

Ruthenium *meso*-Tetrakis(2,6-dichlorophenyl)porphyrin Complex Immobilized in Mesoporous MCM-41 as a Heterogeneous Catalyst for Selective Alkene Epoxidations

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A ruthenium complex of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin, [Ru^{II}(TDCPP)(CO)(EtOH)], is immobilized into mesoporous MCM-41 molecular sieves; the supported Ru catalyst can effect highly selective heterogeneous alkene epoxidations using 2,6-dichloropyridine *N*-oxide as terminal oxidant. Aromatic and aliphatic alkenes can be efficiently converted to their epoxides in good yields and selectivities, and *cis*-alkenes such as *cis*-stilbene, *cis*- β -methylstyrene, and *cis*- β -deuteriostyrene are epoxidized stereospecifically. Oxidation of cycloalkenes, e.g., norbornene and cyclooctene, can be carried out effectively using the heterogeneous Ru-catalyzed reaction while these alkenes are unreactive in the zeolite-based titanium silicate (TS-1)-catalyzed conditions (Murugavel, R.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 477). On the other hand, the Ru/M-41(m) catalyst displays size selectivity in the (+)-limonene oxidation where the terminal C=C bond (vs internal trisubstituted C=C bond) becomes more readily oxidized. Bulky 3,4,6-tri-*O*-benzyl-D-glucal has failed to react under the heterogeneous Ru-catalyzed conditions, whereas the smaller acetyl derivative is converted to a 3:1 mixture of α - and β -glycol epoxides. The Ru/M-41(m) catalyst can be used repeatedly, and 67% of its initial activity is retained after 11 691 turnovers (three runs). The loss of activity is attributed to catalyst leaching and/or deactivation. On the basis of Hammett correlation ($\rho^+ = -0.72$, $R = 0.997$) and product studies (cyclohexene and *cis*-alkenes as the substrates), a reactive dioxoruthenium(VI) porphyrin intermediate is not favored. An oxoruthenium(V) complex or oxoruthenium(IV) porphyrin cation radical could be the key intermediate for this highly selective epoxidation reaction.

Introduction

Epoxidation is one of the most important C=C bond functionalization methods, and epoxides are valuable intermediates for laboratory syntheses as well as chemical manufacturing.¹ Although the reaction is typically carried out by peracid oxidation in a laboratory-scale reactor with remarkable selectivities,² the pursuit of highly efficient and selective catalytic methods that are simple and safe to operate on a large scale remains an area of current interest. Transition metal catalysts, for instance, Mo/W(VI),^{3,4} Re(VII),⁵ and Ru(III)⁶ complexes, are known to effect homogeneous selective alkene epoxidations by employing the more tractable and economical oxidants such as dilute H₂O₂ and *tert*-butyl hydroperoxide (TBHP). Apparently, heterogeneous catalysis can offer additional advantages over its homogeneous counterpart for easy catalyst recycling and product isolation; however,

few heterogeneous catalysts are able to attain high catalytic turnovers (>1000) and product selectivity. Notably, the zeolite-based titanium silicate (TS-1) can bring about selective heterogeneous epoxidation by aqueous H₂O₂; its catalytic activity is limited by the small pore diameter (ca. 7 Å) of the zeolite support, and the oxidation of cycloalkenes (size > 7 Å) is ineffective.⁷

The use of ruthenium porphyrin complexes for epoxidations,⁸ and recently aziridinations,⁹ has been extensively studied by us and others.¹⁰ Indeed, this class of complexes, among other metalloporphyrins,¹¹ display promising selectivities toward organic oxidations using dioxygen,¹² as well as other mild oxidizing reagents such as N₂O¹³ and 2,6-dichloropyridine *N*-oxide (Cl₂pyNO).¹⁴ Previously, we prepared a heterogeneous oxidation cata-

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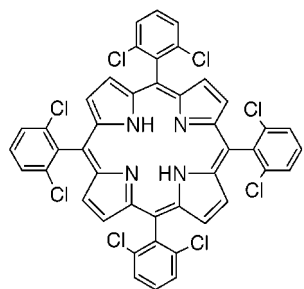


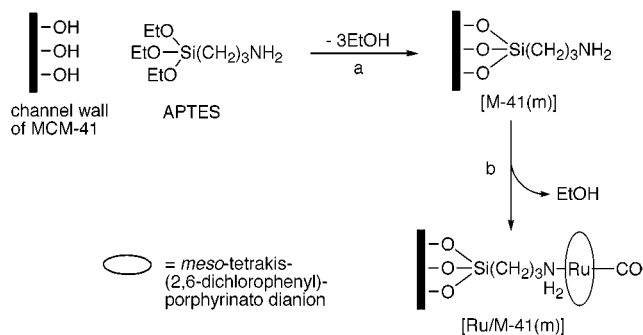
Figure 1. *meso*-Tetrakis(2,6-dichlorophenyl)porphyrin (TD-CPP).

