Catalysis Today 140 (2009) 162–168

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Manganese octahedral molecular sieve catalysts for selective styrene oxide ring opening

Shanthakumar Sithambaram [a], Linping Xu [a], Chun-Hu Chen [a], Yunshuang Ding [b], Ranjit Kumar [a], Craig Calvert [a], Steven L. Suib [a,b,*]

[a] Department of Chemistry, University of Connecticut, U-3060, 55 North Eagleville Rd., Storrs, CT 06269-3060, USA
[b] Department of Chemical, Materials, and Biomolecular Engineering, University of Connecticut, U-3060, 55 North Eagleville Rd., Storrs, CT 06269-3060, USA

ARTICLE INFO

Article history:
Available online 20 November 2008

Keywords:
Heterogeneous catalysis
Manganese
Octahedral molecular sieves
Ring opening
Epoxides
Oxidation

ABSTRACT

Manganese octahedral molecular sieve (OMS) catalysts prepared by different methods have been employed for terminal ring opening of epoxides. Conversions ranging from 14% to 80% were obtained depending on the properties of the OMS catalysts. The catalysts act as Lewis acids in the reaction to facilitate nucleophilic attack on styrene oxide. Doping with other transition metals such as V, W, and Mo may alter the Lewis acidity of the materials and hence, leads to significant enhancement in conversions (100%) and selectivities for the ring opening. Effects of different solvents and nucleophiles were also studied in the reaction. This process using OMS catalysts is environmentally friendly and the catalysts can be reused without loss of activity.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

β-Amino alcohols are versatile building blocks in the synthesis of a wide range of biologically active natural and synthetic products [1], artificial amino acids [2], and chiral auxiliaries [3]. The classical synthesis of β-amino alcohols involves the ring opening of epoxides with amines [4]. However, these reactions, which are generally carried out with a large excess of amines at elevated temperatures, often fail when poorly nucleophilic amines or sterically crowded amines or epoxides are used. In addition, these reactions are accompanied by the poor regio-selectivity of ring opening. Transition metal based catalysts are widely used for successful ring opening reactions. $CoCl_2$, VCl_3, and $Zn(OAc)_2$ were used as Lewis acids to catalyze the reaction [5–7]. Onaka et al. have used zeolites for the ring opening of unsymmetrical epoxides with aniline [8]. Recently, Chakraborti et al. have reported silica gel catalysis for ring opening under solvent free conditions [9]. The use of transition metal based catalysts or zeolites for the ring opening of epoxides reduces the reaction time and enhances regio-selectivity. However, these processes which require expensive and stoichiometric amounts of reagents, suffer from poor regio-selectivity and most of the times the catalyst cannot be reused.

Here, we describe a route to styrene oxide ring opening to produce β-aminoalcohols in an environment friendly manner using inexpensive, reusable manganese octahedral molecular sieve (OMS) catalysts. In this reaction, OMS-2 acts as a Lewis acid to catalyze the reaction. OMS materials have been shown to possess excellent catalytic properties in oxidation [10,11] and condensation reactions [12]. These materials can be synthesized by various methods and their characteristics are well documented [13]. OMS-2 materials have a one-dimensional tunnel structure formed by 2 × 2 edge shared MnO_6 octahedra (Fig. 1). The composition of K-OMS-2 is $KMn_8O_{16}\cdot nH_2O$ and the tunnels have dimensions of 4.6 Å × 4.6 Å. The average oxidation state of Mn in OMS-2 is ~3.8 with the presence of Mn^{4+}, Mn^{3+}, and Mn^{2+} ions in the framework. Doping other metals can enhance the catalytic properties of OMS-2 materials. Chen et al. have successfully doped Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} into OMS-2 materials [14]. The catalytic activities of these OMS-2 materials were evaluated for the decomposition of 2-propanol [15]. Cu-OMS-2 showed significantly enhanced activity towards decomposition of propanol. In the present study, OMS-2 materials prepared by different methods from our laboratory were evaluated for catalytic activity for the ring opening of epoxides. Furthermore, V, Mo, and W doped OMS-2 prepared by reflux methods were studied for terminal ring opening of styrene oxide. This environmentally friendly process produces either expensive or commercially unavailable amino alcohols from cheaper starting materials.

---

* Corresponding author at: Department of Chemistry, University of Connecticut, U-3060, 55 North Eagleville Rd., Storrs, CT 06269-3060, USA. Tel.: +1 860 486 2797; fax: +1 860 486 2981.
E-mail address: Steven.Suib@uconn.edu (S.L. Suib).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.10.007

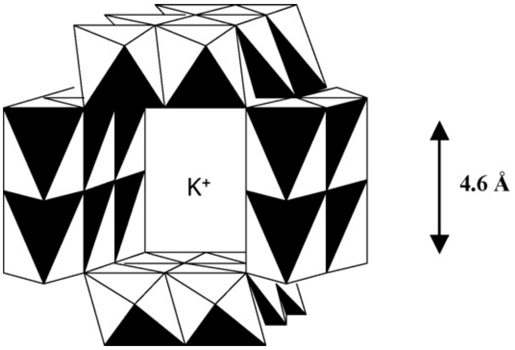


Fig. 1. Structure of 2 × 2 OMS-2.

