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Research Article

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Unrevealing the Structure–Activity Relationship of Ru Catalysts Supported on MCM-41, ZSM-5, ZSM-22, and γ - Al_2O_3 for Selective Acetophenone Hydrogenation

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ABSTRACT

The pore architecture and acid-site distribution of catalyst supports have a major impact on controlling the conversion and selectivity of Ru-supported catalysts in the hydrogenation of acetophenone. In this work, Ru catalysts were prepared and evaluated on mesoporous (MCM-41 and γ - Al_2O_3) and microporous (ZSM-5 and ZSM-22) supports. The combination of high surface area, ordered mesoporous structure, moderate acidity, and efficient Ru dispersion in Ru/MCM-41 promoted complete hydrogenation of both the aromatic ring and the carbonyl group, achieving a conversion of 99% and a selectivity of 88.96% toward 1-cyclohexylethanol under optimized reaction conditions (140°C and 40 bar H_2). The Lewis acid sites of Ru/ γ - Al_2O_3 instead promoted selective carbonyl hydrogenation to 1-phenylethanol, while the microporous catalysts Ru/ZSM-5 and Ru/ZSM-22 showed comparatively lower conversion and selectivity toward complete hydrogenation due to their shape selective pore architecture. Characterization by XRD, N_2 physisorption, FTIR, H_2 -TPR, NH_3 -TPD, and TEM revealed the influence of support properties on Ru dispersion, surface area, porosity, acidity, and reducibility; TPD data further reveal the role of acid-site distribution in governing the depth of hydrogenation of the aromatic ring and the C=O group. The effects of temperature, H_2 pressure, and reaction time on conversion and selectivity toward 1-cyclohexylethanol were also examined, and the catalyst retained steady activity over five successive reaction cycles. This study establishes a clear structure–activity–selectivity relationship for Ru-supported micro- and mesoporous catalysts in acetophenone hydrogenation.

Keywords: Ru nanoparticles; hydrogenation; mesoporous/microporous supports; acid-site distribution; structure–activity relationship; catalyst recyclability.

1. INTRODUCTION

Catalytic hydrogenation of aromatic aldehydes and ketones plays a fundamental role in organic synthesis.[1] Hydrogenation of aromatic ketones such as acetophenone can proceed selectively over a suitable catalyst to give a variety of products, notably 1-phenylethanol, which is an important intermediate in the synthesis of fragrances and flavours.[2, 3] Aromatic rings are thermodynamically stable but can undergo to hydrogenation under sufficiently forcing catalytic conditions, which can give rise to ring-hydrogenated products such as cyclohexylethanol.[4, 5] The product distribution and hydrogenation pathway of a particular metal catalyst depend on its surface area, electronic structure, and metal–support interactions.[6]

Among the transition-metal catalysts used for the hydrogenation of aldehydes and ketones, transition metals such as platinum,[7] ruthenium,[8] copper,[9] nickel,[10] and palladium[11] exhibit excellent conversion and high selectivity toward alcohols. In these metals, ruthenium is particularly more useful for hydrogenation reactions because of its ability to activate hydrogen and promote both carbonyl and aromatic-ring hydrogenation under appropriate reaction conditions.[12, 13] However, the catalytic behaviour of supported Ru is strongly influenced by the nature of the support, which can affect Ru dispersion, metal–support interaction, hydrogen activation, and the accessibility of reactants to the active sites. [14, 15]

Porous supports such as Al_2O_3 and MCM-41 favour a homogeneous distribution of metal particles and improve reactant/product diffusion, both of which govern the extent of hydrogenation and the conversion rate of acetophenone. [16–18] Microporous zeolites such as ZSM-22 and ZSM-5, by contrast, impose a shape-selective channel environment due to their well-defined micropore structure, but this same confinement can restrict reactant and product diffusion and thereby limit conversion. [19, 20] These characteristics promote superior dispersion of metal nanoparticles, which in turn broadens catalytic selectivity and

activity. These factors together strongly influence both the hydrogenation product distribution and the conversion rate of the carbonyl compound. [21-23] MCM-41 is additionally valued as a support because of its tunable pore size, thermal stability, and high surface area; its silanol-rich surface may further modulate the acidity and dispersion of immobilized metal species. [24-28]

Several studies have examined the hydrogenation of acetophenone using different metal catalysts, each showing distinct selectivity patterns. In bimetallic Bi–Pt/Al₂O₃, [29] Pt/SiO₂, [30] and Ru complexes [31-33] under moderate conditions, the C=O group is preferentially hydrogenated; however, under more demanding conditions, Ru/SiO₂, [34] Ru/FCN, [35] Pd/SiO₂, [36] and Rh/Al₂O₃ [37] catalysts hydrogenate both the aromatic ring and the carbonyl group. These studies collectively emphasize the importance of catalyst properties and metal–support interaction for achieving deep hydrogenation of aromatic ketone substrates. However, no comparable study has correlated pore structure and the distribution of weak and strong acid sites of micro- and mesoporous supports with acetophenone hydrogenation selectivity.

This study investigates the catalytic performance of Ru supported on microporous zeolites (ZSM-5 and ZSM-22) and mesoporous materials (MCM-41 and γ -Al₂O₃), to establish how metal dispersion, metal–support interaction, pore architecture, and acid-site distribution jointly govern product selectivity. Recent reviews on metal species confined within zeolites for hydrogen-related reactions [38] similarly emphasize that acid-site proximity and micropore confinement rather than metal loading alone are decisive for selectivity in these systems, reinforcing the motivation for the present comparative study.

Ru catalysts are extensively used for the hydrogenation of ketones; however, the influence of support pore structure and acid-site properties on activity and product distribution is not well characterised. The present work addresses this issue by performing a comparative study of Ru catalysts supported on MCM-41, γ -Al₂O₃, ZSM-5, and ZSM-22 under identical reaction conditions. Strong structure–property–performance linkages can be established by correlating the catalytic performance with textural parameters, surface acidity and metal dispersion. The findings demonstrate that the interplay between pore topology and acidity governs hydrogen activation, substrate accessibility, and reaction pathways, thereby determining the selective formation of 1-phenylethanol, cyclohexylethanone, and 1-cyclohexylethanol.