lyst by grafting a *meso*-tetrakis(4-chlorophenyl)porphyrinatoruthenium(II) carbonyl complex into mesoporous siliceous molecular sieves MCM-41 modified with (3-aminopropyl)triethoxysilane (APTES).^{15,16} The immobilized ruthenium complex exhibits enhanced stability in the oxidizing medium, as well as good catalytic activity. The MCM-41 solid support consists of an ordered array of hexagonal channels with an average pore diameter of 36 Å, which permits a lower diffusional resistance (cf. nanoporous zeolite support) for the reactant molecules to access the metal active sites located within the channels.¹⁷ Herein is described a heterogeneous catalytic system for highly selective alkene epoxidations based on a supported ruthenium *meso*-tetrakis(2,6-dichlorophenyl)porphyrin, [Ru^{II}(TDCPP)(CO)(EtOH)], complex on mesoporous MCM-41 molecular sieves using Cl₂pyNO as terminal oxidant (Figure 1).

Results and Discussion

The parent MCM-41 was prepared by the literature method¹⁸ using C₁₆H₃₃N(CH₃)₃Br (RBr) as the template according to the following molar composition: 1.0 SiO₂/0.37 RBr/0.23 Na₂O/83.3 H₂O. The solid product was washed with deionized water at ambient temperature and then calcined in air at 550 °C for 3–5 h to afford a white powder product. The X-ray powder diffraction (XRD) pattern of this material shows a very intense absorption at 2θ ≈ 2.25°, the *d* spacing of the peak = 39.74 Å. Although direct encapsulation of the [Ru^{II}(TDCPP)(CO)(EtOH)] complex into MCM-41 by surface

Scheme 1. Encapsulation of *meso*-Tetrakis-(2,6-dichlorophenyl)porphyrinatoruthenium(II) Carbonyl Complex into Mesoporous MC-41^a



^a Key: (a) modification of MCM-41 channel wall: APTES/CHCl₃; (b) encapsulation of ruthenium porphyrin complex: [Ru^{II}(TDCPP)(CO)(EtOH)]/CH₂Cl₂.

adsorption was proven to be unsuccessful, the ruthenium complex was effectively immobilized after modification of the channel surface with (3-aminopropyl)triethoxysilane (APTES) (see the Experimental Section).¹⁹ The amino groups of the surface-bound APTES should serve as anchoring sites for the ruthenium complex via axial coordination (Scheme 1). This can be implicated by the failure to graft the coordinatively saturated [Ru^{IV}(TDCPP)(pz)₂] complex (pz⁻ = pyrazolate)²⁰ into the surface-modified MCM-41 [M-41(m)].

Encapsulation of the Ru complex was undertaken by vigorous stirring of M-41(m) (400 mg) in the methylene chloride solution of [Ru^{II}(TDCPP)(CO)(EtOH)] (10 mL, 0.17–0.28 mM) at ambient temperature for 1 h. The supported catalyst, designated as Ru/M-41(m), was isolated by filtration, washed thoroughly with methylene chloride, and then dried in a vacuum. Its solid diffuse-reflectance UV/vis and FT Raman spectra resemble to those of the unbound ruthenium complex, indicating that the molecule remains intact during the process of encapsulation (Table 1). To estimate the loading of [Ru^{II}(TDCPP)(CO)] in Ru/M-41(m), the catalyst sample was first dissolved into an aqueous 3% HF solution, followed by exhaustive extraction with methylene chloride. The ruthenium content in the combined organic extracts can then be evaluated using UV/vis spectrophotometry by monitoring the absorbance of the Soret band at λ_{max} = 409 nm (Table 2, see the Experimental Section for detailed procedures).

Figure 2 depicts the XRD pattern of 8.3 wt % Ru/M-41(m), which shows the characteristic peaks of MCM-41 without any peaks arisen from [Ru^{II}(TDCPP)(CO)(EtOH)]. This suggests that the solid support is structurally unchanged and the ruthenium porphyrin should be dispersed molecularly within the channels. The regular porosity of the MCM-41 is preserved during the transformations based on the XRD analyses (2θ = 2.25°, *d* spacing = 39.75 Å) and nitrogen sorption studies (see Table 2).