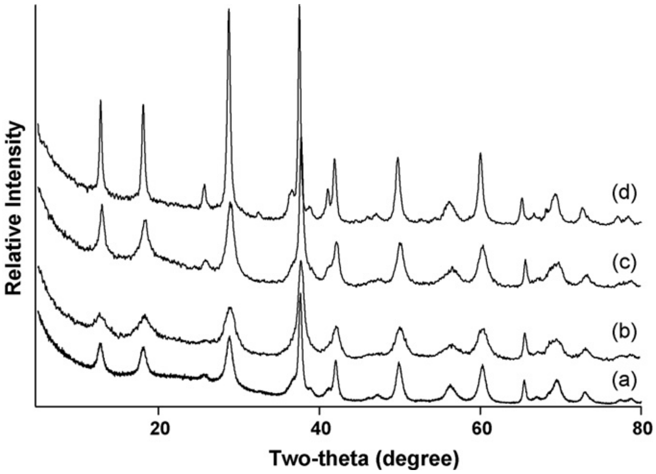


Fig. 2. X-ray diffraction patterns of (a) K-OMS-2 (reflux), (b) K-OMS-2 (solvent free), (c) K-OMS-2 (hydrothermal) and (d) K-OMS-2 (high temperature).

2. Experimental

2.1. Preparation of catalysts

K-OMS-2_{SF} was prepared using a solvent free method by Ding et al. [16] by mixing 9.48 g of $KMnO_4$ and 22.05 g $Mn(Ac)_2{\cdot}4H_2O$ and was ground homogeneously in an agate mortar. The mixed powders were then placed in a capped glass bottle and maintained at 80 °C for 4 h. The resulting black powder was thoroughly washed with deionized water several times to remove any ions that may be present and was finally dried overnight at 80 °C.

The high temperature K-OMS-2_{HT} was prepared by a combination of sol–gel and combustion methods by Shen [17] with the Mn source being $Mn(NO_3)_2$. KNO_3 and $Mn(NO_3)_2$ in a molar ratio of 1:5 were dissolved in distilled deionized water (solution A). Glycerol and KNO_3 were mixed in a 1:10 molar ratio (solution B). Solutions A and B were mixed in deionized water with vigorous stirring to form a clear solution and then heated to 120 °C to form a gel (usually 5 h). The gel was then heated to 250 °C for 2 h to complete the combustion reaction. The black powder was then calcined at 600 °C for 3 h to obtain the final product.

K-OMS-2_R was prepared by a reflux method according to literature [18]. To a 500 ml of round-bottomed flask with a condenser, potassium permanganate solution (0.4 M, 225 ml) was added to a mixture of manganese sulfate hydrate solution (1.75 M, 67.5 ml) and concentrated nitric acid (6.8 ml). The dark brown slurry was refluxed for 24 h, then filtered and washed with deionized water several times. The catalyst was dried at 120 °C overnight before use.

K-OMS-2_{HY} was prepared by a hydrothermal method according to literature [19]. The synthesis mixture was composed of a total of 32 mmol of K_2SO_4, $K_2S_2O_8$, and $MnSO_4.H_2O$ in a 3:3:2 molar ratio dissolved in 70 ml of DDW. The mixture was transferred to a 125 ml Teflon vessel held in a stainless-steel vessel. The vessel was sealed and placed in an oven and heated at 250 °C for four days.

2.2. Catalyst characterization

2.2.1. X-ray powder diffraction studies

X-ray powder diffraction (XRD) experiments were carried out using a Scintag Model PDS 2000 diffractometer. Samples were loaded on glass slides, and Cu Kα radiation was used at a beam voltage of 45 kV and 40 mA beam current. The X-ray patterns of the catalysts were compared to that of the standard OMS-2 materials (JCPDS file #29-1020) (Fig. 2).

2.2.2. Surface area measurements

The surface areas of the OMS-2 materials were measured using the Braunuer–Emmet–Teller (BET) method on a Micrometrics ASAP 2010 instrument. Using N_2 as the absorbent and a multipoint method the determined areas of K-OMS-2 (reflux) and K-OMS-2 (hydrothermal) were found to be ~90 and ~70 $m^2\,g^{-1}$. The surface areas of K-OMS-2 (high temperature) and K-OMS-2 (solvent free) were ~10 and ~160 $m^2\,g^{-1}$, respectively.

2.2.3. Scanning electron microscopy

Scanning electron micrographs were taken on a Zeiss DSM 982 Gemini field emission scanning microscope with a Schottky Emitter at an accelerating voltage of 2 kV with a beam current of 1 μA. The images showed a characteristic fibrous morphology of OMS-2 materials (Fig. 3).

2.3. Catalytic testing

Reactions in a stirred glass reactor were carried out in a 50 ml round-bottomed flask connected to a reflux condenser. About 50.0 mg of the catalyst was suspended in a solution of 1 mmol of styrene oxide and 2 mmol of aniline and 10 ml toluene as the solvent. The reaction mixture was stirred under reflux for 24 h.