2. EXPERIMENTAL

2.1. *Materials and reagents*

All mesoporous and microporous supports used, namely MCM-41, [39] γ -Al₂O₃, [40] ZSM-5, [41] and ZSM-22 [42] were synthesized in the laboratory. RuCl₃ (Aldrich) was used as the metal precursor for catalyst synthesis. Hydrogenation tests were carried out using acetophenone (99%, Aldrich), hydrogen gas, and isopropanol (L.R. grade) as solvent. Acetophenone, 1-phenylethanol, cyclohexylethanol, and cyclohexylethanone (Aldrich) were used as standards for GC calibration; a mixture of all four compounds in solvent was used to construct the calibration curve, and reaction products were additionally confirmed by GC-MS.

2.2. *Catalyst preparation*

MCM-41 was synthesized following a previously reported method. Briefly, 12.8 g of NaOH was dissolved in water, and 60 g of fumed silica was added slowly with continuous stirring. A second solution was prepared by dissolving 72.93 g of CTAB in distilled water with stirring for 30 min. The CTAB solution was then added dropwise to the silica solution, and the resulting gel was stirred for 1 h to ensure homogenization, with the pH maintained at 11.3–11.5. The final molar gel composition was 1.0 : 0.2 : 0.32 : 125 (SiO₂ : CTAB : NaOH : H₂O). The gel was transferred to an autoclave and held at 373 K for 24 h under constant stirring. The solid product was washed, filtered, and dried in an air oven at 353 K for 12 h, and the as-synthesized sample was calcined in flowing air at 823 K for 8 h.

The 0.5% Ru/MCM-41 catalyst was prepared by wet impregnation. RuCl₃ (0.10 g) was dissolved in acetone, and MCM-41 was dispersed with continuous stirring in the resulting solution. After 2 h of impregnation, the solvent was removed under reduced pressure using a rotary evaporator. The recovered solid was dried overnight at 393 K, calcined in air at 723 K for 4 h, and reduced under flowing H₂ at 623 K for 2 h before catalytic evaluation.

The Ru catalysts supported on γ -Al₂O₃, ZSM-5, and ZSM-22 were prepared using the same impregnation, drying, calcination, and reduction protocol to allow direct comparison between mesoporous and microporous supports. All catalysts were prepared with a nominal 0.5 wt.% Ru loading.

2.3. Catalytic hydrogenation reaction and performance evaluation

Catalytic hydrogenation was carried out in a 400 mL stainless-steel autoclave reactor (Amar Equipment) fitted with a heating jacket. Acetophenone (5 g) and catalyst (0.5 g) were charged together with 100 g of isopropyl alcohol (IPA) as solvent. The reactor was purged with nitrogen at room temperature and then flushed and charged with hydrogen at room temperature. The initial hydrogen pressure of 40 bar was monitored throughout the run. Samples were withdrawn from the reactor at 60-min intervals and analysed by GC using a Restek Stabilwax-MS capillary column (30 m $\times$ 0.25 mm i.d. 0.25 μ m film thickness). Acetophenone conversion (X%) and product selectivity (S%) were calculated from the resulting chromatograms.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterisation

All support materials and catalysts were characterized by surface-area and pore-volume measurements (BET method), X-ray diffraction (XRD), ICP, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), FTIR, and temperature-programmed desorption/reduction (NH₃-TPD / H₂-TPR). Analysis conditions and instrumentation are detailed elsewhere.

3.1.1. XRD analysis

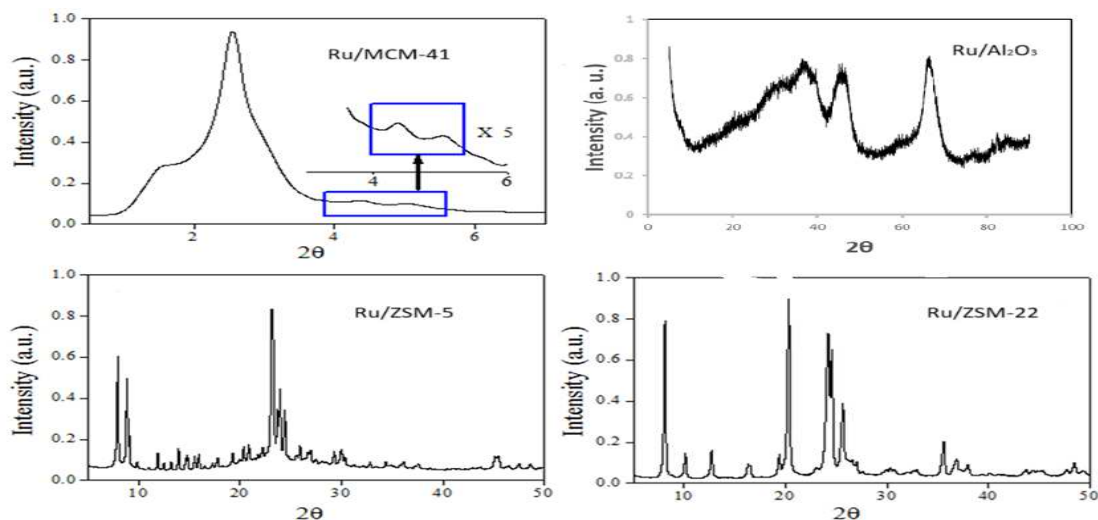


Fig. 1. XRD patterns of Ru/MCM-41, Ru/ γ -Al₂O₃, Ru/ZSM-5, and Ru/ZSM-22 catalysts.