Aromatic and aliphatic alkenes (1 mmol) react with Cl₂-pyNO (1.1 mmol) to produce epoxides selectively in good yields using 50 mg of 0.4 wt % Ru/M-41(m) as catalyst (substrate/oxidant/Ru ratio = 5245:5769:1) in methylene

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Table 1. Characterization Data (UV/vis, FT-Raman, and XRD) of MCM-41, M-41(m), and Ru/M-41(m)

| entry | compd | solid diffuse-reflectance UV/vis (λ_{\max}/nm) | FT-IR (cm^{-1}) | FT-Raman (cm^{-1}) | XRD 2θ (deg), d-spacing (\AA) | pore size ^g (\AA) |
|-------|--------------------------------------|--|---|--|--|--|
| 1 | MCM-41 | | 3410–3100 (br) ^a | | 2.25, 39.74 | 38 |
| 2 | M-41(m) | | 3510–3250 (br), ^b 3000–2780 (br) ^c | | 2.25, 39.74 | 36 |
| 3 | [Ru ^{II} (TDCPP)(CO)(EtOH)] | 409, 529, 558 ^d | 1948 ^{e,f} | 2251, 2070, 1552, 1490, 1363, 1232, 339, 287, 220 | | |
| 4 | 8.3 wt % Ru/M-41(m) | 410, 531, 560 | 1947 ^f | 2241, 2063, 1552, 1490, 1363, 1232, 393, 287, 220 | 2.25, 39.74 | 35 |

^a (br) broad peak, ^vOH. ^b ν NH. ^c ν CH₂. ^d In CH₂Cl₂. ^e KBr. ^f ν CO. ^g Determined by N₂ adsorption isotherm.

Table 2. Preparation of the MCM-41 Supported Ruthenium Porphyrin Catalysts^a

| entry | [Ru] ₀ /mM | V ₀ /mL | wt of M-41(m) used for encapsulation/mg | [Ru] _e /mM | V _e /mL | Ru content/ wt % |
|-------|-----------------------|--------------------|---|-----------------------|--------------------|---------------------|
| 1 | 0.48 | 20.0 | 100 | 7.91 | 100.0 | 8.3 |
| 2 | 0.29 | 20.0 | 100 | 4.76 | 100.0 | 5.0 |
| 3 | 0.16 | 10.0 | 400 | 1.52 | 25.0 | 0.4 |
| 4 | 0.042 | 10.0 | 400 | 0.95 | 10.0 | 0.1 |

^a [Ru]₀ = concentration of the stock CH₂Cl₂ solution of [Ru^{II}(TDCPP)(CO)(EtOH)] used for immobilization into M-41(m). V₀ = volume of the Ru stock solution used for immobilization into M-41(m). [Ru]_e = concentration of the Ru complex in CH₂Cl₂ after dissolution of 10.0 mg of Ru/M-41(m) into 3% HF. V_e = final volume of CH₂Cl₂ solution used for UV/vis spectrometry.

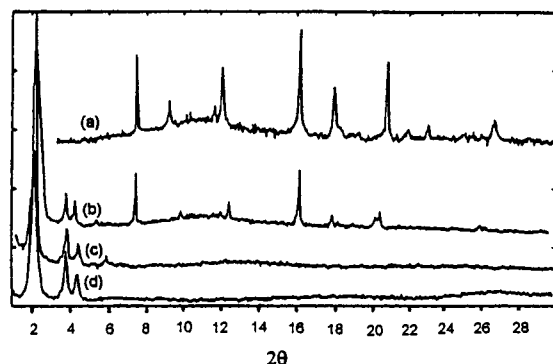


Figure 2. XRD patterns of (a) [Ru^{II}(TDCPP)(CO)(EtOH)], (b) a 8:92 (w/w) physical mixture of [Ru^{II}(TDCPP)(CO)(EtOH)] and MCM-41(m), (c) 8.3 wt % Ru/M-41(m), and (d) MCM-41(m).

chloride (5 mL) containing a small quantity of hydrochloric acid (0.03 mL of 36% HCl, ~0.3 mmol). The CH₂-Cl₂/HCl mixture was predried by anhydrous sodium sulfate before use, and the suspension was stirred at 40 °C under an argon atmosphere for 18–30 h. The results for the catalytic oxidation of some representative alkenes are summarized in Table 3.

Styrene was oxidized to styrene oxide in 91% yield (Table 3, entry 1) under the heterogeneous Ru-catalyzed conditions, and only traces of undesirable benzaldehyde (C=C bond cleavage) and phenylacetaldehyde (rearrangement) were detected. Turnovers of 4550 for the epoxide production were attained in 24 h. In addition, the oxidation of *cis*-stilbene (entry 2) and *cis*- β -methylstyrene (entry 3) took place stereospecifically with full retention of configuration of the starting alkenes, and the *cis*-epoxides were formed in >90% yields. The concertedness of the reaction was further tested by employing *cis*- β -deuteriostyrene (entry 4) as a mechanistic probe.²¹ Applying the standard reaction conditions, i.e., alkene

