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Double Metal Cyanides as Efficient Solid Acid Catalysts for Synthesis of *β*-Amino Alcohols Under Solvent-Free Conditions

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Abstract A novel application of Fe–Zn double metal cyanide complexes as solid, acid catalysts for regioselective synthesis of *β*-amino alcohols under solvent-free conditions via ring-opening of epoxides with amines is reported for the first time. The conversion of epoxides to *β*-amino alcohols is nearly 100%. In the reaction with styrene oxide, regioselective *β*-amino alcohol formation is higher with aromatic than with aliphatic amines. Strong Lewis acidic Zn^{2+} ions in the catalyst are probably the active sites in this reaction.

Keywords Double metal cyanide (DMC) · Solid Lewis-acid catalyst · *β*-Amino alcohols · Regioselective ring-opening of epoxides · Single crystal X-ray structure

1 Introduction

Development of efficient and eco-friendly catalytic routes for stereo- and regio-selective ring-opening of epoxides is an emerging area of investigation in organic synthesis. The *β*-Amino alcohol moiety, obtained by ring opening of epoxides, is a main structural unit in a vast number of naturally occurring and synthetic molecules of pharmaceutical importance. Among several applications, *β*-amino alcohols are used as *β*-blockers, insecticidal agents, oxazolines and as chiral ligands in asymmetric synthesis [1–5]. They are synthesized by nucleophilic addition of amines to epoxides via opening of the epoxide ring (Scheme 1). The classical synthesis of *β*-amino alcohols is generally carried out with a large excess of the amines at elevated temperatures and in the presence of organic solvents. This method is not suitable for poorly nucleophilic amines since regioselectivity is low. A large number of promoters and catalyst system have been reported, e.g. sulfamic acid [6], Amberlyst-15 [7], metal amides, metal triflates [8], transition metal halides [9], ionic liquids [10], and Lewis acids [11]. However, all those required long reaction times, elevated temperatures, high pressures and stoichiometric amounts of catalyst. Brönsted acidic SBA-15 functionalized with sulfonic acid and Lewis acidic Ti-MCM-41 catalyze the reaction at mild conditions yielding high conversion and product selectivity [12, 13].

Double metal cyanide complexes are used as catalysts in the manufacture of polyethers-polyols [14, 15]. They also catalyze the copolymerization of epoxides and CO_2 producing polycarbonates [16], reaction of cyclic carbonates with alcohols yielding dialkyl carbonates [17] and production of biodiesel/lubricants by alcoholysis of vegetable oils [18]. We, now, report, for the first time, their application as solid, Lewis-acid catalysts for nucleophilic ring-opening of epoxides with amines producing *β*-amino alcohols. A series of *β*-amino alcohols was synthesized under solvent-free conditions using this Lewis acid catalyst.

2 Experimental

2.1 Material Preparation and Characterization

Fe–Zn double metal cyanide (DMC) catalysts were prepared [18] using $K_4Fe(CN)_6 \cdot 3H_2O$ as a source of Fe,

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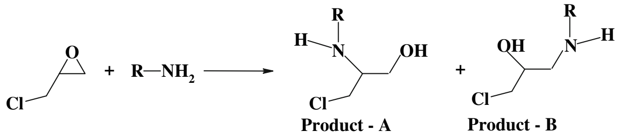


Scheme 1

$ZnCl_2$ as a source of Zn and *t*-butanol as the complexing agent. In a typical preparation of the DMC catalyst, 0.01 mol of potassium ferrocyanide(II), $K_4Fe(CN)_6 \cdot 3H_2O$, was dissolved in 40 mL of double-distilled water to prepare solution A. In a separate a beaker, solution B was prepared by dissolving 0.1 mol of $ZnCl_2$ in 100 mL of distilled water and 20 mL of *t*-butanol. Solution C was prepared by dissolving 15 g of a tri-block copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (average molecular weight = 5800; Aldrich) in 2 mL of distilled water and 40 mL of *t*-butanol. Solution B was added to solution A slowly over 1 h at 323 K under vigorous stirring. Precipitation of a solid occurred during the addition. To that mixture, solution C was added over 5–10 min and stirring continued for another 1 h. The solid was filtered, washed thoroughly with double-distilled water to remove all the uncomplexed ions, and dried at 298 K for several hours. The composition, purity, structural, spectroscopic and acidic properties were determined as reported by us earlier [18].