The synthesized catalysts were examined by X-ray diffraction to determine crystallinity and structural integrity. The XRD pattern of Ru/MCM-41 shows well-resolved low-angle diffraction peaks in the 2θ range 2.0–5.0° and exhibits three distinct reflections indexed to the (100), (110), and (200) of the hexagonally ordered mesoporous structure of MCM-41. No crystalline peaks are observed in the wide-angle region ($2\theta = 5$ –20°), confirming the amorphous nature of the silica framework. After

ruthenium loading, no peaks attributable to Ru or RuO₂ phases were detected, indicating that the ruthenium species are highly dispersed on the surface of the support or present as crystallites below the detection limit of XRD.

Powder X-ray diffraction (XRD) analysis was employed to evaluate the phase composition and structural integrity of the synthesized catalysts. The low-angle XRD pattern of Ru/MCM-41 exhibits three distinct reflections indexed to the (100), (110), and (200) planes within the 2θ range of 2–5°, confirming the preservation of the highly ordered hexagonal mesoporous framework after Ru incorporation. In contrast, the wide-angle diffraction pattern ($2\theta = 5\text{--}20^\circ$) displays only a broad diffuse feature characteristic of amorphous silica, with no evidence of long-range crystalline ordering. Furthermore, diffraction peaks associated with crystalline Ru or RuO₂ are absent, suggesting that the ruthenium species are either highly dispersed on the support surface or present as crystallites below the detection limit of XRD.

The absence of additional broad reflections confirms that the framework integrity of both mesoporous and microporous supports remained intact during catalyst preparation an important requirement for retaining pore accessibility and surface area for catalytic activity. The lack of crystalline ruthenium reflections is consistent with efficient metal dispersion, in line with the elevated hydrogenation activity observed for Ru/MCM-41 and Ru/ γ -Al₂O₃. Together with the BET results below, the XRD data indicate that metal dispersion and support porosity are critical factors governing catalytic activity in acetophenone hydrogenation.

3.1.2. Physicochemical analysis

Table 1 lists the specific surface area, pore volume, and pore diameter of the microporous and mesoporous supports and their corresponding 0.5 wt.% Ru catalysts.

Sample	BET area (m ² /g)	Micropore area (m ² /g)	Pore volume (cm ³ /g)	Avg. pore dia. (Å)	Ru (wt.%)
MCM-41	1297	–	0.88	27.33	–
γ -Al ₂ O ₃	369	–	1.53	167.70	–
ZSM-22	267	220	0.45	68.0	–
ZSM-5	358	194	0.23	26.41	–
Ru/MCM-41	1203	–	0.78	24.11	0.42
Ru/ γ -Al ₂ O ₃	313	–	1.31	153.67	0.43
Ru/ZSM-22	234	217	0.41	63.8	0.38
Ru/ZSM-5	330	172	0.19	23.3	0.41

Table 1. Physicochemical properties of the microporous and mesoporous supports and their 0.5 wt.% Ru catalysts, evaluated for liquid-phase acetophenone hydrogenation.

N₂ adsorption–desorption isotherms (not shown) confirm typical Type IV behaviour for the mesoporous supports, consistent with their mesoporous character. Ru/MCM-41 has a large surface area (1203 m²/g) and pore volume of 0.78 cm³/g, whereas Ru/ γ -Al₂O₃ has a larger pore volume (1.31 cm³/g) but lower surface area (313 m²/g). Unlike the mesoporous supports, Ru/ZSM-5 and Ru/ZSM-22 maintain their microporous zeolitic structures following Ru incorporation, with micropore surface areas of 172 and 217 m² g^{−1}, respectively. after loading 0.5 wt.% Ru, all supports show a decrease in both pore volume and surface area relative to the parent support, indicating partial pore-mouth blockage by Ru particles and pointing to effective, well-dispersed Ru loading. Overall, the catalysts retain their essential pore structure and surface characteristics required for catalytic hydrogenation.

Taken together, the XRD and textural data show that Ru metal is incorporated and highly dispersed within the support materials, resulting in a modest reduction in surface area and pore volume while preserving structural stability.

3.1.3. TEM analysis

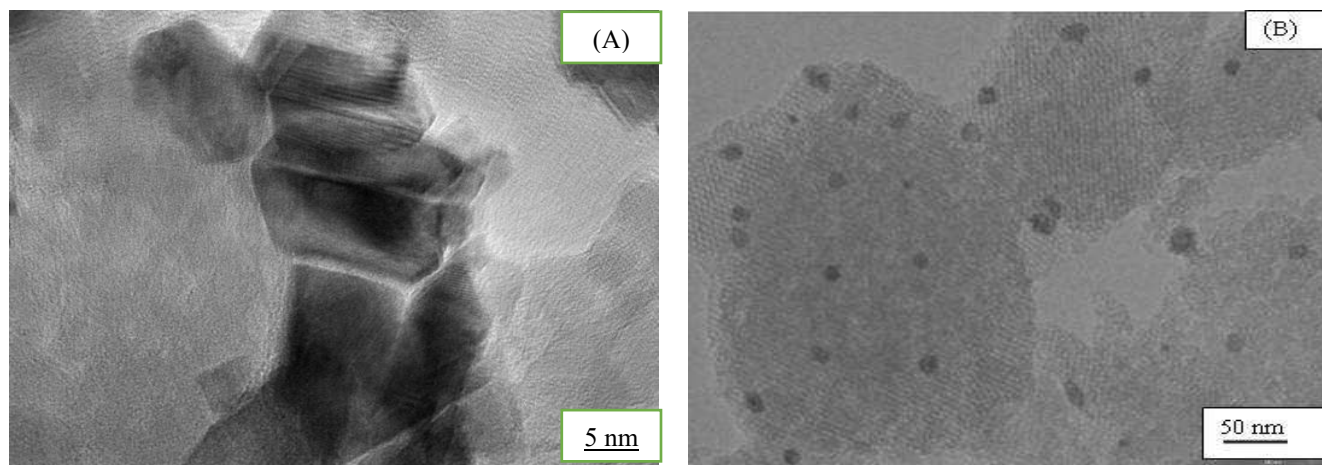


Fig. 2. TEM images of the Ru/MCM-41 catalyst (A: overview; B: high-resolution lattice image).