Table 3. Heterogeneous Alkene Epoxidations Catalyzed by a MCM-41-Supported Ruthenium Porphyrin Complex

| entry | alkene | reaction time (h) | % conversion | products | % yield ^a | turnovers (TOF/h ⁻¹) ^b |
|-------|--------|-------------------|--------------|----------|----------------------|---|
| 1 | | 24 | 98 | | 91 ^b | 4550 (209) |
| 2 | | 30 | 76 | | 98 | 3819 |
| 3 | | 24 | 98 | | 90 ^c | 4546 (202) |
| 4 | | 20 | 91 | | 93 ^{b,d} | 4299 |
| 5 | | 18 | 84 | | 61 ^e | 2628 (142) |
| 6 | | 24 | 81 | | 94 | 3905 (169) |
| 7 | | 20 | 89 | | 91 | 3762 (161) |
| 8 | | 24 | 80 | | 92 | 3774 (158) |
| 9 | | 24 | 74 | | 61 | 2304 |
| | | | | | 27 | |
| | | | | | 10 | |
| 10 | | 24 | n.d. | | 55 ^{d,g} | 1410 |

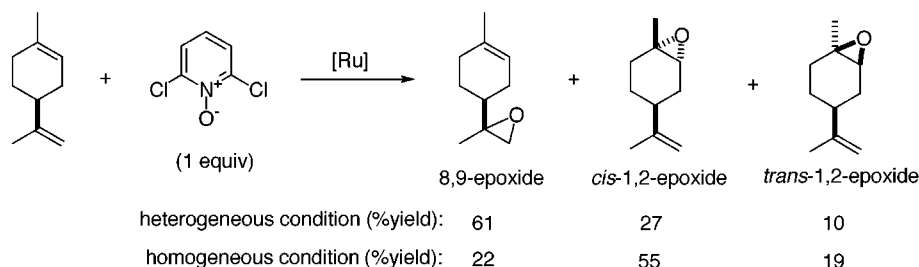
Reaction conditions: alkene (1 mmol), Cl₂pyNO (1.1 mmol), 0.4 wt % Ru/M-41(m) (0.195 μ mol of Ru), HCl (~0.3 mmol), CH₂Cl₂ (5 mL), 40 °C under an Ar atmosphere. ^a Yields are based on the amount of substrates consumed; products were identified and quantified by either GLC or ¹H NMR using the internal standard method unless otherwise stated. ^b Trace amounts of benzaldehyde and phenylacetaldehyde were also detected. ^c Trace amount of benzaldehyde was detected. ^d Isolated yield. ^e 2-Cyclohexen-1-ol (14%) and 2-cyclohexen-1-one (11%) were formed. ^f Glycol (0.5 mmol), Cl₂pyNO (0.62 mmol), 0.4 wt % Ru/M-41(m) (0.195 μ mol of Ru), HCl (~0.3 mmol), CH₂Cl₂ (5 mL), 40 °C under an Ar atmosphere. ^g Overall isolated yield after epoxidation and methanolysis; ratio of α : β -epoxides = 3:1. ^h Turnover frequencies (TOF) were determined by monitoring the reactions using GC within the first 2 h of the reactions. n.d.: not determined.

(1 mmol), Cl₂pyNO (1.1 mmol), HCl (~0.3 mmol), and 50 mg of 0.4 wt % Ru/M-41(m) in CH₂Cl₂ at 40 °C, *cis*- β -deuteriostyrene oxide was produced exclusively in 93% isolated yield, and yet the *trans*-epoxide was not detected using ¹H NMR spectroscopy. Oxidation of *trans*-stilbene is completely ineffective using this Ru-catalyzed reaction.

The heterogeneous oxidation of cyclohexene (entry 5) proceeded smoothly to form cyclohexene oxide (61%) as the major product, though 2-cyclohexen-1-ol (14%) and 2-cyclohexen-1-one (11%) were also generated by allylic C–H oxidation. Bulkier cycloalkenes such as norbornene (entry 6) and cyclooctene (entry 7) can also be effectively converted to *exo*-epoxynorbornane (94%) and cyclooctene oxide (91%), respectively, while these two cycloalkenes

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Scheme 2. Ru-Catalyzed (+)-Limonene Oxidation

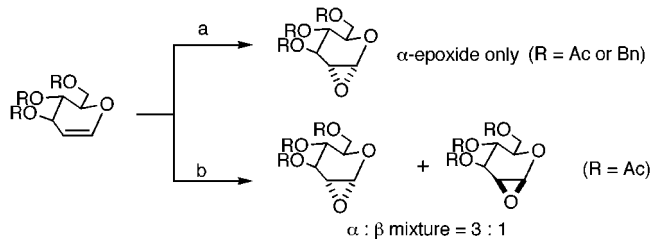


are poor substrates for the TS-1-catalyzed epoxidation.⁷ Terminal alkenes are usually the least reactive, but when 1-octene (entry 8) was treated with Cl₂pyNO under the catalytic conditions, 1-octene oxide was obtained in 92% yield after 24 h of reaction (entry 8).