2.4. Analytical procedure

Analyses of products in the reaction were carried out using gas chromatography–mass spectrometry (GC–MS) and NMR. An HP 5890 series gas chromatograph coupled with an HP 5971 mass detector was used for the identification and quantification of the reaction products using an internal standard. An HP-1 column (non-polar cross-linked siloxane) with dimensions of 12.5 m × 0.2 mm × 0.33 μm was used for the gas chromatograph. ^1H and ^{13}C NMR were collected on Brucker DRX-400 (400.144 MHz ^1H, 100.65 MHz ^{13}C).

3. Results

3.1. Catalytic activity

Styrene oxide and aniline were reacted in toluene with OMS-2 catalysts prepared by hydrothermal, reflux, solvent free, and high temperature methods in our laboratory. According to Table 1, K-OMS-2 prepared by reflux and hydrothermal methods gave higher conversions for the reaction than K-OMS-2 prepared by other methods. Apart from the anticipated β-amino alcohol, imines were also formed as side products in the reactions. Moreover, metal-doped M-OMS-2 catalysts [M = V, Mo and W] prepared by the reflux method were used for the styrene

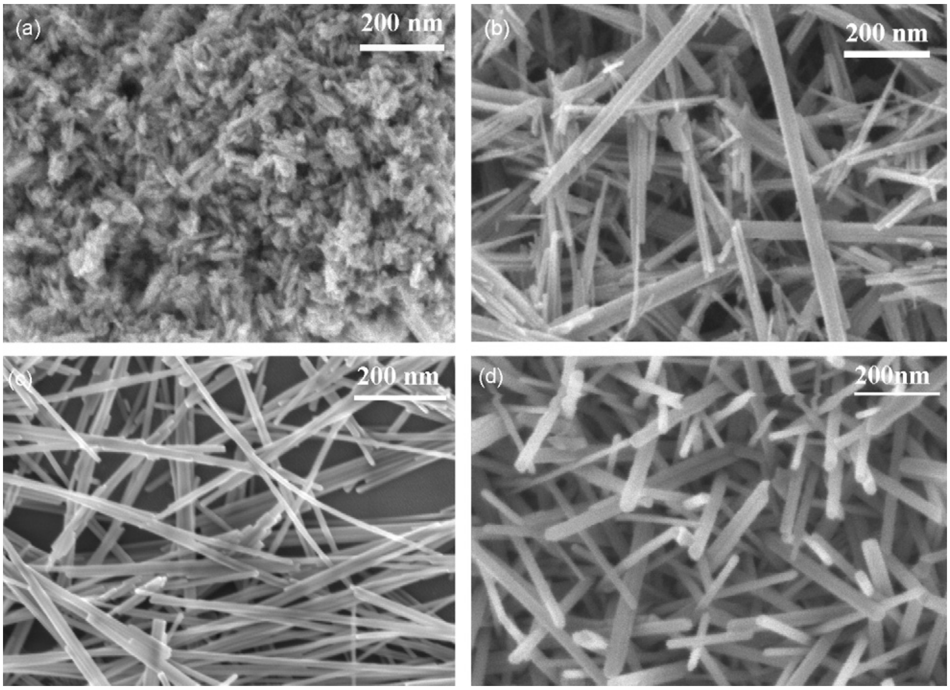
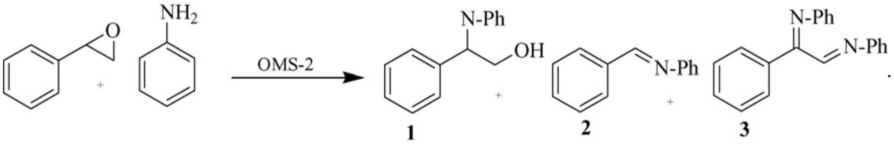


Fig. 3. FESEM images of K-OMS catalysts, (a) solvent free, (b) conventional (c), hydrothermal and (d) high temperature.

Table 1
Conversion of styrene epoxide by OMS-2 catalysts.



Catalyst	TON[a]	Conversion (%)[b]	Selectivity (%)[c]		
			β-Amino alcohol	Imine	Diimine
K-OMS-2_R	12.2	76	88	12	0
K-OMS-2_{HY}	12.8	80	69	28	3
K-OMS-2_S	7.5	47	95	3	2
K-OMS-2_{HT}	2.2	14	0	100	0
No catalyst	0	0	0	0	0

Reaction conditions: 50.0 mg of catalyst; 1 mmol of styrene oxide; 2 mmol of aniline; t = 24 h and 10 ml of toluene as solvent; T = 110 °C.

[a] TON – $[(\mathrm{mol}_{\mathrm{substr}})(\mathrm{mol}_{\mathrm{catalyst}})^{-1}]$, where $\mathrm{mol}_{\mathrm{substr}}$ is the moles of styrene oxide converted.

[b] Conversion (%) based on substrate = ← [1 ⊆ ← (concentration of substrate left after reaction)initial concentration of substrate)] ← 100.