Fig. 2 shows well-dispersed Ru nanoparticles on the mesoporous silica support in the Ru/MCM-41 catalyst. Both images show uniformly distributed dark spots, indicating that Ru is homogeneously dispersed without sintering. The high-resolution image (Fig. 2B) shows lattice fringes with an interplanar spacing corresponding to the (101) plane of metallic Ru, confirming successful metal reduction, with particle sizes in the range of 10 nm and a well-ordered MCM-41 morphology retained around the particles. These observations point to a strong metal–support interaction and a structurally stable catalyst, consistent with the mesoporous character established by N₂ physisorption and BET analysis.

3.1.4. FTIR analysis

FTIR spectroscopy was used to identify functional groups and confirm the structural framework of the support materials. The FTIR spectrum of Ru/MCM-41 (4000–500 cm⁻¹) shows a band at ~1635 cm⁻¹ assigned to H–O–H bending, a broad band at ~3400 cm⁻¹ assigned to O–H stretching (confirming surface hydroxyl groups), and a strong, intense band near 1100 cm⁻¹ confirming the mesoporous silica framework of MCM-41. Similarly, the FTIR spectra of Ru/γ-Al₂O₃, Ru/ZSM-5, and Ru/ZSM-22 showed no significant changes in the characteristic framework vibrations after Ru incorporation, indicating that the support structures remain intact. The absence of significant shifts in framework vibrations after Ru loading indicates that the catalyst preparation method did not alter the underlying support structure and that Ru species were well dispersed on the support surface — a factor that directly impacts catalytic performance.

3.1.5. Acidity measurement (NH₃-TPD)

The acidity of the supports before and after Ru formation was assessed by NH₃ temperature-programmed desorption (NH₃-TPD). Following Ru integration, there was a steady decrease in overall acidity, indicating that well-dispersed Ru species partially covered accessible acid sites. In addition, the acid sites were found to vary enormously in density and strength across the supported catalysts. Such variations are expected to influence the adsorption of the substrate and reaction pathways, hence controlling the activity and selectivity of the products in the hydrogenation of acetophenone.

MCM-41, by contrast, had a relatively low total acidity that fell further, from 507.58 to 259.09 μmol g⁻¹, after Ru loading, consistent with its weakly acidic mesoporous character. These acidity results clearly show that Ru incorporation modifies both the concentration and strength of acid sites in a support-dependent manner - a modification that is central to the product selectivity and adsorption behaviour observed during hydrogenation.

Catalyst	Weak acidity ($\mu\text{mol g}^{-1}$)	Strong acidity ($\mu\text{mol g}^{-1}$)	Total acidity ($\mu\text{mol g}^{-1}$)
ZSM-5	625.76	574.24	1200.00
Ru/ZSM-5	468.18	298.48	766.67
MCM-41	68.18	439.39	507.58
Ru/MCM-41	62.12	196.97	259.09
Al_2O_3	303.03	469.70	772.73
Ru/ Al_2O_3	63.64	409.09	472.73
ZSM-22	237.88	374.24	612.12
Ru/ZSM-22	230.30	33.33	263.64

Table 2. NH_3 -TPD acidity data for the parent supports and Ru-incorporated catalysts.

3.1.6. H_2 -TPR analysis

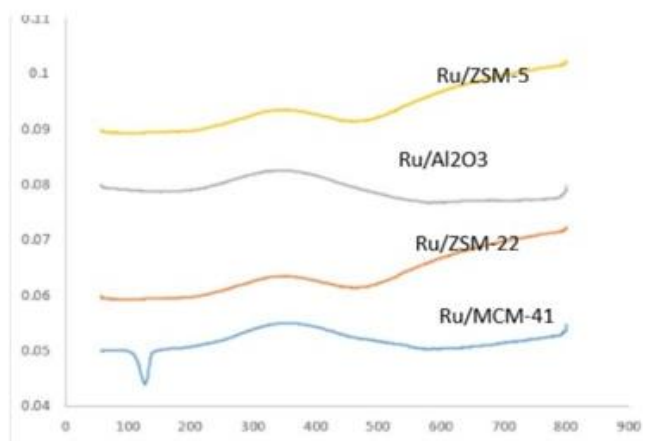


Fig. 3. H_2 -TPR profiles of Ru/MCM-41, Ru/ $\gamma\text{-Al}_2\text{O}_3$, Ru/ZSM-5, and Ru/ZSM-22 catalysts.

The reducibility of the supported Ru species and the strength of the metal-support interaction were assessed by H_2 -temperature-programmed reduction (H_2 -TPR). The reduction behaviour is strongly support dependent (Fig. 3), which is indicative of the different electronic environment of Ru and the effect on catalytic performance.

The Ru/MCM-41 has the lowest reduction temperature, which suggests a weak interaction between Ru and support and easily reducible Ru species. These properties, along with low total acidity ($259.09 \mu\text{mol g}^{-1}$; Table 2) and open mesoporous structure, favour hydrogen activation and complete hydrogenation, leading to the highest selectivity to 1-cyclohexylethanol. Ru/ZSM-5 has the highest reduction temperature, implying strongest Ru-support interaction. The high residual acidity after Ru loading ($766.67 \mu\text{mol g}^{-1}$; Table 2) is expected to promote stronger adsorption of the substrate and to limit the hydrogen availability on the Ru surface, thus favouring the formation of cyclohexylethanone.

Ru/ $\gamma\text{-Al}_2\text{O}_3$ exhibits an intermediate reducibility and retains a high concentration of strong acid sites ($409.09 \mu\text{mol g}^{-1}$; Table 2). The balanced metal-support interaction and surface acidity favour selective hydrogenation of the carbonyl group, giving mainly 1-phenylethanol.

The hydrogen consumption of Ru/ZSM-22 is lower than that of Ru/MCM-41, indicating less reducibility and less efficient activation of hydrogen. These features, together with the strong reduction of strong acid sites after Ru incorporation and the

one-dimensional microporous framework, limit full hydrogenation and favour the formation of cyclohexylethanone. The overall H₂-TPR results indicate that the activity and product selectivity in acetophenone hydrogenation are determined by the synergic effects of Ru reducibility, metal-support interaction, pore architecture and surface acidity.