2.2 Reaction Procedure

In a typical reaction, equimolar quantities of epoxide and amine were taken in a double-necked round-bottomed flask (50 mL) placed in a temperature-controlled oil bath and fitted with a water-cooled condenser. The reaction was conducted at a specific temperature and for a specific period. The progress of the reaction was monitored by taking out aliquots of the sample, diluting it with a known quantity of dichloromethane, separating the catalyst by centrifugation and subjecting the diluted liquid to gas chromatographic analysis (Varian 3400; CP-SIL8CB column; 30 m-long and 0.53 mm-i.d.). The products were identified using GC-MS (Varian CP-3800; 30 m-long, 0.25 mm-i.d., and 0.25 µm-thick CP-Sil8CB capillary column). They were also isolated by column chromatography (eluent: petroleum ether–ethyl acetate mixture) and characterized by ^{1}H NMR studies. The characteristics of some isolated products are as follows:

2-Phenylamino-2-phenyl ethanol: GC-MS (*m/e*): 214.8, 213.8, and 182.0. ^{1}H NMR: 3.7 (1H, dd), 3.9 (1H, dd), 4.4 (1H, dd), 6.5 (2H, d), 6.7 (1H, t), 7.1 (2H, t), 7.3 (5H, m).

2-(4-Chlorophenylamino)-2-phenyl ethanol: GC-MS (*m/e*): 249.1, 248.2 and 246.3. ^{1}H NMR: 3.7 (1H, dd), 3.9 (1H, dd), 4.4 (1H, dd), 6.5 (2H, d), 7.05 (2H, d), 7.4 (5H, m).

2-(3-Methylphenylamino)-2-phenyl ethanol: GC-MS (*m/e*): 228.0, 227.4, 197.3, 196.4, and 118.1. ^{1}H NMR: 2.3 (3H, s), 3.7 (1H, dd), 3.9 (1H, dd), 4.5 (1H, dd), 6.5 (3H, m), 7.0 (1H, t), 7.3 (5H, m).

2-(2-Methylphenylamino)-2-phenyl ethanol: GC-MS (*m/e*): 228.0, 227.4, 197.3, 196.4, and 118.1. ^{1}H NMR: 2.3 (3H, s), 3.8 (1H, dd), 3.9 (1H, dd), 4.5 (1H, dd), 6.37 (1H, d), 6.63 (1H, t), 6.95(1H, t), 7.07 (1H, d), 7.35 (5H, m).

2-(1-Piperidino)-1-phenyl ethanol: ^{1}H NMR: 1.45–1.51 (2H, m), 1.6–1.7 (4H, m), 2.35–2.45 (4H, m), 2.6–2.7 (2H, m), 4.7 (1H, dd), 7.3–7.4 (5H, m).

Single crystals of 2-(4-chlorophenylamino)-2-phenyl ethanol (**1**), 2-(2-methylphenylamino)-2-phenyl ethanol (**2**) and 2-(1-piperidino)-1-phenyl ethanol (**3**) were grown from dichloromethane solutions by slow evaporation. Single crystal X-ray intensity data measurements were carried out at 297 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized ($MoK_\alpha = 0.71073$ Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. Data were collected with ω-scan width of 0.3° at three different settings of φ (0°, 90° and 180°) keeping the sample-to-detector distance fixed at 6.145 cm and the detector position (2θ) fixed at $-28°$. X-ray data collection was monitored by the SMART program (Bruker 2003). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker 2003). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2. Some of the hydrogen atoms were located from a difference Fourier map in all the three structures, and their positional coordinates and isotropic thermal parameters were refined. H-atoms were included in the refinement as per the riding model option in SHELXL. Compound **1** crystallized with dichloromethane as solvent of crystallization. The structure of compound **3** was already reported [19]. But in this study we present a more refined structure and compare it with the structures of compounds **1** and **2**.

3 Results and Discussion

3.1 Physicochemical Properties

3.1.1 Structural and Spectroscopic Characterization

The double metal cyanide (DMC) complex has a molecular formula: $K_4Zn_4[Fe(CN)_6]_3 \cdot 6H_2O \cdot 2(\text{tert.-BuOH})$ with two molecules of tert.-butanol included in the structure. The complex is characterized by a cubic unit cell (unit cell parameter = 9.04 Å) with a powder X-ray diffraction (XRD) pattern as shown in Fig. 1. The XRD pattern also confirms that the DMC complexes are free from the starting precursor compounds (metal chlorides and

