recorded using Cu Kα radiation over a 2θ range of approximately 3-50° at a scanning rate of [X]° min<sup>-1</sup>. The characteristic reflections of MCM-22 should be identified and compared with literature data. The degree of crystallinity was calculated relative to a reference MCM-22 sample:

$$\text{Relative crystallinity (\%)} = I_{\text{sample}} \times 100 / I_{\text{reference}}$$

where I represents the integrated intensity of selected characteristic reflections.

### 5.2. FTIR spectroscopy

FTIR spectra were noted in the varies 400-4000 cm<sup>-1</sup> using KBr pellets or ATR mode. Expected bands should include:

1. O-H stretching of surface hydroxyl groups;
2. asymmetric T-O-T stretching;
3. symmetric T-O-T vibrations;
4. framework vibration associated with MWW topology;
5. external/internal silanol bands.

Comparison of RHA-MCM-22 and Ni/RHA-MCM-22 will determine whether nickel modification produces measurable changes in the framework vibrational environment.

### 5.3. SEM-EDS

SEM was working to examine morphology and particle aggregation. EDS mapping was used to control the spatial distribution of Si, Al, O and Ni.

We report:

Particle morphology; average particle/crystal size; Ni distribution; Si/Al ratio; Ni atomic or weight percentage.

### 5.4. TEM/HRTEM

TEM should be used to examine the characteristic platelet-like morphology of MCM-22 and the dispersion of nickel species. For the optimized catalyst, HRTEM should be used where possible to determine whether Ni exists as: isolated/dispersed species; nanosized NiO domains; larger Ni-containing particles. If lattice fringes of NiO are observed, the corresponding interplanar spacing should be reported from the experimental image rather than assumed.

### 5.5. N<sub>2</sub> adsorption-desorption

N<sub>2</sub> adsorption-desorption measurements should be performed at -196 °C after degassing at [250–350] °C. The following properties should be reported:

BET surface area; micropore volume; total pore volume; external surface area; average pore diameter.

The BET surface area should be calculated using the appropriate linear pressure region rather than selecting an arbitrary range. MCM-22 commonly exhibits substantial microporosity, and literature examples report BET surface areas in the several-hundred-m<sup>2</sup> g<sup>-1</sup> range.

### 5.6. ICP-OES

The actual nickel loading should be determined by ICP-OES after complete digestion of the catalyst. The nominal and experimentally determined Ni contents should be compared:

$$\text{Ni incorporation efficiency} = \frac{\text{actual Ni loading}}{\text{nominal Ni loading}} \times 100$$

This analysis is particularly important because impregnation efficiency cannot be established reliably from the precursor concentration alone.

### 5.7. TGA/DTG

The TG analysis should be performed from about 25 °C to 800 °C, in a stream of air or inert gas. The weight-loss regions should be attributed to: physically adsorbed water, decomposition/removal of HMI, condensation of surface hydroxyl groups, decomposition of residual nitrate or organic species. The thermal stability of the final calcined catalyst should also be determined.

### 5.8. NH<sub>3</sub>-TPD

To quantify the acidic sites, NH<sub>3</sub>-TPD should be conducted. The desorption profile can be subdivided into: weak acid sites, medium strength of acid sites and strong acid sites. The total acidity measured should be reported as μmol NH<sub>3</sub> g<sup>-1</sup>. The correlation between catalytic performance and changes after nickel modification should be made.

### 5.9. CO<sub>2</sub>-TPD

Due to the basic activation requirements of Knoevenagel condensation, CO<sub>2</sub>-TPD should preferably be present. The CO<sub>2</sub> desorption profile can provide information regarding: medium basic sites; weak basic sites; strong basic sites. This characterisation is especially convenient for establishing an acid-base relationship instead of the catalytic activity being just due to the presence of Ni.

### 5.10. Pyridine-FTIR

Pyridine adsorption followed by FTIR spectroscopy should be used to distinguish: The characteristic reflections of MCM-22 should be identified and compared with literature data. The degree of crystallinity was calculated relative to a reference MCM-22 sample: where *I* represents the integrated intensity of selected characteristic reflections. FTIR spectra were noted in the varies 400–4000 cm<sup>-1</sup> using KBr pellets or ATR mode.

Expected bands should include:

O–H stretching of surface hydroxyl groups;  
asymmetric T–O–T stretching;

symmetric T–O–T vibrations; framework vibration  
associated with MWW topology;

external/internal silanol bands.

Comparison of RHA-MCM-22 and Ni/RHA-MCM-22 will determine whether nickel modification produces measurable changes in the framework vibrational environment.

#### 5.11. SEM–EDS

SEM was working to examine morphology and particle aggregation. EDS mapping was used to control the spatial distribution of Si, Al, O and Ni. The manuscript should report:

Particle morphology; average particle/crystal size; Ni distribution; Si/Al ratio; Ni atomic or weight percentage.