Overall, the combined TPR and acidity results establish that Ru reducibility and support acidity jointly govern hydrogenation selectivity. Catalysts with weaker metal-support interaction, higher reducibility, balanced (moderate) acidity, and pore architecture favour hydrogenation to 1-cyclohexylethanol, whereas catalysts with strong Ru-support interaction and pronounced acidity — whether Lewis-acidic (Al₂O₃) or zeolitic (ZSM-5, ZSM-22) — favour selective carbonyl hydrogenation or aromatic-ring hydrogenation, respectively, depending on the dominant acid-site character and pore architecture.

3.2. Catalytic activity study on acetophenone hydrogenation

3.2.1. Effect of support

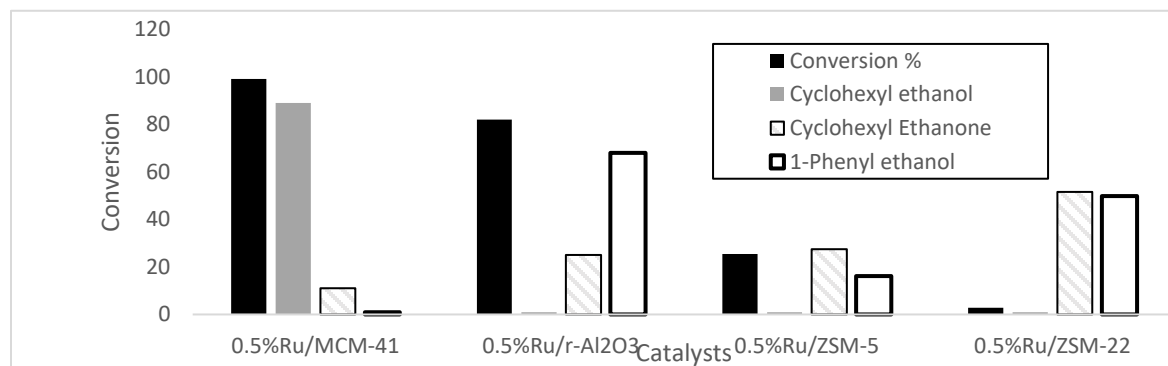


Figure 4. Effect of Ru-based mesoporous and microporous supported catalysts on acetophenone hydrogenation. (Reaction conditions: temperature = 140°C, IPA solvent, catalyst weight = 500 mg, H₂ = 40 bar, time = 8 h.)

Ru/MCM-41 shows the highest selectivity toward 1-cyclohexylethanol (88.96% at the optimized 40-bar condition), attributable to its low weak acidity, moderate strong acidity, mesoporous structure, and high Ru dispersion. The ordered mesoporous channels of MCM-41 allow efficient diffusion of acetophenone and hydrogen while limiting over-adsorption of intermediates. Its moderately strong-acid-site density promotes sequential hydrogenation of both the carbonyl group and the aromatic ring without imposing severe adsorption constraints, allowing complete hydrogenation to proceed efficiently through 1-phenylethanol and cyclohexylethanone intermediates to 1-cyclohexylethanol.

By comparison, Ru/ γ -Al₂O₃ yields predominantly 1-phenylethanol (~60% selectivity). Among the catalysts studied, the Ru/ γ -Al₂O₃ catalyst shows the highest number of strong acid sites after Ru incorporation (409.09 $\mu\text{mol g}^{-1}$; Table 2). The abundance of Lewis acid sites is expected to promote the activation of the carbonyl group, thus favouring selective C=O hydrogenation. In combination with the moderate Ru-support interaction indicated by H₂-TPR, these characteristics suppress extensive hydrogenation of the aromatic ring, resulting in 1-phenylethanol as the predominant product.

The zeolitic catalysts Ru/ZSM-5 and Ru/ZSM-22 show markedly different selectivity from the mesoporous supports. Ru/ZSM-5 retains the highest weak acidity (468.18 $\mu\text{mol g}^{-1}$) and total acidity (766.67 $\mu\text{mol g}^{-1}$), which strongly enhances aromatic-ring adsorption and hydrogenation. This elevated acidity, combined with the microporous framework, favours flat (η^6 -type) aromatic-ring adsorption over carbonyl adsorption, increasing the yield of cyclohexylethanone; the narrow micropore channels additionally restrict diffusion of the bulkier alcohol product, limiting further hydrogenation to 1-cyclohexylethanol. Ru/ZSM-22, despite its lower total acidity, shows the highest selectivity of all catalysts toward cyclohexylethanone (~40%).

Notably, the strong-acid-site density of ZSM-22 decreases sharply after Ru loading, from 374.24 to 33.33 $\mu\text{mol g}^{-1}$, while weak acidity remains dominant. This predominance of weak acid sites, combined with the one-dimensional TON pore structure, promotes aromatic-ring hydrogenation but restricts further hydrogenation of the ketonic intermediate to the corresponding

alcohol; severe diffusion limitations within the narrow channels likely hinder desorption and secondary hydrogenation, resulting in the observed accumulation of cyclohexylethanone.

ZSM-5 and ZSM-22 showed lower conversion due to the diffusion limitation because of pore opening. Typical pore opening of ZSM-5 and ZSM-22 are 5.1×5.5 to 5.3×5.6 Å and 4.5×5.5 Å respectively against that of dimension of acetophenone, measuring approximately $7 \times 6.5 \times 4.5$ Å. High conversion of acetophenone was observed in MCM-41 and γ -Al₂O₃ as their pore opening is in the range of 25–30 Å and 50 Å, which helps in easy diffusion of acetophenone.