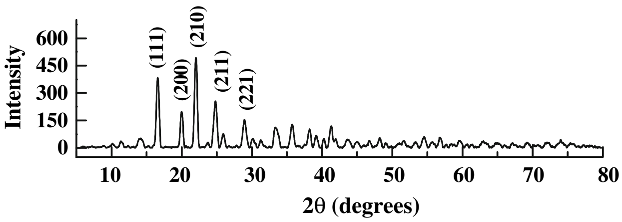


Fig. 1 X-ray powder diffraction pattern of double metal cyanide Fe–Zn complex

$K_4Fe(CN)_6 \cdot 3H_2O$). The particles have a spherical morphology with an average particle size of 0.8 µm (scanning electron microscopy; SEM; figure not shown here) and a specific surface area of 52 m^2/g [18].

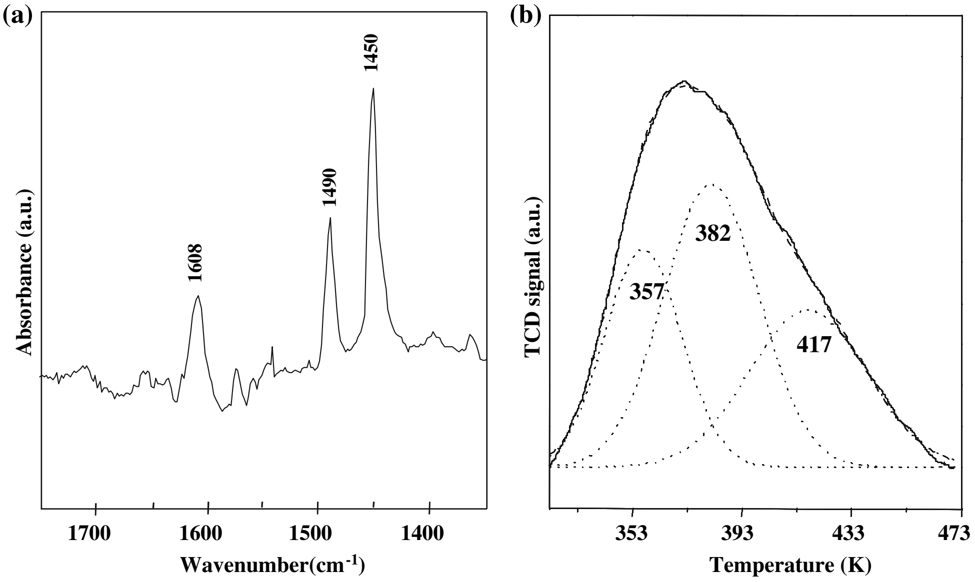
DMC shows FT-IR bands at 2096 cm^{-1} due to $\nu(C{\equiv}N)$ and 2925, 1260–1450 and 1095 cm^{-1} due to C–H and C–O stretching frequencies of tert.-butanol. While $K_4Fe(CN)_6$ $3H_2O$ shows this band, due to $\nu(C{\equiv}N)$, at 2039 cm^{-1}, it shifts to higher wavenumbers in DMC complexes. The presence of coordinated tert.-butanol in the complex was confirmed also from the ^{13}C NMR studies [18]. Characteristic ^{13}C NMR signals were observed in the CP-MAS spectrum at 172.2, 73.2 and 18.0 ppm [18]. The signal at 172.2 ppm corresponds to the cyanide group. The signals at 73.2 and 18.0 ppm are due to tert.-butanol. $K_4Fe(CN)_6 \cdot 3H_2O$ shows a signal for the cyanide groups at 118 ppm. A significant downfield shift (to 172.2 ppm) of the cyanide signal observed in the Fe–Zn DMC complexes reveals a bridging mode of cyanide coordination consistent with the FT-IR data. $K_4Fe(CN)_6 \cdot 3H_2O$ showed an intense band at 236 nm and two medium intensity bands at 278 and 330 nm. While the latter two are attributed to ligand (CN)-to-metal (Fe) charge transfer (LMCT) transitions, the former corresponds to π–π^* charge transfer transitions in the cyanide group [18]. For DMC complexes, the LMCT bands shift to higher energy (265 and 308 nm, respectively; figure not shown) due to the bridging of the cyanide group and the delocalization of electron density on both Fe and Zn orbitals. The binding energy of Zn^{2+} and Fe^{2+} shifts to lower values (1021.4 and 707 eV, respectively) compared to their precursors, $ZnCl_2$ (1023.7 eV) and $K_4Fe(CN)_6 \cdot 3$ H_2O (708 eV), respectively [18]. This shift is due to electron delocalization via the cyano-bridge in the Fe–Zn structural unit.

