

Aerobic epoxidation of olefins catalyzed by Co-SiO₂ nanocomposites

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Abstract

Cobalt-silica nanocomposite catalysts have been prepared using sol–gel process followed by drying under different conditions. The use of amino functionalized silane in the gelation step provided homogeneous distribution of the cobalt through the whole material. TEM, XPS and H₂-TPR data reveal that highly dispersed cobalt(II) sites are present in the samples. The catalysts were evaluated for selective aerobic epoxidation of olefins without the use of sacrificial reductant. Among the Co-SiO₂ nanocomposite catalysts, aerogel prepared catalyst has shown superior activity due to the high porosity clubbed with highly accessible cobalt(II) sites.

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1. Introduction

Catalytic epoxidation of olefins has attracted much attention both in industrial processes and in organic syntheses, as the epoxides are the most useful synthetic intermediates. Despite successes in homogeneous catalysis [1], there is a clear demand for solid materials that catalyze the epoxidations with easily available oxidants such as molecular oxygen, and H₂O₂ [2]. Cobalt-catalyzed epoxidation of alkenes with molecular oxygen is extensively investigated. Raja et al. [3] developed a MAIPO-36 (M = Co or Mn) catalyst for the epoxidation of cyclohexene and other alkenes in the presence of sacrificial aldehyde. CoO-MCM-41 prepared by ultrasonic deposition–precipitation of cobalt tricarbonyl nitrosyl in decalin catalyzes the epoxidation of alkenes by O₂ in the presence of isobutyraldehyde [4]. Timo Pruss et al. [5] reported that cobalt complexes immobilized on modified HMS catalyzed the epoxidation of alkenes with O₂. Wang and co-workers described that the single site Co(II) catalysts present in faujasite zeolites or in MCM-41 are active in the aerobic

epoxidation of styrene without the use of sacrificial reductant [6].

Sol–gel process was found to be a promising method to prepare highly efficient catalysts for oxidation of variety of substrates using molecular oxygen or H₂O₂ as oxidants [7]. Gusevskaya and co-workers [8] reported an active and recyclable heterogeneous catalyst, sol–gel Co/SiO₂ for the oxidation of limonene, 3-carene, α -pinene and β -pinene with dioxygen under solvent-free conditions. Silica supported highly dispersed active components can be obtained by a sol–gel method that allows a nanostructural control of ceramics through process variables [9]. The homogeneously disperse nanometer-sized metal particles in a silica matrix are obtained by tethering the metal precursor to the silica matrix during the sol–gel process [10]. Herein, we report the selective aerobic epoxidation of olefins by using sol–gel prepared Co-SiO₂ catalysts in the absence of the sacrificial reductant (Scheme 1).

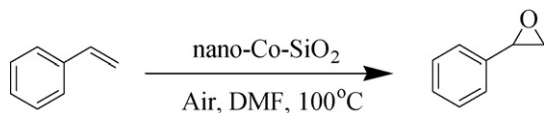
2. Experimental

2.1. Preparation of catalysts

The commercial fumed silica ag-SiO₂ was purchased from Sigma (type 5005, 0.007 μ m particle size). The surface area was 400 m²/g.

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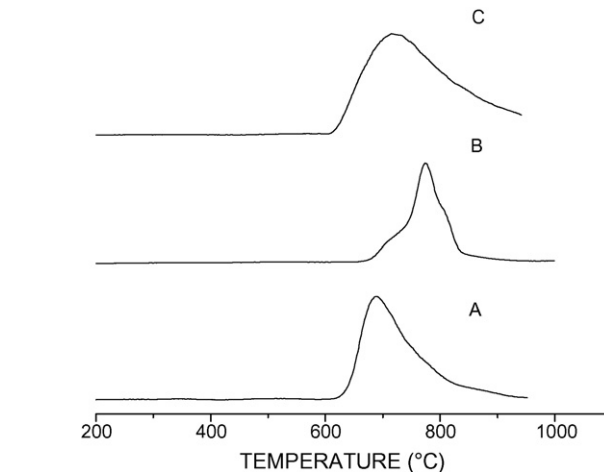


Scheme 1. Aerobic epoxidation of styrene.

Cobalt(III) acetylacetonate and 3-(trimethoxy silyl)propyl] diethyl triamine are mixed together in ethanol. The slurry was stirred at room temperature until a clear solution was obtained. After addition of tetraethoxysilane (TEOS), a solution of aqueous 0.2 N ammonia in ethanol is added to the mixture under vigorous stirring. The vessel is then closed and heated to 70 °C for 3 days. The obtained cogelled samples were dried in an autoclave under hypercritical conditions and dried under vacuum at 100 °C to obtain ag-Co-SiO₂ and xg-Co-SiO₂. The imp-Co-SiO₂ catalyst was obtained by impregnation of cobalt(III) acetylacetonate in ethanol at 85 °C for 12 h. All the catalysts were calcined in a flow of air at 300 °C for 12 h.

2.2. Reaction conditions

The oxidations were carried out in air in a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer and reflux condenser. In a typical run, 0.025 g (3.7 mol%) of catalyst was added to the reactor, which was precharged with alkene (1 mmol) and 5 mL of solvent, at the desired temperature. The reaction was started by bubbling of air into the liquid. The reaction mixture was stirred vigorously during the reaction. The progress of the reaction was monitored by GC analysis. After completion of the reaction, the catalyst was filtered off, and the liquid organic products were analyzed by gas chromatography

Fig. 1. TPR profiles of Co-SiO₂ catalysts. (A) imp-Co-SiO₂, (B) xg-Co-SiO₂ and (c) ag-Co-SiO₂.

graph (Shimadzu 2010) equipped with a B-5 capillary column and a FID detector. The turnover number was calculated from the moles of styrene converted per mole of cobalt present in the catalyst.