These results establish a clear acidity–selectivity relationship for acetophenone hydrogenation over Ru-supported catalysts. Catalysts with low weak acidity and moderate strong acidity favour complete hydrogenation to 1-cyclohexylethanol, catalysts with pronounced Lewis acidity selectively hydrogenate the carbonyl group to 1-phenylethanol, and catalysts combining high weak acidity with microporous confinement favour aromatic-ring hydrogenation to cyclohexylethanone. Mesoporous supports with moderate acidity are best suited to sequential (complete) hydrogenation, whereas highly acidic microporous zeolites alter diffusion behaviour and adsorption geometry in ways that substantially redirect the hydrogenation pathway. The observed selectivity trend indicates that product distribution is governed not only by total acidity but also by the ratio of weak to strong acid sites, the strength of metal–support interaction, and pore architecture.

3.2.2. Effect of temperature

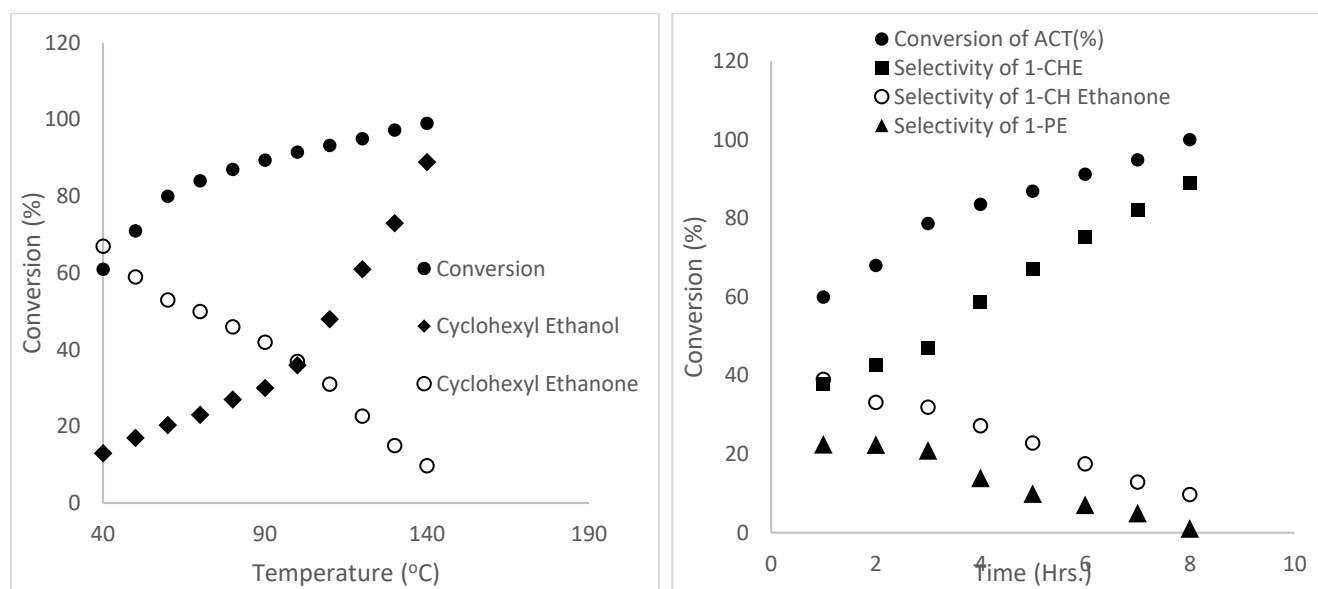


Figure 5(A). Effect of temperature on acetophenone hydrogenation over Ru/MCM-41. (Reaction conditions: catalyst weight = 500 mg, H₂ = 40 bar, time = 8 h, IPA solvent.)

Figure 5(A) shows the effect of reaction temperature on the catalytic hydrogenation of acetophenone over Ru/MCM-41. At 140°C, conversion reaches almost 100% due to enhanced hydrogenation kinetics. Selectivity toward 1-cyclohexylethanol, however, declines slightly at higher temperatures because of increased formation of 1-phenylethanol as a by-product. The optimum reaction-temperature range thus balances high conversion with maximum selectivity, which is essential for an efficient hydrogenation process.

3.2.3. Effect of reaction time

The effect of reaction time on the hydrogenation of acetophenone is shown in Fig. 5(B). Under the conditions studied, acetophenone conversion increases from 60% to 100% with time, indicating progressively increasing hydrogenation activity. Simultaneously, selectivity toward 1-cyclohexylethanol increases markedly from 40% to 89%, indicating effective

hydrogenation of both the C=O group and the aromatic ring at longer reaction times. Selectivity toward cyclohexylethanone and 1-phenylethanol follows a corresponding decreasing trend. This behaviour indicates that partial hydrogenation dominates under milder (shorter-time) conditions, producing intermediate compounds, whereas more extended reaction conditions allow hydrogenation of both the C=O group and the aromatic ring, yielding 1-cyclohexylethanol as the ultimate product. These results confirm that product distribution is strongly governed by reaction time.

3.2.4. Effect of H₂ pressure

Initial pressure (bar)	Conversion (%)	1-Cyclohexylethanol (%)	Cyclohexylethanone (%)	1-Phenylethanol (%)
10	17.34	–	6.09	93.91
20	90.39	–	44.58	55.41
30	93.20	80.07	16.91	3.02
40	99.99	88.96	11.03	–

Table 3. Effect of H₂ pressure on conversion and product selectivity over the 0.5% Ru/MCM-41 catalyst.

The pressure study shows that the Ru/MCM-41 catalyst is highly sensitive to H₂ pressure: both conversion and selectivity toward 1-cyclohexylethanol increase markedly with increasing hydrogen partial pressure, consistent with hydrogen availability being rate-limiting for the sequential (complete) hydrogenation pathway at lower pressures.