[c] Selectivities for **1**, **2** and **3**.

epoxide ring opening under the same conditions. β-Amino alcohol **1** resulting from the ring opening, a monoamine **2,** and a diimine **3** were formed in most cases. However, the selectivity for β-amino alcohol was the highest in all cases. Table 2 shows that doping transition metals in the K-OMS-2 catalysts prepared by reflux methods significantly enhanced the conversion of styrene oxide in the reaction.

3.2. *Effect of nucleophiles*

In a further set of experiments, styrene oxide was reacted with different nucleophiles to study their effect in ring opening. The results are summarized in Table 3. Anilines and phenols with different substituents in the benzene rings were used as nucleophiles. In some cases, two isomers of the β-amino alcohol were observed among the products.

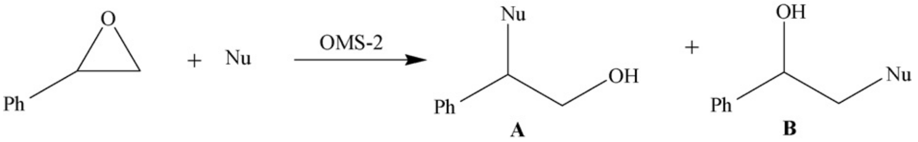
Table 2
Styrene oxide ring opening catalyzed by doped OMS-2 (reflux).

Catalyst	Conversion (%)	Selectivity (%)		
		β-Amino alcohol	Imine	Diimine
OMS-2_R	76	88	12	0
1% V-OMS-2_R[a]	83	86	8	6
2% V-OMS-2_R	88	83	14	3
10% V-OMS-2_R	100	73	20	7
1% Mo-OMS-2_R	91	81	13	6
2% Mo-OMS-2_R	95	84	9	6
10% Mo-OMS-2_R	100	62	31	8
1% W-OMS-2_R	98	81	13	4
Reused OMS-2_R	79	88	11	1

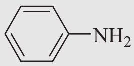
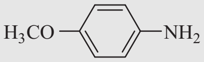
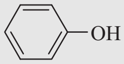
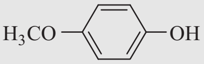
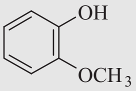
Reaction conditions: 50.0 mg of catalyst; 1 mmol of styrene oxide; 2 mmol of aniline; t = 24 h and 10 ml of toluene as solvent; T = 110 °C.

[a] Initial ratio of V:Mn = 1:100 in the catalyst.

Table 3
Styrene oxide ring opening with different nucleophiles.



.

Entry	Nucleophile	Conversion (%)	Selectivity[a] (%)	A:B[b]
1		76	88	100:0
2		80	59	66:34
3		81	70	94:6
4		84	77	77:23
5		49	45	97:3
6		35	69	76:24
7		19	46	53:47

Reaction conditions: 50.0 mg of K-OMS-2_R catalyst; styrene oxide and nucleophile mmol ratio = 1: 2; t = 24 h and 10 ml of toluene as solvent; T = 110 °C. Ph—phenyl, Nu—nucleophile.

[a] Selectivity for both A and B isomers.

[b] Ratio between A and B.

3.3. *Effect of solvents*

The influence of solvents in the catalytic ring opening of styrene oxide was investigated at 75 °C for the comparison of activity. The results of the effect of solvents are given in Table 4. Both polar and non-polar solvents were evaluated for the reaction and toluene was found to be the best solvent for this reaction system.

4. Discussion

4.1. *Catalytic reactions*

Epoxide ring opening reactions can either proceed along acid or base catalyzed pathways [20]. Transition metals can play the role of Lewis acids to facilitate the ring opening by nucleophilic attack. OMS-2 materials have predominant Lewis acidity arising due to defects, oxygen vacancies, and positive charges in the metals. The Lewis acidity of OMS-2 is believed to primarily catalyze the ring opening reaction of styrene epoxide. Doping other transition metal ions such as V^{5+}, Mo^{6+}, and W^{6+} into mixed valent (Mn^{4+}, Mn^{3+}, and Mn^{2+}) manganese oxide octahedral molecular sieves may alter their Lewis acidity and hence has significant impact on their catalytic activity. Our initial set of experiments investigated the K-OMS-2 mediated epoxide ring opening reaction with styrene oxide and aniline using toluene as the solvent (Table 1). The method of preparation of K-OMS-2 had significant impact on conversions and selectivities. K-OMS-2 catalysts function as Lewis acids in ring opening reactions and the conversions in the reactions can be primarily related to their Lewis acidity.

Table 5 shows Lewis acidity/basicity of K-OMS-2 catalysts determined by NH_3 and CO_2 chemisorption that was reported recently by Ghosh et al. [21]. Furthermore, the temperature

Table 4
Ring opening of styrene oxide with solvents over K-OMS-2_R.