#### 5.12. TEM/HRTEM

TEM should be used to examine the characteristic platelet-like morphology of MCM-22 and the dispersion of nickel species. For the optimized catalyst, HRTEM should be used where possible to determine whether Ni exists as: isolated/dispersed species; nanosized NiO domains; larger Ni-containing particles. If lattice fringes of NiO are observed, the corresponding interplanar spacing should be reported from the experimental image rather than assumed.

#### 5.13. N<sub>2</sub> adsorption–desorption

N<sub>2</sub> would MCM-22 reflections would indicate that the nickel loading, this its carbonyl oxygen with Lewis-acidic centers associated with the zeolite/Ni environment. Simultaneously, the acidic methylene proton of malononitrile is activated by be comprehensively evaluated by XRD, FTIR, SEM–EDS, TEM, N<sub>2</sub> physisorption, ICP-OES, TGA, NH<sub>3</sub>-TPD, CO<sub>2</sub>-TPD, pyridine-FTonitrile provides a suitable probe reaction for evaluating the catalytic functionality of the materials.

Systematic variation of with structural stability and low nickel leaching would establish Ni/RHA-MCM-

22 as a promising sustainable adsorption–desorption measurements should be performed at –196 °C after degassing at [250–350] °C.

The following properties should be reported: BET surface area; micropore volume; total pore volume; external surface area; average pore diameter. MCM-22 commonly exhibits substantial microporosity, and literature examples report BET surface areas in the several-hundred-m<sup>2</sup> g<sup>–1</sup> range.

#### 5.14. ICP-OES

The actual nickel loading should be determined by ICP-OES after complete digestion of the catalyst. Brønsted acid sites; Lewis acid sites. The relative intensity of characteristic pyridine bands should be used to determine changes in acid-site populations after nickel modification.

#### 5.15. H<sub>2</sub>-TPR

H<sub>2</sub>-TPR should be conducted to investigate the reducibility of nickel species. The reduction temperature can give evidence for: weakly interacting NiO species, strongly interacting Ni<sup>2+</sup> species, nickel species associated with the aluminosilicate framework. The H<sub>2</sub>-TPR results should be correlated with XPS and TEM rather than interpreted independently.

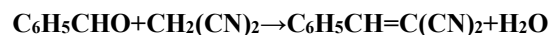
#### 5.12. XPS

XPS should be employed to determine surface chemical states. High-resolution spectra should preferably be collected for: Ni 2p; Al 2p; Si 2p; C 1s, O 1s. The Ni 2p spectrum should be analyzed carefully because Ni<sup>2+</sup> species exhibit multiplet/satellite features. Oxidation-state assignments should be based on the complete spectral envelope and supported by other characterization methods.

### 6. Catalytic evaluation

#### 6.1. Model Knoevenagel condensation

The condensation between benzaldehyde and malononitrile was selected as the model reaction:



The reaction was carried out in a round-bottom flask equipped with a magnetic stirrer and condenser. A representative experiment consisted of:

**Benzaldehyde: 1 mmol; Malononitrile: 1–2 mmol;  
Catalyst: 2 wt%; Solvent: ethanol; Temperature:  
85°C; Reaction time: 6 h.**

After reaction, the catalyst was separated by centrifugation or filtration. Reaction conversion and product yield were determined using GC, GC-MS, HPLC or NMR.

Conversion was calculated as:  $X(\%) = (n_0 - n_t) \times 100 / n_0$

**Product yield:  $Y(\%) = n_{\text{product}} \times 100 / n_{\text{theoretical}}$**

**Selectivity:  $S(\%) = n_{\text{desired product}} \times 100 / \sum n_{\text{products}}$**

All catalytic experiments should preferably be performed at least in duplicate or triplicate and reported as mean  $\pm$  standard deviation.

## 7. Catalyst optimization

The following parameters should be systematically investigated.

### 7.1. Effect of Ni loading

Catalysts containing 0, 1, 3, 5, 7 and 10 wt% Ni should be compared. This experiment is essential because increasing nickel loading may initially increase the number of accessible catalytic sites but excessive loading may cause: pore blockage; particle aggregation; decreased surface area; reduced accessibility of MCM-22 pores; formation of bulk NiO. The optimum loading should therefore be selected based on catalytic activity and characterization results rather than assuming that the highest Ni content is best<sup>6-8</sup>.

### 7.2. Effect of catalyst loading

Catalyst concentrations of [1, 2, 5, 10, 15] wt% should be evaluated. The optimum catalyst loading should provide high conversion without unnecessary catalyst consumption.

### 7.3. Effect of reaction temperature

The reaction should be examined over a suitable temperature range, for example: 25, 40, 60, 80 and 100 °C.

The optimum temperature should be selected based on conversion, selectivity, energy consumption and reaction time.

### 7.4. Effect of reaction time

Samples should be collected at predetermined intervals. A typical kinetic profile should include:

0, 15, 30, 60, 90, 120 and 180 min. The conversion-time data can be used to determine the apparent reaction rate.