3.2.5. Recycling study

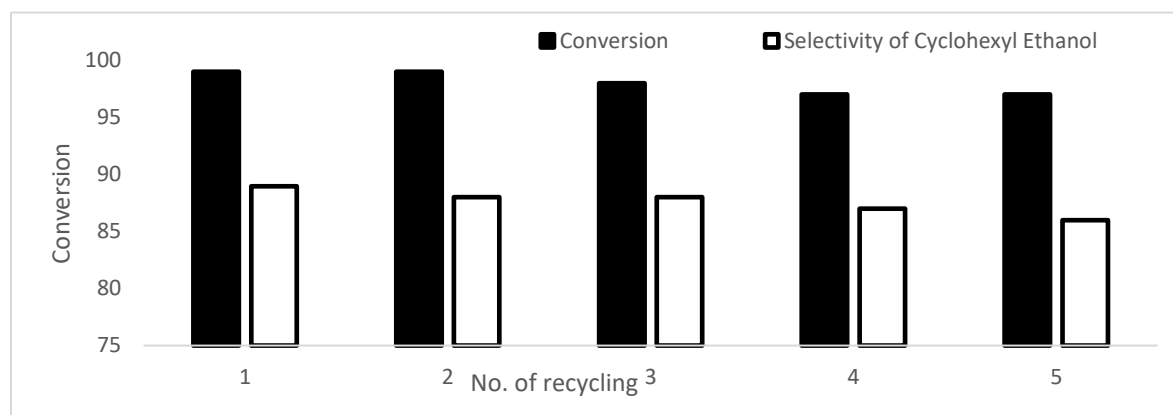


Figure 6. Recycling study of the 0.5% Ru/MCM-41 catalyst in acetophenone hydrogenation. (Reaction conditions: temperature = 140°C, IPA solvent, catalyst weight = 500 mg, H₂ = 40 bar, time = 8 h.)

Heterogeneous catalyst systems offer clear advantages over homogeneous systems in terms of ease of separation and recyclability. The recycling behaviour of the 0.5% Ru/MCM-41 catalyst over five successive runs is shown in Fig. 6. The catalyst exhibited high conversion and product selectivity in 5 consecutive reaction cycles. The minor loss in conversion is mostly due to some pore plugging, some sintering of the metal and the unavoidable loss of catalyst during filtration and handling, and not to significant catalyst deactivation.

Selectivity toward 1-cyclohexylethanol remains high throughout recycling, indicating that the mesoporous support structure and the active Ru sites remain largely intact under repeated use.

3.2.6. Effect of substrate structure

The effect of electron-donating and electron-withdrawing substituents on the acetophenone ring was also examined. Higher conversion and selectivity were observed with an electron-withdrawing substituent (chlorine) at the para position compared with an electron-donating substituent (methyl).

When a bulkier carbonyl-chain substituent is attached to the aromatic ring, only carbonyl-group hydrogenation is observed, an effect attributed to steric hindrance from the longer chain. Ring hydrogenation was not observed for five-membered heteroaromatic carbonyl substrates for example, acetyl furan because the electron-rich furan ring pushes electron density toward the carbonyl group, making the C=O group comparatively more reactive toward hydrogenation than the ring.

3.3. Structure–activity relationship

The physicochemical properties of the supports surface area, pore volume, pore diameter, reduction temperature, acidity, and Ru dispersion together play a decisive role in governing catalytic activity and selectivity in acetophenone hydrogenation over the Ru-supported catalysts studied. The mesoporous supports γ -Al₂O₃ and MCM-41 possess higher surface areas and pore volumes than the microporous supports ZSM-5 and ZSM-22, which benefits homogeneous Ru dispersion and improves reactant accessibility to active sites. Ru/MCM-41 shows the best combination of conversion and selectivity toward 1-cyclohexylethanol among all catalysts tested, attributable to its high surface area, well-defined mesoporous channels, and effective Ru dispersion; its large pore diameter and pore volume promote rapid diffusion of reactants, intermediates, and products, enhancing mass transfer during hydrogenation.

The microporous catalysts Ru/ZSM-5 and Ru/ZSM-22, by contrast, show comparatively lower activity owing to their substantial acidity and to a structural framework that impedes intermediate diffusion and restricts access to active Ru sites. As a result, the hydrogenation reaction over these catalysts is less efficient and tends to stall at partially hydrogenated intermediates.

Overall, these results demonstrate that catalytic activity is governed jointly by surface chemistry, textural properties, and acidity: high surface area, appropriate pore volume, and good metal dispersion together support superior hydrogenation activity and product selectivity.

Correlation between porosity, acidity, and product selectivity

Pore architecture and acid-site distribution directly govern the selective hydrogenation of acetophenone. NH₃-TPD clearly reveals substantial variation in acid-site concentration and strength across the catalysts, while BET measurements reveal marked differences in pore structure and surface area. The mild acidity and highly ordered, wide-pore structure of Ru/MCM-41 allow effective diffusion of reactants and sequential hydrogenation of both the carbonyl group and the aromatic ring, yielding 1-cyclohexylethanol as the major product; the long, open mesoporous channels allow intermediates to diffuse freely, facilitating complete hydrogenation.

For Ru/ γ -Al₂O₃, strong Lewis acidity combined with a mesoporous framework favours selective C=O hydrogenation: interaction between the carbonyl oxygen of acetophenone and the Lewis acid sites results in preferential selectivity toward 1-phenylethanol, with the product distribution indicating that adsorption is predominantly directed through the carbonyl functionality. The zeolitic catalysts Ru/ZSM-5 and Ru/ZSM-22 behave quite differently: their microporous structure imposes diffusion limitations that govern adsorption behaviour, and the high acidity of the zeolitic framework favours stronger interaction with aromatic intermediates. These catalysts therefore favour formation of cyclohexylethanone as the dominant (intermediate) product rather than proceeding to complete hydrogenation.

Overall, these findings confirm that pore architecture governs the accessibility and diffusion of reactants and intermediates, while acid-site character governs adsorption geometry and reaction pathway — together determining the observed hydrogenation selectivity.

