Immobilization of new Mn(salen) complex over MCM-41 and its activity in asymmetric epoxidation of styrene

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New tetradentate chelates of bis-Schiff bases were synthesized and then these chiral salen ligands were immobilized over mesoporous MCM-41 by using the ion-exchange method. The efficiency of the chiral catalyst was examined in the asymmetric epoxidation of styrene. Chiral Mn(salen) complexes immobilized onto mesoporous MCM-41 were stable during the reaction without any leaching and exhibited relatively high enantioselectivity for epoxidation as compared with homogeneous complexes.

Keywords: MCM-41, chiral Mn(salen) ligand, ion exchange, asymmetric epoxidation, styrene

1. Introduction

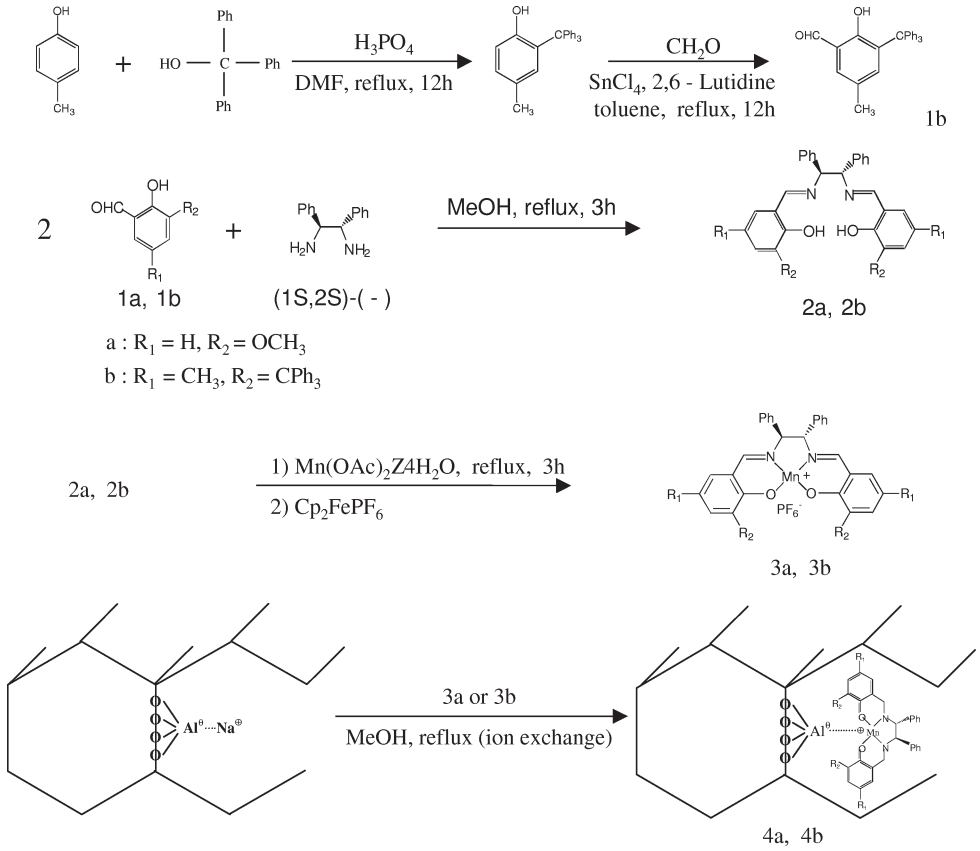
Considerable attention has been given to the enantioselective epoxidation of unfunctionalized olefins and the development of catalysts is an important goal in asymmetric syntheses. The most interesting approach is the use of chiral catalysts capable of asymmetric induction. It has been reported that the combination of titanium(IV) alkoxide, an optically active tartrate ester, and t-butyl hydroperoxide is capable of epoxidizing a wide variety of alcohols with an enantiomeric excess (e.e.) larger than 90%, which is one of the most widely applied reactions in asymmetric synthesis [1–3]. In these cases, substrates must contain specific functional groups to achieve the precoordination required for high enantioselectivity. By contrast, the achievement of high enantioselectivity is determined solely through nonbonded interactions in the epoxidation of olefins bearing no functionality to precoordination to the catalyst such as styrene derivatives [4]. Groves and Myers [5] have examined the asymmetric epoxidation using catalysts of optically active iron porphyrins. Employing FeT($\alpha, \beta, \alpha, \beta$-Binap)PPCl and iodosylbenzene, styrene oxidized to (R)-(+)-styrene oxide in 48% e.e. Styrene is one of the most important prochiral olefins in the chemical industry. Zhang et al. [4] have reported that manganese complexes of chiral Schiff bases catalyze epoxidation of alkyl- and aryl-substituted olefins with high e.e. (%). Catalysts of chiral salen ligands showed $>$90% e.e. for the epoxidation of conjugated *cis*-disubstituted and trisubstituted olefins [6], but using these catalysts only 50–60% e.e. was obtained in the styrene epoxidation [4]. Palucki et al. [7] have performed the low-temperature epoxidation of styrene and obtained the highest e.e. value of 86% using m-CPBA oxidant and excess N-methylmorpholine N-oxide as an additive. Jacobsen et al. [6] reported that introduction of *tert*-butyl groups para to the salen oxygens resulted in an improvement in catalytic selectivity [1].