Solvent	μ[a]	ε[a]	Polarity	Conversion (%)	Selectivity (%)[b]
ACN	3.2	37.5	46	45	92
CH_2Cl_2	1.8	9.1	30.1	8	100
THF	1.75	7.6	21	6	100
Toluene	0.4	2.38	9.9	72	93
Hexane	0	1.9	0.9	44	89

Reaction conditions: 50.0 mg of K-OMS-2_R catalyst; 1 mmol of styrene oxide; 2 mmol of aniline; t = 24 h and 10 ml of solvent; T = 75 °C.

[a] μ: dipole moment, ε: dielectric constant.

[b] Selectivity for β-amino alcohol.

Table 5
Lewis acidity/Lewis basicity of K-OMS-2 catalysts.

Catalyst	Total Lewis acidity (mmol g^{-1})	Lewis acidity due to chemisorption (mmol g^{-1})	Total Lewis basicity (mmol g^{-1})
K-OMS-2_R	0.7	0.4	0.05
K-OMS-2_{HY}	0.63	0.3	0.07
K-OMS-2_S	0.98	0.4	0.2
K-OMS-2_{HT}	0.06	0.02	0.02

programmed desorption (TPD) of ammonia with these catalysts show that the OMS-2 materials have at least one strong Lewis/ Bronsted acid site. These acidic properties are crucial in the ring opening reaction. The Lewis acidity of K-OMS-2_R and K-OMS-2_{HY} are close and they show comparable conversions and selectivities (Table 1) for the epoxide ring opening reaction. The lowest conversion observed with K-OMS-2_{HT} can be attributed to poor Lewis acidity of the material. Although K-OMS-2_S has the highest Lewis acidity and surface area, the conversion was found to be lower. Nevertheless, the selectivity for Lewis acid catalyzed generation of the β-amino alcohol was the highest when K-OMS-2_S was used. A detailed investigation of other properties of catalysts governing this reaction is now under investigation. Turnovers of up to 13 were achieved in a single batch with K-OMS-2 catalysts.

Vanadium, molybdenum, and tungsten based materials have been known to have excellent catalytic properties [22]. V, Mo and W metals were doped into OMS-2 catalysts in different ratios and their detailed characterization properties will be discussed elsewhere [23]. The doped materials available for this study were 1%, 2% and 10% V-OMS-2, 1%, 2% and 10% Mo-OMS-2 and 1% W-OMS-2 (Table 2). As the vanadium loading increased from 1% to 10% in the K-OMS-2_R the conversion of styrene oxide was increased from 83% to 100%. On the other hand, the selectivity for β-amino alcohol decreased from 86% to 73% and the selectivity for the imine increased to 20% from 8%. A 1% loading of molybdenum in K-OMS-2_R raised the conversion from 76% to a significantly higher 91%. Doubling the amount of molybdenum in the catalyst to 2% had only a slight enhancement of conversion to 95%. As the loading of molybdenum increased to 10% the conversion reached 100%. However, the selectivity for the ring opening product decreased dramatically from 88% to 62%. Tungsten showed the highest conversion enhancement to 98% from 76% for just 1% of the tungsten loading into K-OMS-2_R. In general, as the amount of doping increased in OMS-2, there was a significant increase in the conversion of styrene oxide.

The XRD patterns of doped OMS-2 are given in Fig. 4. With the increase in amount of dopant in the OMS-2 catalyst, the crystallinity of OMS-2 decreases. Doping transition metals into OMS-2 may lead to tunnel or framework occupancy. Previous XRD studies with OMS-2 have shown that in V-OMS-2, the vanadium is in the framework [24]. However, the determination of the exact position of vanadium, tungsten, and molybdenum in the M-OMS-2 mixed materials using EXAFS is still in progress. This difference in occupancies of the framework or tunnel sites of OMS-2 may play a crucial role in the reaction.

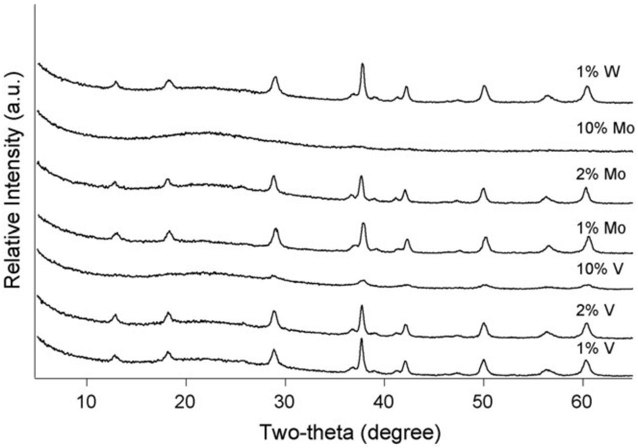


Fig. 4. X-ray diffraction patterns of V, Mo and W doped OMS-2 materials.