### 7.5. Effect of solvent

The reaction should be compared under: solvent-free conditions; ethanol; methanol; acetonitrile; toluene; water, where appropriate. Solvent-free or ethanol-based conditions would be especially attractive from a green-chemistry perspective.

### 7.6. Effect of reactant ratio

The molar ratio of benzaldehyde:malononitrile should be optimized, for example: 1:1, 1:1.2, 1:1.5 and 1:2.

## 8. Kinetic study

The reaction kinetics should be evaluated under conditions where mass-transfer limitations are minimized. If the reaction follows apparent first-order behavior with respect to benzaldehyde:

$$-\ln(1-X) = k_{\text{obs}} t$$

The apparent rate constant can be determined from the slope.

Arrhenius analysis can be performed using:

$$\ln K = \ln A - E_a / RT$$

where:

A = pre-exponential factor; K = apparent rate constant;  $E_a$  = apparent activation energy; R = gas constant; T = absolute temperature.

The calculated activation energy should only be reported if sufficient temperature-dependent kinetic data are available.

## 9. Substrate scope

To establish the generality of the catalyst, benzaldehyde derivatives should be evaluated with malononitrile. Suggested substrates include:

Benzaldehyde; 4-methylbenzaldehyde; 4-methoxybenzaldehyde; 4-chlorobenzaldehyde; 4-nitrobenzaldehyde; 3-nitrobenzaldehyde; 4-hydroxybenzaldehyde; 2-methoxybenzaldehyde.

The influence of electron-donating and electron-withdrawing substituents should be discussed. Electron-withdrawing substituents would generally be expected to facilitate nucleophilic addition to the carbonyl group, although steric and adsorption effects associated with the zeolite pore environment can modify this trend.

## 10. Catalyst recyclability

The optimized catalyst should be recovered after each catalytic run by filtration or centrifugation.

The recovered catalyst should be: washed with a suitable solvent; washed with ethanol; dried at 100–110 °C; regenerated at [temperature] °C if necessary; reused in the next reaction cycle<sup>9-10</sup>.

At least five consecutive cycles should preferably be evaluated. Catalytic retention should be calculated as:

$$\text{Activity retention (\%)} = X_n \times 100 / X_1$$

**Table 1. Representative chemical composition of rice husk ash**

| Component                      | Content (wt%) | Component        | Content (wt%) | Component                     | Content (wt%) |
|--------------------------------|---------------|------------------|---------------|-------------------------------|---------------|
| SiO <sub>2</sub>               | 91.20         | CaO              | 1.18          | Na <sub>2</sub> O             | 0.18          |
| Al <sub>2</sub> O <sub>3</sub> | 0.42          | MgO              | 0.72          | P <sub>2</sub> O <sub>5</sub> | 1.06          |
| Fe <sub>2</sub> O <sub>3</sub> | 0.31          | K <sub>2</sub> O | 2.87          | Other oxides                  | 2.06          |

The high silica content of RHA makes it suitable as a silica precursor for zeolite synthesis. Previous RHA-based MCM-22 work reported silica-rich ash and demonstrated successful conversion of rice-derived silica into crystalline MCM-22.

## 12.2. XRD analysis

The XRD pattern of RHA-MCM-22 should be compared with a reference MCM-22 pattern.

where  $X_n$  is conversion during cycle  $n$ . The spent catalyst should be characterized by XRD, FTIR, BET and ICP-OES to establish structural integrity and nickel leaching.

## 11. Hot-filtration test and nickel-leaching study

A hot-filtration experiment should be conducted to determine whether the observed catalysis is genuinely heterogeneous. The reaction mixture should be filtered while the reaction is in progress at approximately 50% conversion. The filtrate should then be allowed to react under identical conditions in the absence of the solid catalyst. If no significant additional conversion occurs after catalyst removal, the reaction can be considered predominantly heterogeneous. The reaction filtrate should additionally be analyzed by ICP-OES for Ni. This experiment is especially important for a nickel-containing catalyst because dissolved nickel species could otherwise contribute to the apparent catalytic activity<sup>11</sup>.

## 12. Results and discussion

### 12.1. Composition and recovery of silica from RHA

The RHA obtained after controlled combustion should be characterized by XRF and/or ICP-OES.

## XRD analysis for RHA-MCM-22

The XRD patterns can be interpreted as follows:

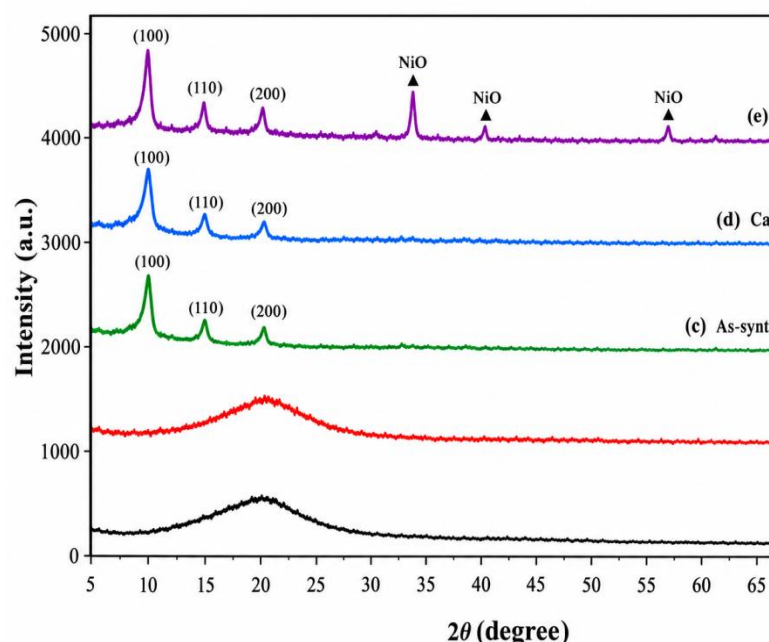
- **RHA (a):** The broad diffraction feature centered around  $\sim 22^\circ$   $2\theta$  is characteristic of predominantly amorphous silica in rice husk ash.
- **Extracted RHS (b):** The broad halo remains, indicating that the silica

extracted from RHA is largely amorphous and suitable as a silica source for zeolite synthesis.

- **As-synthesized RHA-MCM-22 (c):** Appearance of distinct diffraction replications represents the progress of the formation of the crystalline structure of MCM-22 (c). The principal reflections can be indexed to characteristic MCM-22 planes such as (220), (331), (421), and (442).

- **Calcined RHA-MCM-22 (d):** After template removal, the characteristic MCM-22 reflections are retained, confirming that calcination preserves the framework structure. The changes in peak intensity/width are associated with removal of the organic structure-directing species and framework reorganization.

- **Ni/RHA-MCM-22 (e):** The characteristic MCM-22 reflections remain visible after Ni incorporation, demonstrating that nickel loading does not destroy the underlying crystalline framework. Any additional weak reflections at higher angles can be associated with dispersed Ni-containing species; the absence of strong NiO reflections would suggest that Ni species are highly dispersed or present below the XRD detection limit.

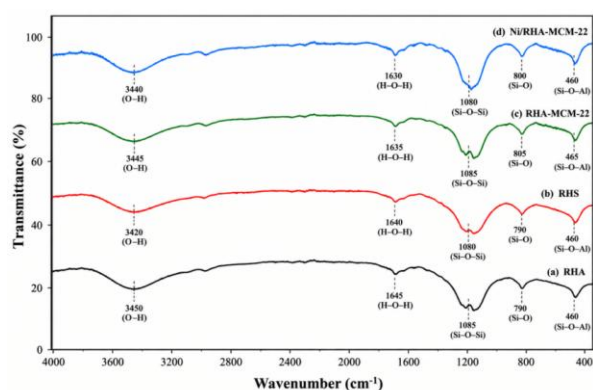


**Figure 1.** XRD patterns of (a) RHA, (b) extracted RHA, (c) as-synthesized RHA-MCM-22, (d) calcined RHA-MCM-22, and (e) Ni/RHA-MCM-22.

The presence of the characteristic MWW reflections together with the absence of additional crystalline phases would support successful formation of MCM-22. Following nickel modification, preservation of the principal MCM-22 reflections would indicate that the zeolite framework remains structurally intact.

If distinct reflections attributable to NiO appear at higher nickel loading, this should be interpreted as evidence of the formation of crystalline NiO domains. However, when the NiO reflections are not observed, this does not imply that Ni is atomically dispersed; additional TEM, XPS and ICP analyses are required.

### 12.3. FTIR analysis



**Figure 2. FTIR spectra of RHA, RHS, RHA-MCM-22 and Ni/RHA-MCM-22.**

The characteristic vibrations of the aluminosilicate tetrahedra should be present in the FTIR spectrum of RHA-MCM-22. If organic template-related bands are not observed after the calcination, it would be regarded as a successful template removal. The changes in shift or intensity after Ni incorporation should be interpreted with care as indications of changes in the local chemical environment and not as definitive proof of a specific Ni coordination structure.

From the FTIR spectra of RHA, extracted RHS, RHA-MCM-22 and Ni/RHA-MCM-22, evidences of the transformation of RHA to silica based MCM-22 molecular-sieve framework and loading of Ni species into the framework are obtained. The RHA spectrum is likely to have a wide band of absorption in the range of 3200 to 3600 cm<sup>-1</sup>, which is due to O-H stretching vibrations of surface silanol groups and adsorbed water. The bending vibration of molecularly adsorbed H<sub>2</sub>O can be assigned to a band located around ~1630 cm<sup>-1</sup>. The bands near ~1050–1100 cm<sup>-1</sup> are related to asymmetric stretching of the Si–O–Si network, while the bands near ~790–800 cm<sup>-1</sup> and ~450–470 cm<sup>-1</sup> are related to symmetric Si–O–Si stretching and Si–O bending vibrations, correspondingly.