Bowers and Dutta [8] have studied the synthesis of a Mn complex of the salen ligand encapsulated in zeolite Y and its catalytic activity for the oxidation of cyclohexene and styrene. But they have never tested salen ligands as catalysts in asymmetric epoxidation reactions. Sabater et al. [9] have synthesized a chiral salen Mn(III) complex of simple structure inside the supercages of zeolite Y, showing catalytic activity very similar to that of the chloride complex in the homogeneous phase. Ogunwumi and Bein [10] have reported that asymmetric manganese salen complexes were assembled and trapped in the cages of zeolite EMT in a multistep synthesis and these heterogeneous catalysts produced high enantiomeric excess in the epoxidation of aromatic alkenes with NaOCl. Recently, Frunza et al. [11] have checked the capability of MCM-41 mesoporous materials as supports for homogeneous chiral salen ligands. They have proposed that the complex is parallelly arranged to the pore walls by the strong hydrogen bonding between the complex and MCM-41 walls. Very few asymmetric catalytic reactions have been examined on zeolites. We have synthesized new tetradentate chelates of bis-Schiff bases and then immobilized these chiral salen ligands by ion exchange over mesoporous MCM-41. We report herein that these new catalysts afforded high level of enantioselectivity in the epoxidation of unsubstituted olefins such as styrene and α-methylstyrene.

2. Experimental

For this study, salen manganese(III) complexes were synthesized according to scheme 1.

Two kinds of chiral salen ligands (**2a**, **2b**) were prepared by the condensation of (1S, 2S)-(−)1,2-diphenylethylenediamine and the appropriate salicylaldehyde derivative. O-valine (**1a**) was chosen as one of the salicylaldehydes and obtained from Aldrich Co. The salicylaldehyde **1b**



Scheme 1.

with –C(Ph_3) group was synthesized by direct formylation according to the method reported by Casiraghi [12] and Zhang [13]. The salicylaldehyde derivatives **1a** and **1b** (2.0 equiv.) were added to the solution of (1S, 2S)-(−)1,2-diphenylethylenediamine (1.0 equiv.) in MeOH solution, respectively. This mixture was heated to reflux for 3 h and then was concentrated to dryness *in vacuo* and recrystallized in ethanol solution. The resulting yellow crystals (**2a**, **2b**) were collected by filtration. The compound of **2a** or **2b** in MeOH solution was heated to reflux for insertion of the Mn(II) center, as indicated in scheme 1. A solution of ferricenium hexafluorophosphate (Cp_2FePF_6) was added to this mixture to obtain the cationic $(Mn–salen)^+PF_6^-$ complex (**3a**, **3b**). The mixture was concentrated to dryness and washed with hexane to remove the side product, ferrocene.

In addition, ion-exchangeable Al-containing MCM-41 (mesoporous material with 35 Å pore diameter) was synthesized hydrothermally, as described in the reported paper [14]. As-synthesized MCM-41 material was washed, filtered and dried overnight at 120 °C. The dried sample was calcined in air at 450 °C to remove the organic templates. In this study, two different methods were adopted to immobilize the Mn(salen) complexes onto MCM-41, as shown in figure 1.