The oxidation of (+)-limonene, which contains an internal trisubstituted and an isolated terminal C=C bond, afforded the 8,9-epoxide as the major product (8,9-/1,2-epoxide = 1.6:1) (entry 9); i.e., the terminal C=C bond reacts preferentially. It should be noted that the reaction with the electron-rich trisubstituted C=C bond prevails when *m*-chloroperoxybenzoic acid is the oxidant (1,2-/8,9-epoxide = 8.9:1).²² Moreover, when (+)-limonene was subjected to a homogeneous condition using [Ru^{II}(TDCPP)(CO)(EtOH)] as the catalyst and 1 equiv of Cl₂pyNO; the 1,2-epoxides were also produced predominantly (1,2-/8,9-epoxide = 3.4:1) (Scheme 2). The apparent selectivity reversal is in good agreement with the theory that the Ru-catalyzed epoxidation reaction should be largely heterogeneous. Since the oxidation has to take place within the MCM-41 channel, the hindered trisubstituted C=C bond should become more inaccessible to the entrapped active metal centers than the terminal one.

On the other hand, if a reactive oxoruthenium intermediate is assumed, the facial selectivity for the oxidation of the trisubstituted C=C bond of (+)-limonene in both the homogeneous and heterogeneous oxidations (respective *cis/trans*-1,2-epoxide ratio = 2.9:1 and 2.7:1) can be understood on the basis of the "side-on approach" model proposed by Groves,^{22a} since the facial approach leading to the *trans*-1,2-epoxide should be more hindered because of the steric repulsion between the vinyl groups of the alkene and the chloro substituents at the *meso*-phenyl rings of the ruthenium complex. On a contrary, the *m*-chloroperoxybenzoic acid-mediated reaction is featured by an equimolar production of the *cis*- and *trans*-epoxides.²²

1,2-Anhydrosugars (glycal epoxides) are important and versatile intermediates for carbohydrates syntheses; the compounds were hitherto derived directly from glycal using dioxirane as the active oxidant.²³ Treatment of 3,4,6-tri-*O*-acetyl- β -D-glucal (0.5 mmol) with Cl₂pyNO (0.62 mmol), HCl (~0.3 mmol), and a catalytic quantity of [Ru^{II}(TDCPP)(CO)(EtOH)] (1.91 μ mol) in methylene chloride (3 mL) under homogeneous conditions afforded the corresponding glycal epoxide, and subsequent methanolysis occurred with an inversion of configuration (77% overall isolated yield). On the basis of ¹H NMR analysis, only

Scheme 3. Ru-Catalyzed Glycal Oxidations^a

^a Key: (a) homogeneous conditions: [Ru^{II}(TDCPP)(CO)(EtOH)], Cl₂pyNO, HCl/CH₂Cl₂; (b) heterogeneous conditions: [Ru/M-41(m)], Cl₂pyNO, HCl/CH₂Cl₂.

methyl 3,4,6-tri-*O*-acetyl- β -D-glucopyranoside (δ_{H} = 3.58 ppm, s, 3H, OCH₃) was obtained, and the isomeric α -glucopyranoside (δ_{H} = 3.44 ppm, s, 3H, OCH₃) was not detected. This indicates that the epoxidation is directed selectively to the α -face, yet a previous report had already showed that the dioxirane oxidation of 3,4,6-tri-*O*-acetyl-D-glucal should result in a mixture of α - and β -glycal epoxides.^{23a} Likewise, the benzyl-substituted glucal derivative can also be transformed selectively to its α -glycal epoxide by adopting the same protocol (Scheme 3). As opposed to the homogeneous reactions, the Ru/M-41(m)-catalyzed oxidation of 3,4,6-tri-*O*-acetyl-D-glucal furnished a 3:1 mixture of α - and β -glycal epoxides based on ¹H NMR analysis of the methanolysis products (55% overall isolated yield). It is noteworthy that the larger 3,4,6-tri-*O*-benzyl-D-glucal did not react effectively under the heterogeneous conditions, and the alkene remained largely unreacted and was recovered after 3 days of continuous reaction.

The Ru/M-41(m) catalyst has been reused successively three times under the typical reaction conditions: styrene (1 mmol), oxidant (1.1 mmol), and HCl (~0.3 mmol) in CH₂Cl₂ (5 mL) at 40 °C for 24 h, except that 100 mg of 0.4 wt % Ru/M-41(m) was used. The solid catalyst was recycled by filtration after each reaction and washed thoroughly with methylene chloride before reuse. The Ru/M-41(m) catalyst still retains ca. 67% of its initial activity after a total of 11 691 turnovers: first run, epoxide yield = 91%, turnovers = 4550, turnover rate = 209 h⁻¹; second run, epoxide yield = 88%, turnovers = 4085, turnover rate = 187 h⁻¹; and third run, epoxide yield = 76%, turnovers = 3056, turnover rate = 171 h⁻¹. No induction period was observed for all reactions, and the turnover rates were obtained by monitoring the epoxide production rate during the first 2 h of reaction using gas chromatography. In addition, when sample was taken from the recovered Ru/M-41(m) after the first reaction run for analysis of the Ru content; an approximately 5% loss of the Ru catalyst was registered, and the decrease of catalytic activity is therefore attributed to leaching and/or catalyst deactivation.