Thermogravimetric experiments in air-flow of the Fe–Zn complexes revealed three-stages of weight loss: stage I (308–503 K) corresponding to desorption of the water and tert.-butanol groups; stage II (513–690 K) due to the decomposition of the cyanide groups to metal nitrates/carbonates and stage III (873–1090 K) due to the complete decomposition of the material into metal oxides-$ZnFe_2O_4$ and ZnO [18]. The weight losses in the three stages are 21.6, 16 and 7.3%, respectively. All the H_2O molecules in the sample are lost below 443 K. Tert.-BuOH desorbed at 443–503 K.

3.1.2 Acidic Properties

The catalyst does not contain basic sites on its surface (CO_2 did not adsorb on these catalyst). Pyridine adsorption followed by DRIFT spectroscopic studies (Fig. 2a) revealed the presence of strong Lewis acid sites as shown by the IR bands at 1608 and 1450 cm^{-1}. Brönsted acid sites (IR bands at 1639 and 1546 cm^{-1}) were absent. The Fe–Zn complex showed a broad, asymmetric desorption peak in

Fig. 2 (**a**) DRIFT spectrum of adsorbed pyridine and (**b**) NH_3-TPD of DMC catalyst

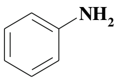
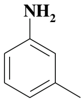
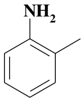
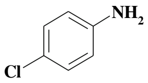
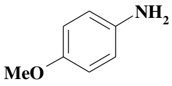
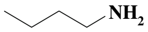
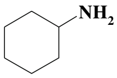
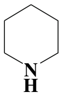


NH_3-TPD, which could be deconvoluted into three peaks with maximum at 357, 382 and 417 K, respectively (Fig. 2b). While the desorption at 357 K is attributed to physisorbed NH_3, those at 382 K and 417 K are assigned to weak and strong Lewis acid sites, respectively. The total amount of NH_3 desorbed was 1.96 mmol/g. The concentration of the strong Lewis acid sites (area of the NH_3-desorption peak at 417 K) and weak Lewis acid sites (area of the desorption peak at 382 K) were 0.57 and 0.85 mmol/g, respectively [18].

3.2 Catalytic Activity

β-Amino alcohols were synthesized at atmospheric pressure by the ring-opening of epoxides with amines over Fe–Zn double metal cyanide catalysts at 333 K under solvent-free conditions. Both the steric hindrance and nucleophilicity of the amines influenced their reactivity. In general, the ring-opening reaction of epoxides with amines yielded two regio-isomers: A and B (Scheme 1). Selectivity for the A-isomer is higher in most of the cases (Table 1).

Table 1 Aminolysis of epoxides over Fe–Zn double metal cyanide catalyst[a]

Run No.	Amine	Epichlorohydrin				Styrene oxide				Cyclohexene oxide			
		Epoxide conv. mol%	Product selectivity		TOF $(h^{-1})^{b}$	Epoxide conv. mol%	Product selectivity		TOF $(h^{-1})^{b}$	Epoxide conv. mol%	Product selectivity		TOF $(h^{-1})^{b}$
			A	B			A	B			A	B	
1		97.8	100	0	86 (25)	94.5	97.9	2.1	83 (24)	7.3	100	0	6 (2)
1a		(89.8)[c]	98.9	1.1	79 (23)								
1b		(64.7)[d]	99.5		57 (16)								
1c		(5.2)[e]	100	0	5 (1)								
2		98	100	0	86 (25)	95	100	0	83 (24)				
3		90.2	100	0	79 (23)					3.1	100	0	3 (1)
4		82.6	98.3	1.7	73 (21)	71.3	83.4	16.6	63 (18)	7.8	100	0	7 (2)
5		100	98.3	1.7	88 (26)	94.6	87	13	83 (24)				
6		100	0	100	88 (26)	23	16.6	83.4	20 (6)				
7	$(Butyl)_2NH$	98.5	2.5	97.5	86 (25)								
8		67.5	49.7	50.3	59 (17)	19.8	52.4	47.6	46 (5)				
9		98	29.2	70.8	86 (25)	96.4	60.2	39.8	85 (25)				

[a] *Reaction conditions*: Epoxide—10 mmol, amine—10 mmol, catalyst—50 mg, temperature—333 K, reaction time—4 h

[b] Turnover frequency (TOF) = moles of epoxide converted per mole of strong Lewis acid per hour. Values in parentheses are those calculated based on total acid sites