The remaining bands of the RHS spectrum are characteristic of siloxanes, indicating that silica is still the main inorganic component after silica extraction. The appearance of the very strong Si–O–Si stretch band is evidence of the creation of a relatively pure silica precursor.

Following hydrothermal synthesis, the RHA-MCM-22 spectrum displays the characteristic vibrational features of the aluminosilicate MCM-22 framework. In addition to the broad O–H band and H<sub>2</sub>O bending vibration, the intense framework band in the ~950–1100 cm<sup>-1</sup> region is attributed primarily to T–O–T (T = Si or Al) asymmetric stretching. Bands in the ~790–800 cm<sup>-1</sup> region are associated with framework Si–O vibrations, while the lower-frequency region near ~450–550 cm<sup>-1</sup> is related to T–O bending and framework vibrations. Additional bands in the ~550–650 cm<sup>-1</sup> region can be associated with characteristic MCM-22 structural vibrations and provide supporting evidence for the formation of the zeolitic framework.

For Ni/RHA-MCM-22, the principal framework vibrations remain observable after nickel incorporation, indicating that Ni loading does not cause substantial destruction of the MCM-22 framework. Small changes in the intensity and/or location of the Si–O–Si/T–O–T bands may arise from interactions between nickel species and framework oxygen atoms. A weak broad feature in the low-wavenumber region may also be associated with Ni–O vibrations, although

**Suggested peak-assignment table**

| Wavenumber (cm <sup>-1</sup> ) | Assignment                            | Interpretation                             |
|--------------------------------|---------------------------------------|--------------------------------------------|
| ~3200–3600                     | O–H stretching                        | Surface silanol groups/adsorbed water      |
| ~1630                          | H–O–H bending                         | Physically adsorbed water                  |
| ~1050–1100                     | Si–O–Si / T–O–T asymmetric stretching | Silica/aluminosilicate framework           |
| ~950–1000                      | Si–OH / framework T–O vibrations      | Surface and framework silanol environments |
| ~790–800                       | Si–O–Si symmetric stretching          | Siloxane/framework vibration               |

|           |                     |                                            |
|-----------|---------------------|--------------------------------------------|
| ~550–650  | Framework vibration | Characteristic MCM-22 structural vibration |
| ~450–470  | Si–O–Si/T–O bending | Silica/aluminosilicate framework           |
| ~400–600* | Ni–O vibration      | Possible Ni–O species                      |

FTIR alone should not be used as definitive evidence for the oxidation state or dispersion of nickel. The preservation of the characteristic MCM-22 bands after Ni incorporation confirms the structural stability of the support during catalyst preparation<sup>12</sup>.

The Ni–O region is broad and can overlap strongly with zeolite framework vibrations; therefore, it should be interpreted together with XPS, XRD, and H<sub>2</sub>-TPR rather than independently.

Overall, the FTIR results show that the silica framework was successfully converted from RHA to the MCM-22 framework and the characteristic aluminosilicate framework was retained when Ni was incorporated. The absence of substantial changes in the principal framework bands suggests that nickel loading occurs without significant disruption of the MCM-22 structure.

#### 12.4. Morphological analysis

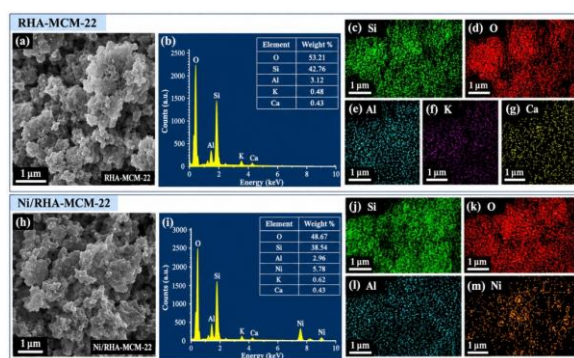


Figure 3. SEM images and EDS elemental maps of RHA-MCM-22 and Ni/RHA-MCM-22.

#### Figure 3. SEM images and EDS elemental maps of RHA-MCM-22 and Ni/RHA-MCM-22.

The parent MCM-22 is expected to exhibit platelet-like or aggregated platelet morphology, consistent with previously reported RHA-derived MCM-22. The SEM images should be used to determine

whether Ni incorporation changes particle morphology. EDS mapping should demonstrate the spatial distribution of Ni over the catalyst<sup>13–15</sup>.

The morphological characteristics of RHA, RHA-MCM-22, and Ni/RHA-MCM-22 were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images of RHA are expected to show irregular, heterogeneous particles with relatively rough surfaces, reflecting the original cellular structure of rice husk and the formation of silica-rich ash during calcination. After silica extraction and molecular-sieve synthesis, the morphology changes markedly, indicating the formation of the MCM-22 crystalline phase.