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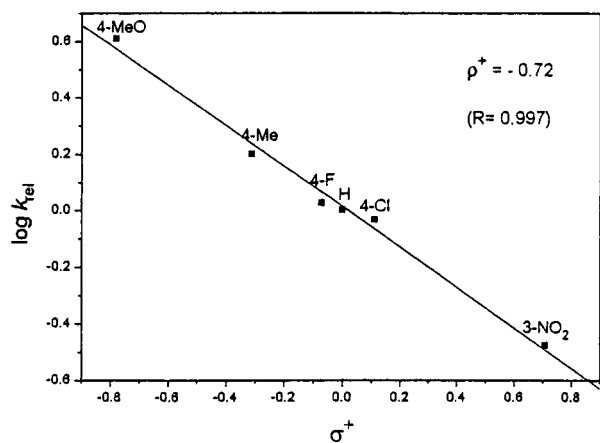


Figure 3. Hammett correlation studies ($\log k_{rel}$ vs σ^+) for the Ru/M-41(m)-catalyzed epoxidation of substituted styrenes by Cl₂pyNO.

Table 4. Listing of $\log k_{rel}$ and σ^+ Values for the Heterogeneous Ru-Catalyzed Alkene Epoxidations

| entry | Y | $\log k_{rel}$ | σ^+ |
|-------|-------------------|----------------|------------|
| 1 | 4-MeO | 0.61 | -0.78 |
| 2 | 4-Me | 0.20 | -0.31 |
| 3 | 4-F | 0.03 | -0.05 |
| 4 | H | 0.00 | 0.00 |
| 5 | 4-Cl | -0.03 | +0.11 |
| 6 | 3-NO ₂ | -0.48 | +0.71 |

The effect of para and meta substituents on the catalytic styrene oxidation has also been examined. The relative rates for the catalytic oxidation of several substituted styrenes (Y-styrene, Y = 4-MeO, 4-Me, 4-F, H, 4-Cl, and 3-NO₂), k_{rel} , were evaluated by monitoring the reactions with gas chromatography (see Experimental Section). Figure 3 depicts a linear correlation ($R = 0.997$) of $\log k_{rel}$ [$k_{rel} = k(Y\text{-styrene})/k(\text{styrene})$] vs substituent constants σ^+ . The slope (ρ^+) of the plot is -0.72 , which is much smaller than those ($\rho^+ = -1.2$ to -2.1) reported for the styrene oxidations by peracids,²⁴ [Fe^{IV}(TMP⁺)O], (TMP = tetramesitylporphyrin),²⁵ [(Br₈TPP)Cr^V(O)(X)] (Br₈TPP = octabromotetraphenylporphyrin),²⁶ and [Ru^{VI}(N₄)O₂]²⁺ (N₄ = macrocyclic tertiary tetramine)²⁷ complexes (Table 4).

The possible intermediary of a dioxoruthenium(VI) complex has been assessed by Hammett correlation studies on the stoichiometric [Ru^{VI}(TDCPP)O₂] epoxidation of styrenes. The $\log k_{rel}$ vs σ^+ plot for the stoichiometric reactions has established a nonlinear Hammett relationship where both electron-donating and -withdrawing substituents can mildly accelerate the epoxidation reactions.²⁰ Furthermore, the cyclohexene oxidation by [Ru^{VI}(TDCPP)O₂] is in favor of allylic C-H oxidation rather than epoxidation: 2-cyclohexen-1-one/2-cyclohexen-1-ol/cyclohexene oxide = 11:33:30.²⁰ These findings had also been encountered in other dioxoruthenium(VI) porphyrin systems.^{8b} In addition, *cis*- β -deuteriostyrene reacts nonstereospecifically with the dioxoruthenium(VI) complex to produce both *cis*- and *trans*- β -deuteriostyrene oxide (*cis/trans* = 87:13).²⁰ These contrasting reactivity