3.4. Comparison with literature

Sr. No.	Catalyst / system	Support type / porosity	Main finding	Ref.
1	Ru-based catalyst	Supported catalyst	Selective hydrogenation of aromatic ketones influenced by catalyst properties	[1]
2	Ru catalysts	Various supports	Catalyst structure affects hydrogenation activity and selectivity	[2]
3	Supported metal catalyst	Porous support	Support properties govern hydrogenation behaviour	[8]
4	Ru catalyst	Mesoporous support	Enhanced hydrogenation via improved metal dispersion	[44]
5	Supported Ru catalyst	Oxide support / metal-support	Metal-support interaction influences product distribution	[28]
6	Bi-Pt/Al ₂ O ₃	Mesoporous oxide	Selective carbonyl hydrogenation to phenylethanol	[29]
7	Pt/SiO ₂	Mesoporous silica	High selectivity toward C=O hydrogenation	[30]
8	Ru/SiO ₂ /Ru/Cr/B	Mesoporous silica/bimetallic catalyst system	Additional metal enhances selective hydrogenation over Ru/SiO ₂ .	[44]
9	Ru/Carbon	Carbon support	High Ru dispersion improves hydrogenation activity	[35]
10	Rh/Al ₂ O ₃	Mesoporous oxide	Efficient aromatic-ring and carbonyl hydrogenation	[43]
11	ZSM-5-based catalyst	Microporous zeolite	Acidity and pore structure affect catalytic selectivity	[41]
12	Zeolite-supported catalyst	Microporous zeolite	Confinement effects influence reaction pathways	[42]
13	Metal@ zeolite (review)	Microporous zeolite (confined metal)	Acid-site proximity/confinement, not metal loading alone, controls selectivity	[38]
14	Pt-Co/ZSM-5-AT	Microporous zeolite (alkali-treated)	Zeolite acid-site tuning boosts unsaturated-alcohol selectivity	[45]
15	Single-site Ru@ zeolite-Y	Microporous zeolite (FAU)	Zeolite cage stabilizes monodisperse Ru sites, aiding selectivity	[46]
16	RuNP/C (electrochemical)	Carbon (non-porous)	Ru nanoparticles enable selective ketone-to-alcohol hydrogenation via H-atom transfer	[47]
17	Ru/MCM-41	Mesoporous silica	Highest 1-cyclohexylethanol selectivity via balanced acidity + high Ru dispersion	[This Paper]
18	Ru/ γ -Al ₂ O ₃	Mesoporous oxide	Selective 1-phenylethanol formation via Lewis acid sites	[This Paper]
19	Ru/ZSM-5	Microporous zeolite (MFI)	High acidity favours cyclohexylethanone formation	[This Paper]

Sr. No.	Catalyst / system	Support type / porosity	Main finding	Ref.
20	Ru/ZSM-22	Microporous zeolite (TON)	1-D pore confinement controls hydrogenation pathway	[This Paper]

Table 4. Comparison of the present findings with representative literature reports on supported-metal hydrogenation catalysts (new entries 25–28 added in this revision are described in the Additional References section).

Most previous studies have focused mainly on the role of the active metal, with comparatively less attention paid to the combined influence of support acidity, pore structure, and metal–support interaction. Mesoporous supports such as SiO₂ and γ -Al₂O₃ typically permit either selective carbonyl hydrogenation or complete hydrogenation, owing to their improved active-site accessibility and surface area. Microporous zeolites, in contrast, govern product distribution mainly through acidity and confinement effects that alter the adsorption and diffusion behaviour of reactants. A systematic study of Ru catalysts on mesoporous (MCM-41 and γ -Al₂O₃) and microporous (ZSM-5 and ZSM-22) materials is therefore needed to establish the relationship between support characteristics and hydrogenation selectivity. The present work addresses this need by showing how changes in acidity and pore structure direct the hydrogenation of acetophenone toward 1-cyclohexylethanol, 1-phenylethanol, or cyclohexylethanone.

Conclusion

This study demonstrates that catalytic hydrogenation of acetophenone over Ru-supported catalysts is strongly governed by the combined influence of support acidity, pore architecture, and Ru reducibility. Among the catalysts tested, Ru/MCM-41 shows the strongest overall catalytic performance and the highest selectivity (88.96% at the optimized 40-bar condition, ~85–89% typical across runs) toward 1-cyclohexylethanol. This behaviour stems from the synergistic effects of balanced acidity, favourable reducibility, moderate metal-support interaction, and a mesoporous framework, which facilitate efficient hydrogen activation and the diffusion of reactants and intermediates.

In contrast, the Al₂O₃-supported Ru catalyst predominantly yields 1-phenylethanol, owing to its strong Lewis acidity, which favours preferential $\eta^1(\text{O})$ -type adsorption and selective hydrogenation of the carbonyl group. The H₂-TPR results indicate a comparatively stronger metal–support interaction for Ru/Al₂O₃, which limits further aromatic-ring hydrogenation. ZSM-5 and ZSM-22, on the other hand, show enhanced formation of cyclohexylethanone owing to their dominant weak acidity and microporous confinement effects: strong adsorption within the zeolitic pores, combined with restricted diffusion, prevents further hydrogenation of the ketonic intermediate to 1-cyclohexylethanol, while their retained weak acidity favours η^6 -type aromatic adsorption and ring hydrogenation. The NH₃-TPD investigation shows that the distribution of weak and strong acid sites significantly impacts adsorption geometry and hydrogenation pathway. Catalysts with low weak acidity and moderate strong acidity promote complete hydrogenation, whereas catalysts with an elevated density of weak acid sites promote aromatic-ring hydrogenation. H₂-TPR further shows that reducibility and metal–support interaction are crucial for hydrogen activation and spillover, and hence for catalytic selectivity: catalysts with higher reducibility and moderate metal–support interaction favour complete hydrogenation, while stronger interaction instead stabilizes Ru species in configurations that redirect the hydrogenation pathway.

Overall, the combined acidity and reducibility studies establish a clear structure–acidity–reducibility–selectivity relationship for Ru-catalysed acetophenone hydrogenation. These results show that tuning support acidity and metal–support interaction offers an effective strategy for controlling adsorption behaviour and product selectivity in selective hydrogenation reactions. The outstanding activity, selectivity, and structural stability of Ru/MCM-41 further demonstrate its strong potential as a viable industrial catalyst for the hydrogenation of aromatic ketones and related fine-chemical synthesis.

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