4.2. Effect of nucleophiles

According to the results listed in Table 3, apart from aniline, both *p*-toluidine and *p*-anisidine exhibited the same conversion of 81%, but selectivities were 70% and 59% respectively. *p*-nitroaniline showed 84% conversion for styrene oxide and 77% selectivity for the corresponding ring opened product. Phenol gave 49% conversion and 45% selectivity. *p*-methoxy phenol showed 35% conversion with an anticipated enhancement in selectivity (69%) for the ring opened product. *o*-methoxy phenol gave only a 19% conversion and 40% selectivity. In a typical situation, the presence of electron donating groups enhances the nucleophilicity of nucleophile and electron withdrawing groups retard the nucleophilicity. Surprisingly, this trend was not observed in these systems and the other regioisomer of the β-amino alcohol also appeared when substituted nucleophiles were used. These observations could be attributed to steric interactions at the nucleophilic centers and Lewis acid sites of the catalyst.

4.3. Effect of solvents

For heterogeneous catalysis in the liquid phase, the solvent can influence the rates of reaction by the solvation of reactants and intermediates in solution. On the other hand, the solvent can also affect the rate by competing with reactant molecules for active sites on the surface of a heterogeneous catalyst [25]. Solvents may stabilize or destabilize transition states and intermediates formed on the catalyst surface. However, in the reaction between styrene epoxide and aniline catalyzed by K-OMS-2 there was no significant difference in conversions when polar (acetonitrile, toluene) or nonpolar (*n*-hexane) solvents were used (Table 4). Toluene showed the highest conversion (72%) followed by acetonitrile (45%) and hexane (44%). For dichloromethane (8%) and tetrahydrofuran (THF) (6%), a dramatic lowering of the conversion was observed. The reason for the low conversion could be that competitive binding of solvent molecules to the active sites (Lewis acid sites) of the catalysts, prevented the reaction process.

4.4. Catalyst reusability

K-OMS-2_R was reused after a simple regeneration procedure by washing with water and acetone and drying at 250 °C. The catalyst was used at least for 4 cycles without any loss in activity. Furthermore, the XRD pattern of the reused K-OMS-2_R catalyst was identical to that of the original, indicating that the crystallinity of the catalyst was not affected during the reaction. Catalyst deactivation may occur due to chemical, mechanical and thermal reasons [26]. The chemical deactivation is common in catalysts and caused by strong chemisorption of species on the catalytic sites, thereby blocking sites for catalytic reaction. The regeneration process used for K-OMS-2, removes the species that cause the deactivation of the catalyst.

4.5. Proposed mechanism of the reaction

The products obtained by reacting styrene oxide and aniline in the presence of OMS-2 indicate that a Lewis acid catalyzed ring opening and an oxidative cleavage process are taking place (Fig. 5). The major product, β-amino alcohol, is formed by OMS-2 Lewis acid catalyzed ring opening via a nucleophilic attack by aniline (Scheme 1). OMS-2 coordinates with the oxirane oxygen to promote nucleophilic attack of the nucleophile leading to two regioisomers **A** and/or **B**. Attack of the nucleophile is governed by the nature of the oxirane and stability of the incipient carbonium ion. In the case of the OMS-2 coordinated styrene oxide, the

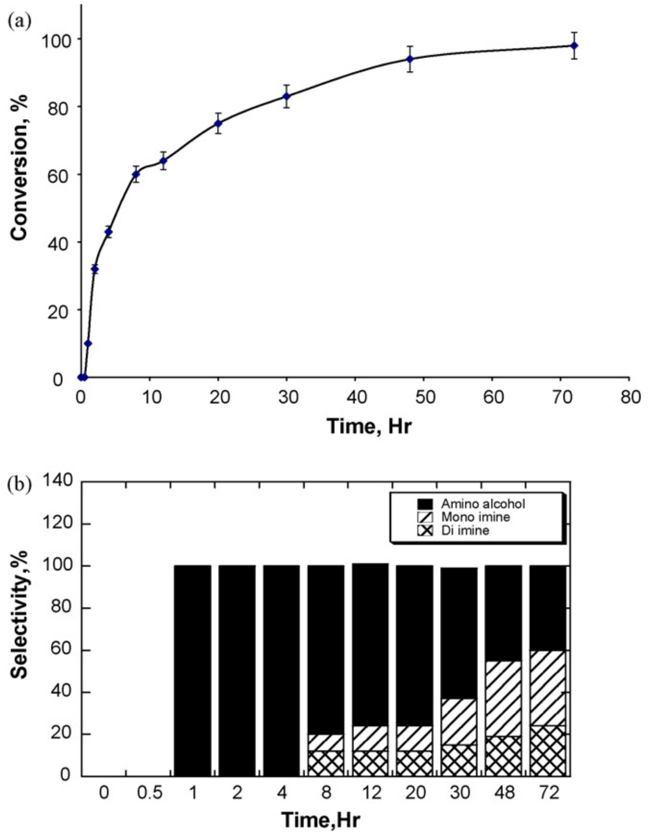
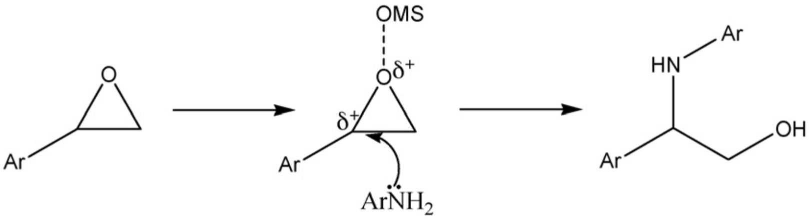


Fig. 5. (a) Conversion and (b) selectivities of products with time for ring opening of styrene oxide.