patterns (catalytic vs stoichiometric reactions) are inconsistent with a dioxoruthenium(VI) porphyrin intermediate. When Ru/M-41(m) was recovered by filtration after the catalytic reaction, ESR analysis of the catalyst sample revealed a signal ($g_{||} = 2.23$, $g_{\perp} = 2.11$) of a paramagnetic species with one unpaired electron, likely to be a ruthenium(III) complex. Since 2,6-dichloropyridine *N*-oxide can be regarded as a two-electron oxygen atom donor, we speculate that an oxoruthenium(V) species may have been generated as the key intermediate for this reaction. Note that oxoruthenium(V) species, e.g., [Ru^V(O)(N₄O)]ClO₄ [N₄O⁻ = [2-hydroxy-2-(2-pyridyl)ethyl]bis[2-(2-pyridyl)ethyl]amine anion],²⁸ can be powerful oxidants capable of oxidizing an unactivated C-H bond and an oxoruthenium(V) intermediate has also been proposed by Groves and co-workers in the ruthenium porphyrin-catalyzed alkane oxidations by Cl₂pyNO.²⁹ However, the involvement of a reactive Ru^{IV}-oxoporphyrin cation radical cannot be excluded.³⁰

Conclusion

A ruthenium complex of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin, [Ru^{II}(TDCPP)(CO)(EtOH)], was immobilized in mesoporous molecular sieves MCM-41; the supported Ru catalyst could bring about heterogeneous selective alkene epoxidations using 2,6-dichloropyridine *N*-oxide as the oxidant. This catalytic system is also effective toward norbornene and cyclooctene oxidations, while these transformations are unsuccessful when the zeolite-based TS-1-catalyzed conditions are applied. Nevertheless, the MCM-41 supported catalyst does exhibit size selectivity in the catalytic (+)-limonene oxidation where the terminal C=C bond (vs the internal trisubstituted C=C bond) reacts more readily. Bulky 3,4,6-tri-*O*-benzyl-D-glucal has failed to react under the heterogeneous Ru-catalyzed conditions, whereas the smaller acetyl derivative is converted to a 3:1 mixture of α - and β -glycol epoxides. The Ru/M-41(m) can be reused, and over 11 000 turnovers are easily attained. The loss of activity after prolonged/repeated usage is attributed to catalyst leaching and/or deactivation, which demands further improvement. Irrespective to this, the Ru/M-41(m)-Cl₂pyNO system is highly active and yet selective, simple, and safe to operate. We anticipate that the present heterogeneous catalytic system would be of potential application to practical organic synthesis.

Experimental Section

Materials. All solvents and alkenes substrates were purified by the standard procedures. Cyclohexene, cyclooctene, and styrene were first washed with 10% sodium hydroxide and then distilled over calcium hydride. Norbornene was purified by sublimation, whereas *cis*-stilbene was passed through a column of activated alumina before use. 2,6-Dichloropyridine *N*-oxide was prepared by Rousseau's method.³¹ Mesoporous MCM-41 was prepared according to the literature procedures by Beck and co-workers.¹⁸ Sodium silicate solution (27 wt % SiO₂, 14 wt % NaOH), cetyltrimethylammonium bromide, and

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(3-aminopropyl)triethoxysilane (APTES) were obtained from Aldrich and used as received. *meso*-Tetrakis(2,6-dichlorophenyl)porphyrin (H₂TDCPP) and [Ru^{II}(TDCPP)(CO)(EtOH)] complex were synthesized by the previously reported procedures.³²

Physical Measurements. UV/vis data for the MCM-41 samples were obtained from a UV/vis/NIR integrating sphere attachment, which employs the diffuse-reflectance technique. X-ray powder diffraction (XRD) studies were performed using monochromatized Cu K α radiation and recorded over the 2θ range from 1.5° to 30° in steps of 0.05° with a count time of 1 s at each point. The tube voltage was 40 kV with a 30 mA current. The pore sizes of the MCM-41 samples were obtained from the total pore volumes and the BET surfaces assuming cylindrical pores using nitrogen adsorption isotherms. Gas chromatography was performed on a SPB-5 capillary column (30 m) using nitrogen as the carrier gas, a flame ionization detector, and an integrator.

Procedure for the Preparation of M-41(m) by Silylation of MCM-41. MCM-41 (500 mg) was suspended in a chloroform solution (0.1 M, 50 mL) of (3-aminopropyl)triethoxysilane (APTES) at room temperature for 8–12 h with stirring. The solid product was collected by filtration, washed with chloroform, and then dried in a vacuum.

General Procedure for the Preparation of Ru/M-41(m) Catalyst. MCM-41(m) (400 mg) was suspended with adequate stirring in a methylene chloride solution of [Ru^{II}(TDCPP)(CO)(EtOH)] (0.17–0.28 mM, 10 mL) at room temperature for 1 h. The resulting solid product was isolated by filtration, washed with methylene chloride, and then dried in a vacuum at room temperature for 1 day. Ru/M-41(m) catalysts containing 0.1–8.3 wt % of [Ru(TDCPP)(CO)] were prepared.