First, the complex of the form $(Mn–salen)^+PF_6^-$ was synthesized by direct reaction according to the method shown in scheme 1. A similar procedure for the preparation of cationic Mn(salen) complex has been reported by Noda et al. [15]. $(Mn–salen)^+$ complex (**3a**, **3b**) was ion exchanged by Na^+ on MCM-41 at 80 °C in ethanol solvent, followed by washing with hexane and CH_2Cl_2 drying at 100 °C (method A).

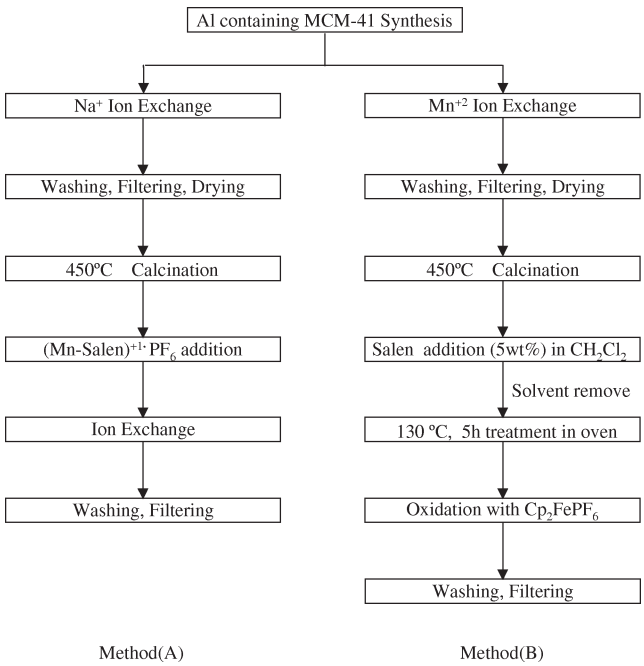


Figure 1. Schematic diagrams for the preparation of chiral salen containing MCM-41 catalyst.

Second, Mn^{2+} was introduced into MCM-41 by ion exchange in $Mn(II)(OAc)_2$ aqueous solution. Then the Mn^{2+}-exchanged MCM-41 was calcined at 450 °C and it was mixed with a predetermined amount of chiral salen ligand (**2a**, **2b**) in dichloromethane solvent. After removal of solvent, the mixture was kept in an oven at 130 °C for 5 h in air. The obtained product was transferred into a flask containing Cp_2FePF_6 in acetonitrile solution and the resulting mixture was stirred for 6 h at room temperature. The residue was washed with hexane to remove uncomplexed salen ligand (method B).

The epoxidation of styrene was carried out with m-chloroperoxobenzoic acid (m-CPBA) as a terminal oxidant. Reactions were run at 0 and −80 °C.

The solution of styrene or α-methylstyrene (0.96 mmol), N-methylmorpholine N-oxide (NMO, 4.80 mmol) and salen Mn complex (0.077 mmol) in 10 ml of CH_2Cl_2 was cooled to 0 °C (or −80 °C). m-CPBA (1.92 mmol) was added as a solid in five roughly equal portions over a 5 min period. The reaction mixture was stirred for 6 h. After finishing the reaction, 10 ml of 1 N NaOH was added and the organic phase was separated and washed with brine. The organic phases were dried over $MgSO_4$. The e.e. (%) values were determined by capillary GC using a chiral column (Astec γ-cyclodextrin trifluoroacetyl, 40 m × 0.25 mm i.d.).

3. Results and discussion

Even though the manganese complex of salen ligand encapsulated in the supercage of zeolite Y (13 Å) by Bowers and Dutta [8] was not a chiral catalyst, this preparation method can be also applied to immobilize the chiral salen complexes over mesoporous materials. In the zeolite Y system, salen ligand of appropriate size (10–11 Å) formed in the supercage (13 Å) cannot escape through the pore opening (7 Å). But this encapsulation method may not be suitable for MCM-41 because of its one-dimensional large pore system (35 Å). Optically active salen manganese(III) complexes of cationic form have been found to be efficient catalysts for the asymmetric epoxidation of simple alkenes [15] and these bulky chiral salen ligands are too large to exist in the supercage of zeolite Y. Instead the ion exchange ability of MCM-41 mesoporous material is capable of immobilizing the chiral salen ligands of cationic type as a heterogeneous catalyst, without any steric hindrance effect. As a result, the ion exchange method was chosen to immobilize the large chiral ligands over MCM-41 in this study. The characterization of the samples was carried out using UV-vis reflectance spectroscopy after immobilizing the Mn(salen) complexes onto MCM-41. The obtained UV spectra are shown in figure 2. (Mn–salen)$^+PF_6^-$ solution of **3b** showed the bands at near 230, 280, 315, 350 and 385 in the spectra. The UV spectra of the complex in solution and of the immobilized form were the same, indicating that the chiral salen Mn complex maintained its structure on the MCM-41. The immobilized salen ligand prepared by