Reaction was carried out at: [c] 323 K, [d] 313 K, and [e] 298 K

The intrinsic catalytic activity (turnover frequency; TOF) of Fe–Zn double metal cyanide catalysts is higher than most of the known catalysts for this reaction [6–11]. For the reaction between styrene oxide and aniline conducted under similar conditions, the TOF values over sulfamic acid, amberlyst-15, $Sc(OTf)_3$, NaY, SBA-15-*pr*-SO_3H and Ti-MCM-41 catalysts were 32, 2, 7, 0.8, 68 and 169 h^{-1}, respectively [6–11, 13]. The corresponding value for the DMC catalyst is 86 h^{-1} (Table 1). Interesting to note that the isomer-A selectivity is greater for the DMC (98%) than for SBA-15-*pr*-SO_3H (90%) and Ti-MCM-41 (94%) catalysts.

Epichlorohydrin is a reactive molecule due to the electron withdrawing Cl atom; the epoxide conversion is, hence, high, about 82.6–100% (Table 1) with isomer-A being the major product. We did not observe products other than the amino alcohols by gas chromatography. The conversions estimated based on the disappearance of either of the two reactants (epoxide/amine) were about the same. When cylcohexylamine was used the product yield was low and both the isomers formed with equal selectivity. On the other hand, in the reaction of epichlorohydrin with aliphatic amines (e.g. *n*-butyl amine, dibutyl amine and piperidine), the formation of the regio-isomer-B was prominent. The reactivity of styrene oxide (epoxide conversion and turnover frequency) was more dependent on the nature and type of the amine molecule (Table 1). The conversion of the epoxide and the selectivity for the A isomer are higher when aromatic instead of aliphatic amines were used. We have also carried out the reaction of

Table 2 Summary of crystallographic data

Crystal data	2-(4-Chlorophenylamino)-2-phenyl ethanol (**1**)	2-(2-Methylphenylamino)-2-phenyl ethanol (**2**)	2-(1-Piperidino)-1-phenyl ethanol (**3**)
Formula	$C_{14}H_{14}N_1O_1 \cdot 0.13(CH_2Cl_2)$	$C_{15}H_{17}N_1O_1$	$C_{13}H_{19}N_1O_1$
M_r	253.64	227.3	205.29
Crystal size, mm	0.13 × 0.09 × 0.07	0.22 × 0.07 × 0.06	0.24 × 0.14 × 0.08
Temp. (K)	297(2)	297(2)	297(2)
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	$I\ 4_1$	$C2/c$	$P\ 2_1/c$
a [Å]	31.343(4)	26.699(11)	12.249(3)
b [Å]	31.343(4)	11.200(5)	6.0070(16)
c [Å]	5.5736(10)	8.786(4)	17.150(4)
β [°]	90	101.269(11)	108.386(4)
V [$Å^3$]	5475.4(14)	2577(2)	1197.5(5)
Z	16	8	4
F(000)	2126	976	448
D calc [g cm^{-3}]	1.231	1.172	1.139
μ [mm^{-1}]	0.288	0.073	0.071
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.9635	0.9841	0.9831
T_{max}	0.9801	0.9956	0.9943
Reflns. collected	19925	8832	5555
Unique reflns.	4792	2272	2093
Observed reflns.	2503	1162	1577
Index range	$-37 \leq h \leq 36$	$-31 \leq h \leq 31$	$-14 \leq h \leq 13$
	$-37 \leq k \leq 36$	$-13 \leq k \leq 13$	$-7 \leq k \leq 6$
	$-6 \leq 1 \leq 6$	$-10 \leq 1 \leq 10$	$-20 \leq 1 \leq 14$
R_1 [I>2σ(I)]	0.0861	0.056	0.0439
wR_2	0.2178	0.1137	0.1028
R_1 (all data)	0.1654	0.1269	0.617
WR_2 (all data)	0.2663	0.139	0.1123
Goodness-of-fit	1.027	1.01	1.037
$\Delta\rho_{max}$, $\Delta\rho_{min}$($eÅ^{-3}$)	0.653, −0.324	0.128, −0.099	0.175, −0.141
CCDC number	668192	668193	668191