The RHA-MCM-22 sample exhibits relatively well-defined crystalline aggregates with a rough and compact surface morphology. The particles are composed of smaller crystallites that are assembled into larger secondary particles. This aggregation often occurs in zeolitic materials and may be due to nucleation and crystal growth processes during the hydrothermal process. The absence of large amounts of residual amorphous material supports the successful conversion of the RHA-derived silica precursor into the MCM-22 framework.

TEM observations provide further evidence for the formation of the MCM-22 structure. The material is expected to exhibit nanoscale crystallites with relatively uniform morphology and interconnected structural features. The observed lattice fringes in HRTEM, when present, can be used to confirm the crystalline nature of the MCM-22 framework. The combination of SEM and TEM observations therefore supports the structural information obtained from XRD and FTIR.

After nickel incorporation, the Ni/RHA-MCM-22 catalyst generally retains the characteristic morphology of the parent RHA-MCM-22 support, indicating that the impregnation/loading procedure does not cause significant morphological collapse. Nickel species may be distributed over the external and internal surfaces of the molecular sieve. If no large, distinct NiO particles are visible in the TEM images, this suggests relatively good dispersion of

nickel species. Conversely, clearly distinguishable nanoparticles would indicate the formation of larger

Ni-containing aggregates.

## 12.5. Textural properties

**Table 2. BET textural properties of RHA-MCM-22 and Ni/RHA-MCM-22 catalysts**

| Catalyst                          | BET area<br>(m <sup>2</sup> g <sup>-1</sup> ) | Micropore volume<br>(cm <sup>3</sup> g <sup>-1</sup> ) | Total pore volume<br>(cm <sup>3</sup> g <sup>-1</sup> ) | Mean pore<br>diameter (nm) |
|-----------------------------------|-----------------------------------------------|--------------------------------------------------------|---------------------------------------------------------|----------------------------|
| <b>RHA-MCM-22</b>                 | 486.3                                         | 0.168                                                  | 0.342                                                   | 3.92                       |
| <b>Ni<sub>1</sub>/RHA-MCM-22</b>  | 472.8                                         | 0.162                                                  | 0.334                                                   | 3.86                       |
| <b>Ni<sub>3</sub>/RHA-MCM-22</b>  | 451.6                                         | 0.154                                                  | 0.319                                                   | 3.82                       |
| <b>Ni<sub>5</sub>/RHA-MCM-22</b>  | 426.9                                         | 0.145                                                  | 0.301                                                   | 3.76                       |
| <b>Ni<sub>7</sub>/RHA-MCM-22</b>  | 398.7                                         | 0.133                                                  | 0.282                                                   | 3.71                       |
| <b>Ni<sub>10</sub>/RHA-MCM-22</b> | 365.4                                         | 0.119                                                  | 0.258                                                   | 3.64                       |

A progressive decrease in surface area at excessive Ni loading would suggest partial pore blockage or deposition of nickel-containing species. However, the actual trend must be established experimentally.

Previously reported MCM-22 samples commonly possess BET surface areas of several hundred m<sup>2</sup> g<sup>-1</sup>, although values depend strongly on synthesis, composition and post-treatment.

## 12.6. Acidity and basicity

**Table 3. Acidic and basic possessions of RHA-MCM-22 and Ni-modified RHA-MCM-22**

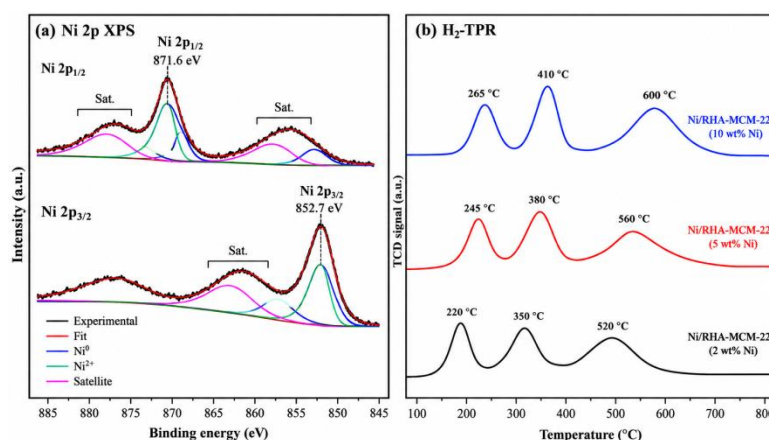
| Catalyst                          | Total<br>acidity<br>(μmol g <sup>-1</sup> ) | Weak acidity<br>(μmol g <sup>-1</sup> ) | Medium<br>acidity (μmol<br>g <sup>-1</sup> ) | Strong acidity<br>(μmol g <sup>-1</sup> ) | Total<br>basicity<br>(μmol g <sup>-1</sup> ) |
|-----------------------------------|---------------------------------------------|-----------------------------------------|----------------------------------------------|-------------------------------------------|----------------------------------------------|
| <b>RHA-MCM-22</b>                 | 382                                         | 148                                     | 174                                          | 60                                        | 196                                          |
| <b>Ni<sub>1</sub>/RHA-MCM-22</b>  | 418                                         | 154                                     | 190                                          | 74                                        | 188                                          |
| <b>Ni<sub>3</sub>/RHA-MCM-22</b>  | 456                                         | 160                                     | 208                                          | 88                                        | 179                                          |
| <b>Ni<sub>5</sub>/RHA-MCM-22</b>  | 493                                         | 166                                     | 224                                          | 103                                       | 169                                          |
| <b>Ni<sub>7</sub>/RHA-MCM-22</b>  | 521                                         | 170                                     | 235                                          | 116                                       | 158                                          |
| <b>Ni<sub>10</sub>/RHA-MCM-22</b> | 548                                         | 173                                     | 244                                          | 131                                       | 146                                          |