Determination of Catalyst Loading in Ru/M-41(m). Ru/M-41(m) (10.0 mg) was digested in a 3% aqueous HF solution (10 mL). After 10 min of stirring, a clear red solution resulted, and the ruthenium porphyrin was extracted with methylene chloride (3 \times 15 mL). The organic extracts were combined, and solvent was removed by rotary evaporation to dryness. The residue was redissolved in a small amount of methylene chloride, transferred to a volumetric flask, and then diluted to 10.00–100.0 mL with methylene chloride. The Ru concentrations were determined by measuring the absorbance of the Soret band (410 nm) with reference to a linear calibration curve [0.76–8.6 μ M of [Ru^{II}(TDCPP)(CO)(EtOH)] in CH₂-Cl₂, $R = 0.999$] of absorbance vs concentration.

General Procedure for the Ru/M-41(m)-Catalyzed Alkene Epoxidations. A mixture of alkene (1.0 mmol), 2,6-dichloropyridine *N*-oxide (1.1 mmol, 200 mg), HCl (~0.3 mmol), and 0.4 wt % [Ru/M-41(m)] (50 mg, 0.195 μ mol of Ru) in CH₂-Cl₂ (5 mL) was stirred in a sealed vial for 24 h at 40 °C under an argon atmosphere. After the mixture was cooled to room

temperature, the solid catalyst was filtered, and the organic products were analyzed and quantified by gas–liquid chromatography and/or ¹H NMR spectroscopy. The recovered Ru catalyst may be reused two to four times. Controlled experiments using metal free M-41(m) as catalyst under identical reaction conditions did not afford any epoxides.

Homogeneous Oxidation of Glucal. A mixture of 3,4,6-tri-*O*-acetyl-D-glucal or 3,4,6-tri-*O*-benzyl-D-glucal (0.5 mmol), Cl₂pyNO (0.62 mmol), HCl (~0.3 mmol), and [Ru^{II}(TDCPP)(CO)(EtOH)] (2 mg, 1.91 μ mol) in CH₂Cl₂ (5 mL) was stirred in a sealed vial under an argon atmosphere at room temperature. The reaction was completed in 24 h as shown by TLC. The solvent was evaporated under high vacuum to dryness to yield the 1,2-anhydro sugars as colorless oils. To these oily compounds were added anhydrous methanol under nitrogen, and the resulting solutions were stirred at room temperature. The progress of methanolysis was monitored by TLC. After 1 h, methanol was removed by rotary evaporation, and the crude products were purified by flash column chromatography.

Methyl 3,4,6-tri-*O*-acetyl- β -D-glucopyranoside.^{23a} white crystalline solid; yield 60%; R_f (50% EtOAc in hexane) 0.54; ¹H NMR (300 MHz, CDCl₃) δ 5.20 (t, $J = 9.4$ Hz, 1H), 5.06 (t, $J = 9.7$ Hz, 1H), 4.27 (d, $J = 7.8$ Hz, 1H), 4.11–4.19 (dd, $J = 12.0, 2.1$ Hz, 1H), 3.96–4.05 (dd, $J = 12.1, 6.0$ Hz, 1H), 3.67–3.75 (m, 1H), 3.58 (s, 3H), 3.50–3.55 (br t, 1H), 2.44 (br s, 1H), 1.25 (s, 9H); MS-EI $m/z = 289$ (M⁺ – OMe); HRMS calcd for C₁₃H₂₀O₉ 320.290, found 320.288.

Methyl 3,4,6-tri-*O*-benzyl- β -D-glucopyranoside.^{23a} white solid; yield 63%; R_f (50% EtOAc in hexane) 0.58; ¹H NMR (300 MHz, CDCl₃) δ 7.42–7.10 (m, 15H), 4.98 (t, $J = 8.5$ Hz, 1H), 4.86–4.75 (m, 1H), 4.55–4.73 (m, 2H), 4.30 (d, $J = 7.8$ Hz, 1H), 3.83–3.62 (m, 2H), 3.49 (s, 3H), 3.55–3.43 (m, 1H).

Determination of the Relative Reactivities (k_{rel}) for the Heterogeneous Ru/M-41(m)-Catalyzed Oxidation of Substituted Styrenes. To a CH₂Cl₂ solution containing styrene (1.0 mmol), substituted styrene (1.0 mmol), 1,4-dichlorobenzene (1.0 mmol as internal standard), and Cl₂pyNO (0.5 mmol, 80 mg) was added 0.4 wt % Ru/M-41(m) (50 mg, 0.195 μ mol of Ru). The suspension was stirred for 12 h, and the amount of styrenes before and after the reaction was determined by GLC. The relative reactivities were determined by the following equation:

$$k_{rel} = k_Y/k_H = \log(Y_f/Y_i)/\log(H_f/H_i)$$

where Y_f and Y_i are the final and initial quantities of the substituted styrenes and H_f and H_i are the final and initial quantities of styrene.

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