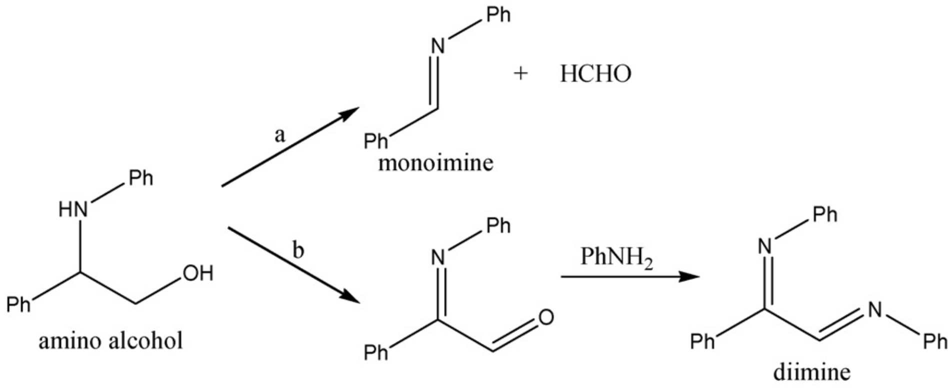
positive charge on the oxygen appears to be localized on the more highly substituted benzylic carbon. The nucleophile attacks the benzylic carbon of the styrene oxide leading to amino alcohol **A** as the major product. With the use of aniline as a nucleophile, amino alcohol **A** is exclusively produced. However, when substituted anilines and phenols were used as nucleophiles both regioisomers were observed, predominantly resulting in isomer **A**. A reasonable explanation for this observation is that steric factors predominate over electronic factors under these reaction conditions [27].

The appearance of monoimines and diimines in the reaction mixture may be due to the oxidation of the β-amino alcohol (Scheme 2). N-phenyl benzylamine, the monoimine is formed by an oxidative cleavage of the β-amino alcohol [28]. Benzalanilines can be oxidized to imines by a variety of oxidants, including manganese oxide [29]. Pratt and McGovern have successfully transformed a series of benzalanilines to imines using manganese oxide [30]. Their mechanism suggests that Mn^{4+} changes to Mn^{2+} in the manganese oxide catalyst used in the oxidation process (Scheme 3). However, Makwana et al. suggested that in an oxidative process with OMS-2 materials, lattice oxygen of OMS-2 participates in the oxidation reaction and is later replenished by fluid-phase oxygen. Hence the structure and catalytic properties of OMS-2 are retained (A Mars–van Krevelen type mechanism) [31]. The formation of diimines in the reaction can be explained in terms of a double oxidation. Along with C–N bond oxidation, the terminal hydroxyl group in the β-amino alcohol is also oxidized to form a carbonyl group. OMS-2 catalysts have been known to oxidize alcohols to aldehydes or ketones [10]. The β-amino alcohol is also oxidized by OMS-2 to form a carbonyl and subsequently the *in situ* formed carbonyl reacts with aniline to form an imine [32]. The formaldehyde believed to be produced during this process was not detected by GC–MS.

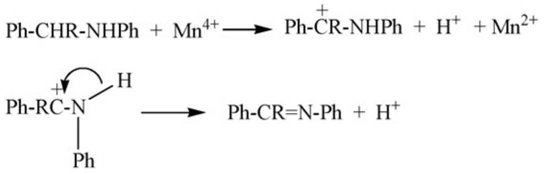
To test the above-proposed oxidation mechanism a substrate similar to β-amino alcohol was reacted with OMS-2. Oxidation of 2-amino-2-phenylethanol with K-OMS-2 catalyst in the absence of aniline gave rise to 2-amino-2-phenylactaldehyde and phenylmethanamine. The products obtained in this reaction support the reaction mechanism proposed for the formation of monoimine and diimines from β-aminoalcohols. XRD studies on the catalyst after the reaction show that the structure of K-OMS-2 is retained; hence lattice oxygen is not consumed in the reaction.



Scheme 1. OMS catalyzed epoxide ring opening.



Scheme 2. Formation of monoimine by (a) oxidative cleavage and diimine by (b) oxidation–condensation processes.



Scheme 3. Mechanism of imine formation from amine.

5. Conclusions

In summary, an efficient method to produce β-amino alcohols from styrene epoxide using OMS-2 materials as catalysts has been proposed. OMS-2 acts as a Lewis acid to catalyze the reaction between styrene oxide and aniline. K-OMS-2 materials prepared by different synthetic methods possess different chemical and physical properties. Hence, the conversions and selectivities for the ring opening reaction vary depending primarily on the Lewis acid strengths of the catalysts. Moreover, conversions and selectivities of products can be enhanced or altered by doping other transition metals into manganese oxide based OMS-2. Among the metals doped into OMS-2, tungsten gave the highest conversion (100%). However, as the conversion increased, the selectivity for the β-amino alcohol diminished. An oxidation process clearly occurs, producing imines from β-amino alcohol. The results suggest that the catalytic activity of doped M-OMS-2 are in the decreasing order of W > Mo > V. Aniline gives the best regioselectivity for β-amino alcohol of all the nucleophiles used for reaction with styrene oxide. OMS-2 catalysts can be tuned by doping metals into the structure to obtain desirable amounts of selective products. OMS-2 catalysts are cheap and easy to prepare, can be reused, and they are environmentally benign.