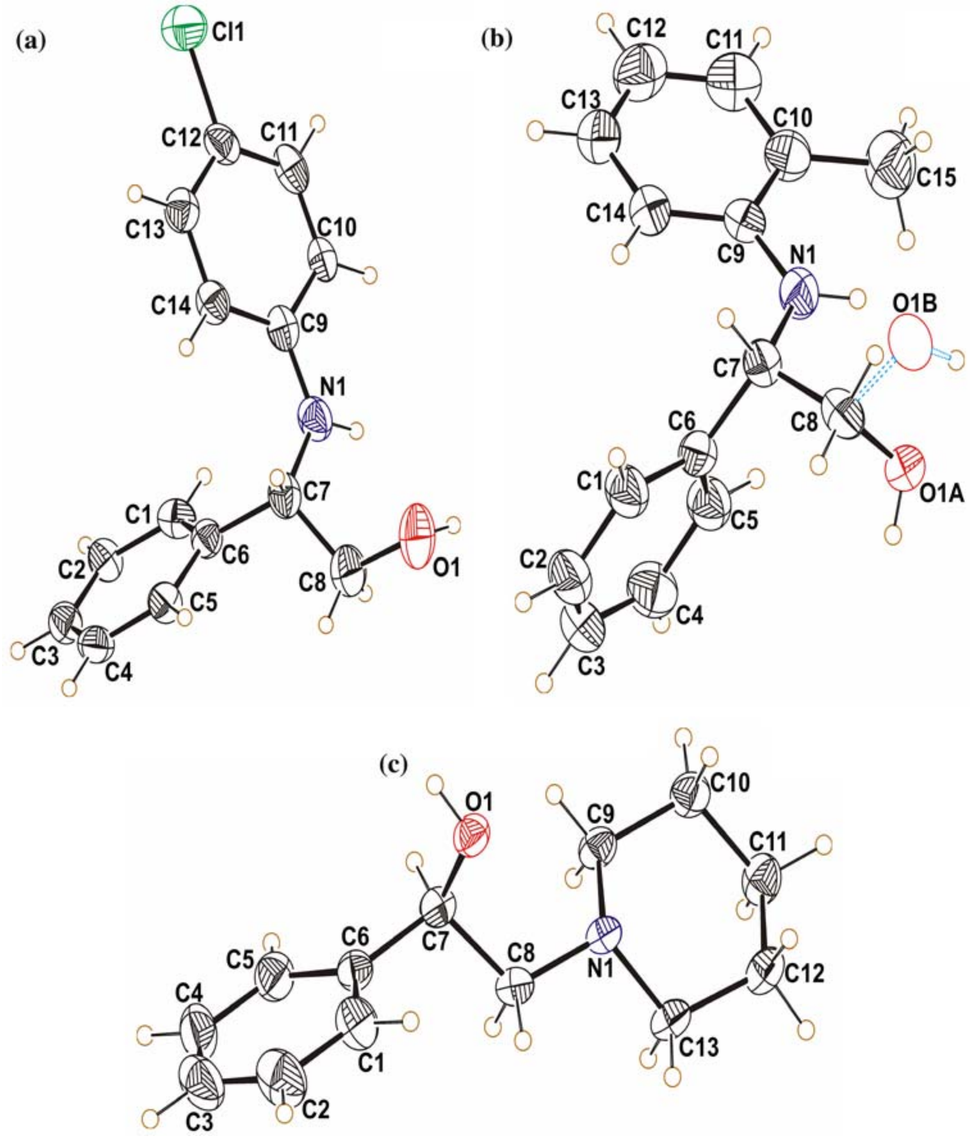


Fig. 3 Single crystal X-ray structures and ORTEP diagrams of (**a**) 2-(4-chlorophenylamino)-2-phenyl ethanol, (**b**) 2-(2-methylphenylamino)-2-phenyl ethanol and (**c**) 2-(1-piperidino)-1-phenyl ethanol

cyclohexene oxide with a few amines; very low yields of amino alcohol were obtained (Table 1) and the isomer A was formed exclusively. The regioselectivity among isomers A and B in the products was determined by NMR spectroscopy (Sect. 2.2). In some cases the results were confirmed by single crystal X-ray diffraction. The individual isomers were isolated by column chromatography and crystallized by slow evaporation. The three dimensional structures of three of the products—2-(4-chlorophenylamino)-2-phenyl ethanol (**1**), 2-(2-methylphenylamino)-2-phenyl ethanol (**2**) and 2-(1-piperidino)-1-phenyl ethanol (**3**) were determined by single crystal X-ray diffraction; the crystallographic data are listed in Table 2. In confirmation to the gas chromatographic and ^{1}H NMR results, the ORTEP views of **1**–**3** (Fig. 3) reveal that the reaction of styrene oxide and aromatic amines results predominantly the regioisomer-A. The reaction of styrene oxide with aliphatic amines like butyl amine, cyclohexyl amine and piperidine yields relatively greater quantities of the B-isomer. In compound **2** the oxygen of the alcoholic group is disordered (O1A: O1B = 70: 30). The geometry of N1–C7–C8–O1 adopts more of a *syn*-conformation in **1** and **3** while it adopts preferentially an *anti*-conformation in compound **2**. The solvent of crystallization (dichloromethane) stabilizes the *syn*-conformation in **1**.