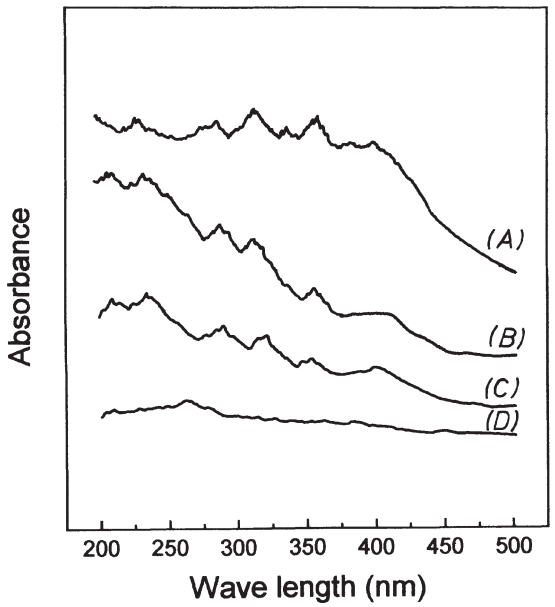


Figure 2. The UV spectra of chiral Mn(III) salen ligands and immobilized complexes over MCM-41. (A) Sample **3b**, (B) sample **4b**, (C) sample **6b**, (D) Mn^{2+}-exchanged MCM-41.

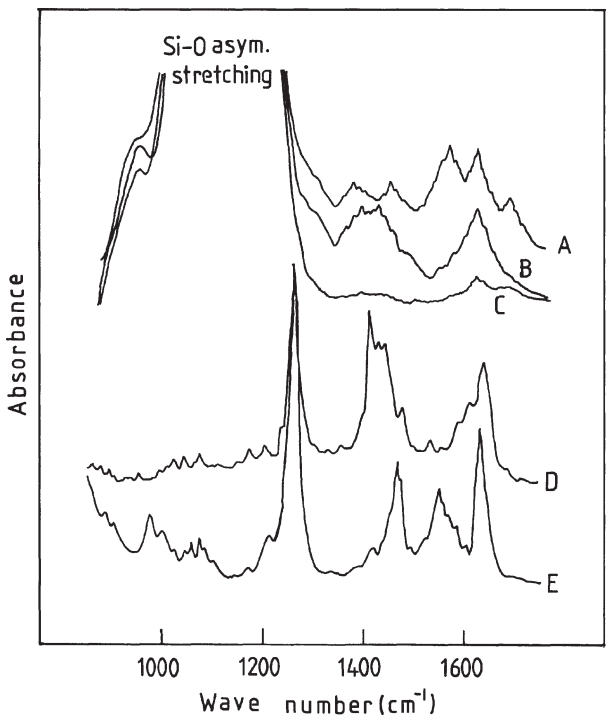
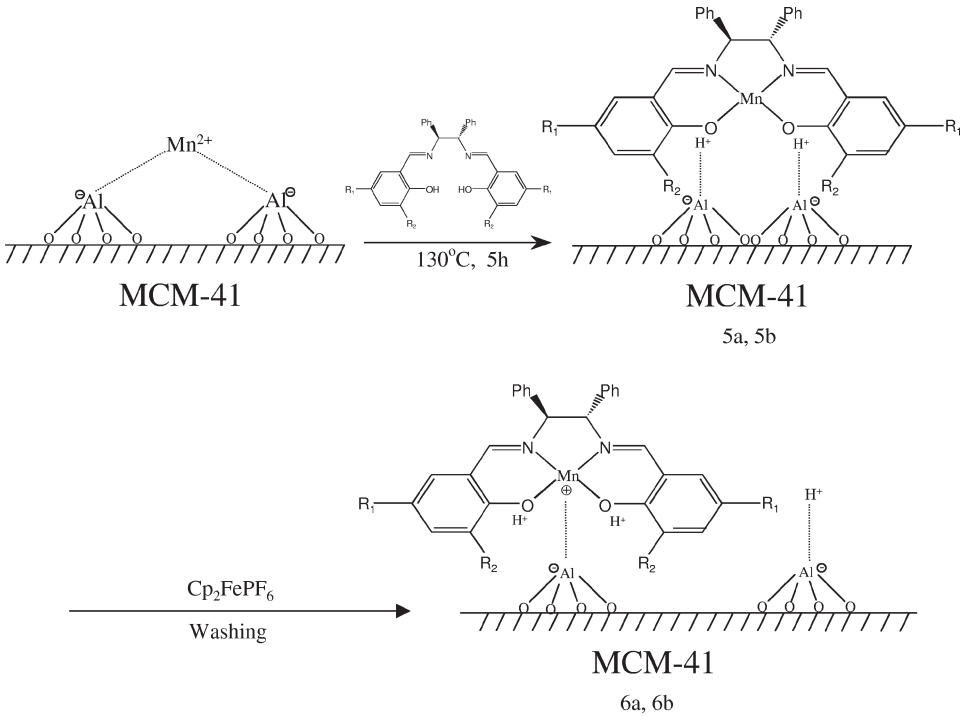