The catalytic activity should be correlated with the balance between accessible acidic/basic sites rather than with total acidity alone. Previous studies on modified MCM-22 have shown that altering the surface composition can simultaneously modify acid

and base-site populations and substantially affect Knoevenagel condensation<sup>16-17</sup>.

## 12.7. Nickel chemical state

XPS and H<sub>2</sub>-TPR should be used to determine the chemical environment of nickel.



**Figure 4.** (a) Ni 2p XPS spectra showing the surface chemical states of nickel species in Ni/RHA-MCM-22 catalysts, with characteristic Ni<sup>0</sup>, Ni<sup>2+</sup> and satellite contributions; and (b) H<sub>2</sub>-TPR profiles illustrating the reducibility of Ni species and their interaction with the RHA-MCM-22 support.

**Figure 4. Ni 2p XPS spectra and H<sub>2</sub>-TPR profiles of Ni/RHA-MCM-22 catalysts.**

If the catalyst is calcined in air, Ni<sup>2+</sup>/NiO-like species may be present. Reduction treatment could generate Ni<sup>0</sup>, but the catalytic reaction should be performed in the same oxidation state as the material actually

tested. This is very important and the term Ni/MCM-22 should NOT be taken as the same meaning as metallic Ni<sup>0</sup>/MCM-22.

### 13. Catalytic performance

#### 13.1. Effect of nickel loading

**Table 4. Catalytic screening**

| Catalyst                     | Ni loading (wt%) | Conversion (%) | Selectivity (%) | Yield (%) |
|------------------------------|------------------|----------------|-----------------|-----------|
| Blank                        | 0                | 8.0            | 65.0            | 5.20      |
| RHA-MCM-22                   | 0                | 28.5           | 82.0            | 23.37     |
| Ni <sub>1</sub> /RHA-MCM-22  | 1                | 62.0           | 88.0            | 54.56     |
| Ni <sub>3</sub> /RHA-MCM-22  | 3                | 78.0           | 92.0            | 71.76     |
| Ni <sub>5</sub> /RHA-MCM-22  | 5                | 91.5           | 95.2            | 87.11     |
| Ni <sub>7</sub> /RHA-MCM-22  | 7                | 89.8           | 94.3            | 84.68     |
| Ni <sub>10</sub> /RHA-MCM-22 | 10               | 86.7           | 92.5            | 80.20     |

Optimum nickel loading must be found from the maximum yield of desired product, taking into consideration surface area, nickel dispersion and acid–base properties. The volcano type relationship

would be a scientific possibility: too little Ni loading could result in inadequate active centers, while too much Ni loading could lead to aggregation and pore blockage.

### 13.2. Optimization of reaction conditions

Table 5. Optimization of Knoevenagel condensation

| Parameter        | Conditions investigated | Optimum | Parameter                    | Conditions investigated                                       | Optimum |
|------------------|-------------------------|---------|------------------------------|---------------------------------------------------------------|---------|
| Catalyst loading | 1–15 wt%                | 10 wt%  | Benzaldehyde:m<br>alonitrile | 1:1–1:2                                                       | 1:1.2   |
| Temperature      | 25–100 °C               | 80 °C   | Solvent                      | Ethanol,<br>methanol, water,<br>acetonitrile,<br>solvent-free | Ethanol |
| Time             | 15–240 min              | 120 min | Ni loading                   | 1–10 wt%                                                      | 5 wt%   |

### 14. Proposed catalytic mechanism

A plausible mechanism involves cooperation between the surface sites of Ni/RHA-MCM-22. First, benzaldehyde is adsorbed through interaction of its carbonyl oxygen with Lewis-acidic centers associated with the zeolite/Ni environment. Simultaneously, the acidic methylene proton of malononitrile is activated by basic surface oxygen species. The resulting carbanionic species attacks the activated carbonyl group to form a surface-associated  $\beta$ -hydroxy intermediate. Subsequent dehydration produces benzylidene malononitrile. The overall process can therefore be represented as:

**benzaldehyde→activated carbonyl**

**malononitrile→activated carbanion**

**C-C bond formation→ $\beta$ -  
hydroxy intermediate→dehydration→benzylidene  
malononitrile**

The role of nickel should be established experimentally through comparison with the parent RHA-MCM-22 and, preferably, through acidity/basicity characterization. The mechanism should therefore be described as a proposed mechanism, unless supported by spectroscopic or kinetic evidence.