The conversion verses time plot (Fig. 4) follows a sinusoidal variation. Conversion of the epoxide increased with the amount of catalyst (Fig. 5a) but decreased with the epoxide concentration (Fig. 5b). The reusability of the catalyst has been confirmed (Table 3). The catalyst was separated by filtration after each reaction, washed with acetone and methanol, dried at 363 K for 2–3 h and reused.

In the ring-opening polymerization of propylene oxide over double metal cyanide catalysts [15], Lewis acidic,

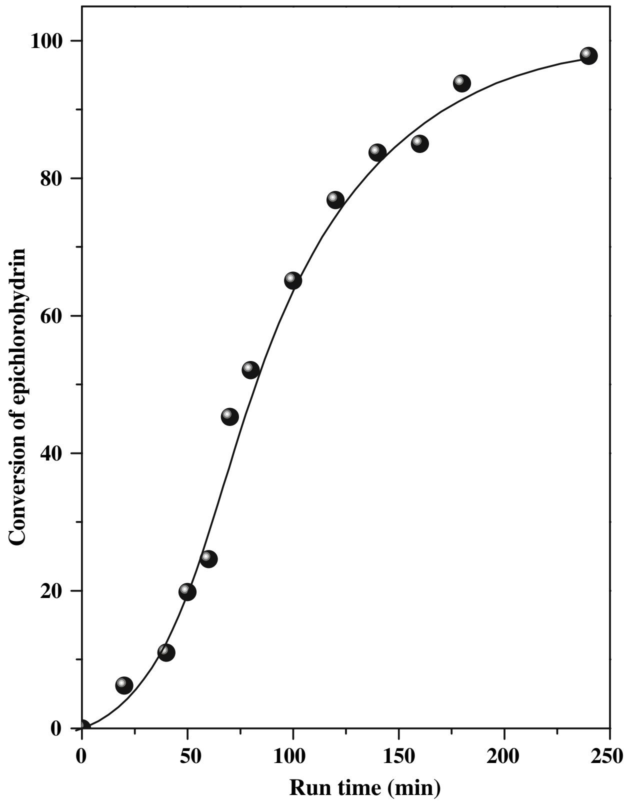


Fig. 4 Influence of reaction time on aminolysis of epichlorohydrin with aniline. Reaction conditions: epichlorohydrin, 10 mmol; aniline, 10 mmol; catalyst, 50 mg; reaction temperature, 333 K

terminal Zn^{2+} ions are the active sites. We had found earlier that the Zn^{2+} sites are also the active sites in transesterification reactions [17, 18]. In the present case also, it is probable that the terminal Zn^{2+} ions activate the epoxide ring facilitating the subsequent nucleophilic attack by the amine on the resulting carbocation.

3.3 Mechanistic Considerations

Most of the reactions of epoxides involve the opening of the oxirane ring, the addition of a proton to the epoxide oxygen and the deprotonated molecule of the substrate to one of the carbon atoms of the oxirane ring [20]. The reaction can occur under neutral, basic or acidic conditions. Reaction under neutral or basic conditions, involves the attack of a nucleophile on one of the epoxide carbon atoms. Under acidic conditions, the addition of the nucleophile is considerably accelerated due to the reversible formation of the more reactive conjugate acid of the epoxide. The ring-opening reactions of epoxides take place by ionic mechanisms. The bond, which is broken, is the highly polar carbon–oxygen bond, which would be expected to break ionically. Possible exceptions are the reactions with hydrogen and a metal catalyst, which may take place by a free-radical mechanism [20].