Figure 3. The IR spectra of complexes in solution and those of immobilized complexes over MCM-41. (A) Sample **6a**, (B) sample **6b**, (C) pure MCM-41, (D) sample **3b**, (E) sample **3a**.

method B (**6a**, **6b**) also showed the characteristic bands of a Mn(III) salen complex.

The characterization of the samples was also carried out using FT-IR spectroscopy after synthesizing the Mn(salen) complexes and immobilizing them onto the MCM-41. In the IR spectra, as shown in figure 3, all the salen complexes as well as MCM-41 loaded chiral salen ligand exhibited the



Scheme 2.

characteristic imine band at 1630 cm^{-1}. This peak is assigned to the stretching vibration of the C=N bond. Frunza et al. [11] have observed the large decrease of the relative intensity and a shift to lower wavenumber for the band at 1611 cm^{-1}. They suggested an alignment of the plane of the complex to the MCM walls by observing the IR band shifts to higher wavenumber due to the changes of electronic structures of the complex caused by guest/host interaction. In this work, it is not clear to find a band shift on the spectra because of the peak broadening. The appearance of the spectrum of the homogeneous complex is relatively similar to that of the complex embedded on MCM-41. Bowers and Dutta [8] have proposed that the encapsulated product is the form of Mn(III) salen OH which is obtained by aerobic oxidation of Mn(II) salen complexes. In this study, the solid sample of **5a** or **5b** exhibited a yellow color but turned to brown after oxidation in ethanol solution, which is indicative of Mn(III) salen complexes formation (**6a**, **6b**). In the preparation of catalyst **6a** and **6b**, the coordination of salen ligand **2a** and **2b** to a divalent Mn^{2+} cation would result in the production of the electrically neutral Mn(II) salen complex and the liberation of two protons. Therefore, the released protons become the charge compensators of the anionic MCM-41 framework, replacing the Mn^{2+} ion in the pore [16]. The produced neutral Mn(II) salen complex will be converted into $(Mn(III)–salen)^{+}$ form by treatment with Cp_2FePF_6 and adhere at the cationic site inside the MCM-41 pore. The possible scheme is shown in scheme 2.

The trends in reactivity and enantioselectivity of the immobilized chiral Mn(salen)/MCM-41 and the same complex in solution were examined for the epoxidation of styrene. As shown in table 1, chiral Mn(salen) immobilized onto mesoporous MCM-41 exhibited relatively high enantioselectivity for epoxidation as compared with homogeneous complexes, respectively. Solutions of buffered commercial bleach (NaOCl) have proven to be useful oxygen atom sources for epoxidation reactions catalyzed by chiral salen Mn(III) complexes [6,13]. But NaOCl buffer solution was not suitable for our study, because exchangeable Na^{+} cation existed in the reaction mixture. To prevent this possibility of ion exchange, m-chloroperoxobenzoic acid (m-CPBA) was used as a terminal oxidant in the presence of N-methylmorpholine N-oxide additive. The epoxidation with m-CPBA was remarkably rapid even at 195 K, as examined by Palucki et al. [7]. The increase in enantioselectivity was also obtained at low reaction temperature over all catalysts. High enantioselectivity was obtained

Table 1
Asymmetric epoxidation of styrene and α-methylstyrene.