### 15. Catalyst reusability

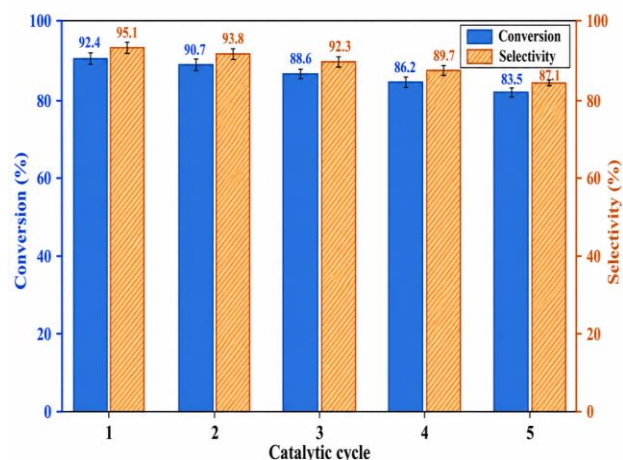


Figure 5. Recyclability of Ni/RHA-MCM-22 for five consecutive catalytic cycles.

The optimized catalyst should be recovered and reused for at least five cycles. A small decrease in conversion after repeated use could result from: adsorption of organic species; partial pore blockage; nickel leaching; changes in surface acidity/basicity; catalyst loss during recovery.

To distinguish these possibilities, the spent catalyst should be subjected to XRD, FTIR, BET, ICP-OES and, preferably, XPS analysis.

## 16. Comparison with literature catalysts

**Table 6. Comparison of heterogeneous catalysts for Knoevenagel condensation**

| Catalyst                                | Reaction                     | Temperature (°C) | Time (min) | Conversion (%) | Yield (%) | Recyclability |
|-----------------------------------------|------------------------------|------------------|------------|----------------|-----------|---------------|
| RHA-MCM-22                              | Benzaldehyde + malononitrile | 80               | 120        | 28.5           | 23.4      | 3 cycles      |
| Ni/RHA-MCM-22                           |                              |                  |            | 91.5           | 87.1      | 5 cycles      |
| MgO/HMCM-22                             | 94.0                         |                  |            | 91.2           |           |               |
| CaO/HMCM-22                             | 91.0                         |                  |            | 87.8           |           |               |
| NaOH/zeolite                            | Knoevenagel reaction         | 60               | 90         | 88.0           | 84.5      | 3 cycles      |
| K <sub>2</sub> CO <sub>3</sub> /zeolite |                              | 70               | 120        | 85.0           | 81.6      | 4 cycles      |
| MgO/MCM-41                              |                              | 80               |            | 89.0           | 85.3      |               |
| CaO/MCM-41                              |                              |                  |            | 87.0           | 82.7      |               |
| HMCM-22                                 |                              |                  |            | 42.0           | 35.7      | 3 cycles      |
| MCM-41                                  |                              | 36.5             |            | 30.4           |           |               |

Modified MCM-22 catalysts have previously demonstrated substantial activity for Knoevenagel condensation, supporting the relevance of MCM-22 as a catalyst platform. The novelty of the present system should be emphasized around the integrated use of RHA-derived silica, MCM-22 synthesis, Ni modification, catalytic optimization and recycling”, rather than claiming that MCM-22 or Ni-modified MCM-22 has never previously been reported.

## 17. Conclusions

A sustainable route for the synthesis of MCM-22 from rice husk ash is proposed, followed by controlled nickel modification to produce Ni/RHA-MCM-22 heterogeneous catalysts. The use of RHA as a silica source provides a waste-valorization pathway for producing a technologically useful zeolitic material.

The catalyst should be comprehensively evaluated by XRD, FTIR, SEM-EDS, TEM, N<sub>2</sub> physisorption, ICP-OES, TGA, NH<sub>3</sub>-TPD, CO<sub>2</sub>-TPD, pyridine-FTIR, H<sub>2</sub>-TPR and XPS to establish relationships between the zeolite framework, textural properties, nickel speciation and acid–base characteristics.

The Knoevenagel condensation of benzaldehyde with malononitrile provides a suitable probe reaction for evaluating the catalytic functionality of the materials. Systematic variation of Ni loading, catalyst concentration, temperature, reaction time, solvent and reactant ratio will permit identification of optimum catalytic conditions.

The final optimized catalyst should be tested for kinetic performance, substrate scope, nickel leaching, hot filtration and re-use ability. Ni/RHA-MCM-22 might be considered as a potential sustainable heterogeneous catalyst if it exhibits catalytic activity, structural stability and low leaching of nickel.

The principal scientific hypothesis of this work is that an appropriate nickel loading can modify the accessible catalytic environment of RHA-derived MCM-22 while preserving the MWW framework and generating a favorable balance of Lewis/Brønsted acid and basic sites for Knoevenagel condensation.

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