Aminolysis of epoxides is a bimolecular reaction. An additional factor, not present in homogeneous catalysis, can influence the rate and mechanism of the reaction in catalysis over solid catalysts: The competitive access of the epoxide and amine molecules to the acidic, active sites on the surface. The different basicities of the amine and epoxide can influence their relative surface coverages and, consequently, reaction rates. Another interesting feature of our results of relevance to the mechanism of this reaction is

Fig. 5 Influence of amount of catalyst and epoxide on the conversion and product selectivity in aminolysis of epichlorohydrin with aniline. (**a**) Reaction conditions: epichlorohydrin, 10 mmol; aniline, 10 mmol; reaction temperature, 333 K, reaction time, 4 h. (**b**) epichlorohydrin: aniline, 1: 1; catalyst, 50 mg; reaction temperature, 333 K; reaction time, 4 h

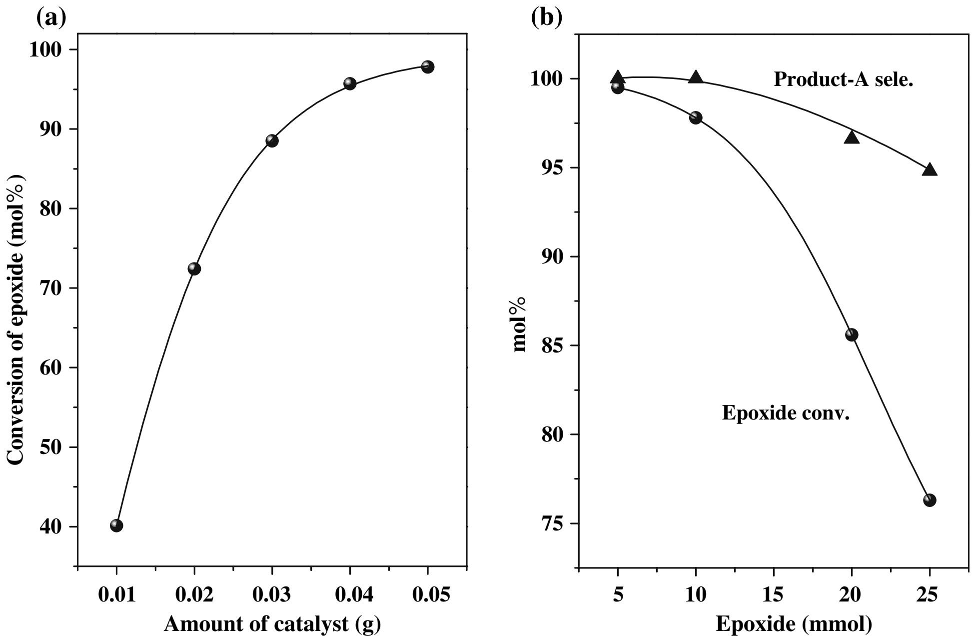


Table 3 Catalyst recycling studies—aminolysis of epoxides

No. of Recycles	Styrene oxide conversion (mol %)	Isomer-A selectivity (%)
0	98.7	99
1	96.8	100
2	95.5	100
3	97.3	100
4	96.0	100
5	95.7	100

Reaction Conditions: epichlorohydrin—20 mmol, aniline—20 mmol, catalyst—100 mg, temperature—333 K, reaction time—4 h

the orientation of the epoxide ring opening. As shown in Scheme 1, two regioisomers are theoretically possible. In almost all our studies (Table 1), the A isomer predominates. Substituent groups on the epoxide influence the orientation of the incoming moiety (RNH_2) by steric as well as electronic effects [20]. Bulky R groups favor the B isomer. Similarly, under basic or neutral conditions, when an S_N2 attack of the reagent molecule (RNH_2) on the epoxide ring carbon atom leads to products, the B isomer is dominant. Under acidic conditions, on the other hand, electronic effects (inductive and conjugative) determine the orientation [20]. These effects can stabilize a positive charge on the carbon atom (of the epoxide ring) adjacent to R. This is facilitated if the reaction occurs by a S_N1 mechanism in which the transition state for the rate-determining step carries a partial positive charge on the carbon atom adjacent to R. Protonation of the epoxide oxygen (in the case of Bronsted acid catalysts) or its coordination to Lewis acids sites (Zn^{2+} in Fe–Zn DMC) apparently favors the S_N1 mechanism and the consequent predominance of the A isomer.

4 Conclusions

Lewis-acidic, Zn^{2+} ions in double metal cyanide Fe–Zn complexes exhibit good catalytic activity and high regioselectivity for β-amino alcohols synthesis via ring-opening of epoxides with amines at near-ambient conditions under solvent-free conditions. The intrinsic catalytic activity of these novel solid, acid catalysts is higher than most of the known catalysts for this reaction.

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