Entry	Olefin	Catalyst	Reaction temp. (°C)	Conversion (%)	e.e. (%)
1	styrene	**3a**	0	93	18
2	″	**4a**	0	85	31
3	″	**6a**	0	82	27
4	″	**3b**	0	95	56
5	″	**3b**	−80	87	78
6	″	**4b**	0	82	70
7	″	**4b**	−80	75	86
8	″	**6b**	0	76	66
9	″	**6b**	−80	66	84
10	α-methylstyrene	**3b**	0	71	23
11	″	**6b**	0	56	38
12	″	**6b**	−80	47	54

Table 2
The catalytic activity and selectivity of chiral Mn(salen) complexes immobilized on MCM-41 during the recycling in styrene epoxidation.[a]

Recycling number	Catalyst	Reaction temp. (°C)	Conversion (%)	e.e. (%)
1st	**6b**	0	76	66
2nd	**6b**	0	78	64
3rd	**6b**	0	75	64

[a] Reaction time 6 h; catalyst 8 mol% of olefins.

particularly with more hindered catalysts such as **3b**, **4b** and **6b**, as shown in table 1. In addition, the e.e. (%) value obtained over immobilized catalysts of Mn(salen)/MCM-41 was higher than that over homogeneous catalyst. The homogeneous salen catalyst of **3a** which has less steric hindrance exhibited comparatively moderate enantioselectivity in epoxidation of styrene. Especially, the reaction using Mn(salen)/MCM-41 of **4a** and **6a** gave improved optical yield. However, we expected that lower enantioselectivity would be attained over this salen derivative. Because it is well known that the introduction of a bulky group such as *tert*-butyl in the salen complexes usually results in a further improvement in catalytic selectivity. The increase in the enantioselectivity over catalyst **3a** may be attributed to the presence of electron-donating methoxy groups. Jacobson et al. [17] showed that a Mn(salen) catalyst containing an electron-donating group exhibited higher asymmetric induction than that bearing an electron-withdrawing group. It is assumed that different electronic environment of Mn cation and steric restriction in the mesoporous zeolite pore may provide strong influence on the stereoselectivity. Jacobson et al. have emphasized that the use of an unhindered precursor opens a quadrant to olefin approach (side-on approach) in which stereochemical communication between ligand and incoming substrate is maximized [6]. For instance, the epoxidation of styrene and α-methylstyrene with the chiral Mn(salen) containing t-butyl groups para to the salen oxygens showed a maximum enantioselectivity of 57 and 30% e.e., respectively, [4]. However, higher enantioselectivity over chiral Mn(salen) complexes immobilized over mesoporous zeolite indicates the free accessibility of the complexes on MCM-41 for the reactant molecules.

Homogeneous chiral Mn(salen) complexes and the prepared solid samples were dark brown color. After using Mn(salen) complexes immobilized on MCM-41 as catalysts, the resultant solution exhibited no color and no Mn was detected in the solution. This means that Mn(salen) complexes immobilized on mesoporous materials are stable during the reaction and exsist in the pore system without any extraction. The catalytic activity and selectivity of immobilized Mn(salen) complexes have not changed more or less after three times of reusing. The catalyst was washed with CH_2Cl_2 solvent and dried under vacuum at 60 °C. The result is given in table 2.

In conclusion, a new chiral Mn(salen) complex containing a $-C(Ph)_3$ group could be synthesized and the immobilization of this complex was performed with the ion exchange method. The asymmetric catalytic epoxidation using Mn(salen) complexes which are bound to MCM-41 can be applied with success and unexpectedly high enantioselectivities are attainable in styrene epoxidation. On the basis of asymmetric epoxidation results, chiral Mn(salen) complexes immobilized on cation exchangeable mesoporous material by the present procedure can be applied as an effective asymmetric heterogeneous catalyst for the epoxidation of unsubstituted olefins. The ligands and catalysts prepared in this study may provide a rather unique approach to (asymmetric) heterogeneous catalyst design.

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