Acknowledgements

We thank the Chemical Sciences, Geosciences, and Bio-sciences Division of the Basic Sciences, Office of Sciences, U.S. Department of Energy, and Office of Basic Energy Science for support of this research. The authors also thank Dr. Frank Galasso and Dr. James Bobbit for helpful discussions.

References

[1] S.C. Bergmeier, Tetrahedron 56 (2000) 2561, and references therein.
[2] P. O'Brien, Angew. Chem. Int. Ed. 38 (1999) 326.
[3] D.J. Ager, I. Prakash, D.R. Schaad, Chem. Rev. 96 (1996) 835.
[4] R.M. Hanson, Chem. Rev. 91 (1991) 437.
[5] G. Sundararajan, K. Vijayakrishna, B. Varghese, Tetrahedron Lett. 45 (2004) 8253.
[6] G. Sabitha, G. Reddy, J.S. Yadav, Synthesis 15 (2003) 2298.
[7] H. Eshghi, M. Rahimizadeh, A. Shoryabi, Synth. Commun. 35 (2005) 791.
[8] M. Onaka, M. Kawai, Y. Izumi, Chem. Lett. (1985) 779.
[9] A.K. Chakraborti, S. Rudrawar, A. Kondaskar, Org. Biomol. Chem. 2 (2004) 1277.
[10] Y.C. Son, V.D. Makwana, A.R. Howell, S.L. Suib, Angew. Chem. Int. Ed. 40 (2001) 4280.
[11] R. Ghosh, Y.C. Son, V.D. Makwana, S.L. Suib, J. Catal. 224 (2004) 288.
[12] R. Kumar, L.J. Garces, Y.-C. Son, S.L. Suib, R.E. Malz, J. Catal. 236 (2005) 387.
[13] S.L. Suib, Curr. Opin. Solid State Mater. Sci. 3 (1998) 63.
[14] X. Chen, Y.-F. Shen, S.L. Suib, C.L. O'Young, Chem. Mater. 14 (2002) 940.
[15] X. Chen, Y.-F. Shen, S.L. Suib, C.L. O'Young, J. Catal. 197 (2001) 292.
[16] Y.-S. Ding, X. Shen, S. Sithambaram, S. Gomez, R. Kumar, M.B. Vincent, S.L. Suib, Chem. Mater. 17 (2005) 5382.
[17] X.F. Shen, Ph.D. Thesis, University of Connecticut, 2007.
[18] R.N. DeGuzman, Y.-F. Shen, E.J. Neth, S.L. Suib, C.L. O'Young, S. Levine, J.M. Newman, Chem. Mater. 6 (1994) 815.
[19] J. Yuan, K. Laubernds, J. Villegas, S. Gomez, S.L. Suib, Adv. Mater. 16 (2004) 1729.
[20] K. Daasbjerg, H. Svith, S. Grimme, M. Gerenkamp, C. Muck-Lichtenfeld, A. Gansauer, A. Barchuk, Top. Curr. Chem. 263 (2006) 39.
[21] R. Ghosh, X.-F. Shen, J.C. Villegas, Y. Ding, K. Malinger, S.L. Suib, J. Phys. Chem. B 110 (2006) 7592.
[22] L. Giebeler, P. Kampe, A. Wirth, A.H. Adams, J. Kunert, H. Fuess, H. Vogel, J. Mol. Catal. A: Chem. 259 (2006) 309.
[23] C. Chen, C.A. Calvert, L. Xu, S. Sithambaram, S.L. Suib, manuscript in preparation.
[24] M. Polverejan, J.C. Villegas, S.L. Suib, J. Am. Chem. Soc. 126 (2004) 7774.
[25] R.L. Augustine, R.W. Warner, M.J. Melnick, J. Org. Chem. 49 (1984) 4853.
[26] C.H. Barthalomew, Appli. Catal. 212 (2001) 17.
[27] S.K. De, R.A. Gibbs, Synth. Commun. 35 (2005) 2675.
[28] M. Shimizu, H. Makino, Tetrahedron Lett. 42 (2001) 8865.
[29] T. Mukiyama, A. Kawana, Y. Fukuda, J. Matsuo, Chem. Lett. (2001) 390.
[30] E.F. Pratt, T.P. McGovern, J. Org. Chem. 29 (1964) 1540.
[31] V.D. Makwana, Y.C. Son, A.R. Howell, S.L. Suib, J. Catal. 210 (2002) 46.
[32] S. Sithambaram, Y.-C. Son, S.L. Suib, US Patent Appl. 0,027,344 (2007).