3. Results and discussion

Sol-gel processing of the Co-SiO₂ nanocomposites is depicted in Scheme 2. Metal silane complex obtained from cobalt(III) acetylacetonate and two equivalents 3-(trimethoxysilyl)propyl]diethyltriamine was co-gelled with tetraethoxysilane by using ammonia and large excess of ethanol. An important advantage of the co-gelation method is homo-

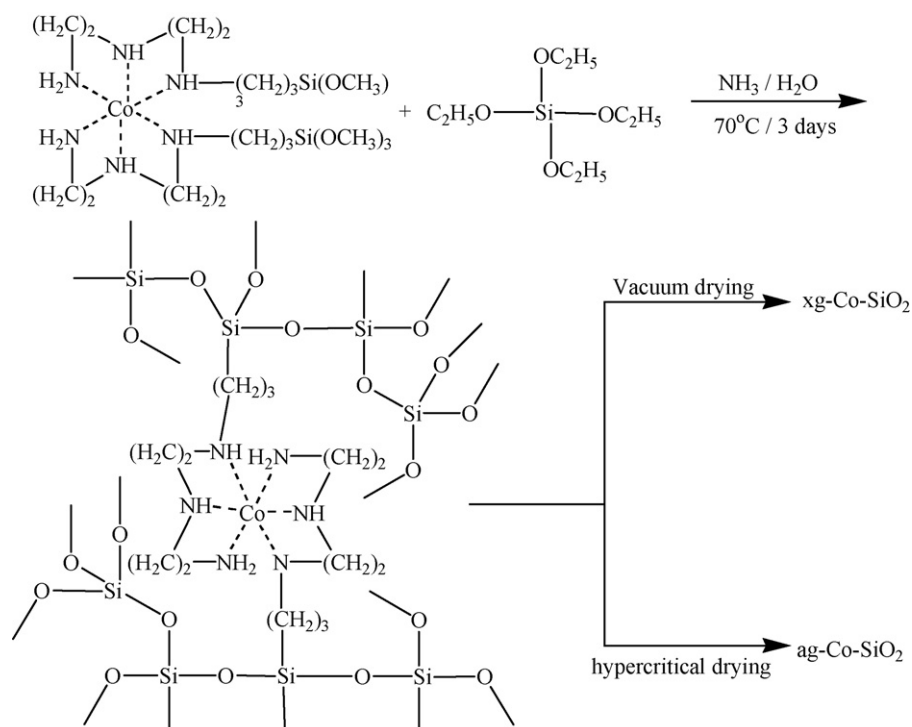
Scheme 2. Synthesis of Co-SiO₂ nanocomposite catalysts in sol-gel method.

Table 1
Textural properties, Binding energies, particle size of Co-SiO₂-nanocomposites

Catalyst	Co (% w/w) ^a	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Binding energies (eV)	Particle size (nm)	TPR (°C)
imp-Co-SiO ₂	6.60	290	2.68	0.75	782.2	<10 nm	687
xg-Co-SiO ₂	8.20	658	0.40	0.22	782.9	<10 nm	774
ag-Co-SiO ₂	8.53	597	9.39	0.93	781.0	<2 nm	720

^a Analyzed by AAS.

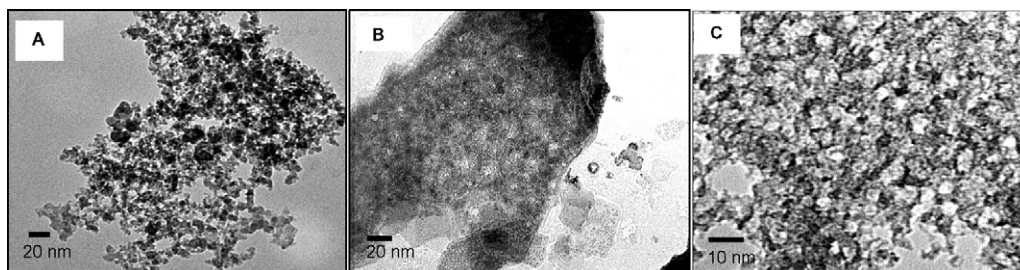


Fig. 2. TEM images of Co-SiO₂ catalysts. (A) imp-Co-SiO₂, (B) xg-Co-SiO₂ and (C) ag-Co-SiO₂.

geneous distribution of the catalytic metal through the whole material. The cobalt localization in the co-gelled samples is probably as a consequence of the ligand used and the hydrolyzable functions in Si₃C₁₀N₃H₂₇ which allow the formation of Si–O–Si bonds all around the complex [10c]. After gelation is completed the samples were subjected to different drying conditions in order to obtain a high porosity and then perhaps a good accessibility to the active sites. Supercritical drying provides aerogel catalysts (ag-Co-SiO₂) and vacuum drying provides xerogel catalysts (xg-Co-SiO₂). For comparison, the impregnated catalyst (imp-Co-SiO₂) was prepared from cobalt(III) acetylacetonate and fumed silica in ethanol.

The chemical analysis and textural properties of different Co-SiO₂ composites were given in Table 1. The surface areas of xg-Co-SiO₂ and ag-Co-SiO₂ are high when compared to the Co-SiO₂ prepared in sol–gel method in the absence of a ligand [11]. The surface area of imp-Co-SiO₂ is less when compared to the parent silica. The ag-Co-SiO₂ shows large pore volume, which is characteristic of aerogels. The XRD pattern of all three catalysts showed amorphous phases. The intense satellite struc-

ture and high energy of the XPS Co 2p_{3/2} peaks (781–782.9 eV) indicate the presence of Co²⁺ ions in the impregnated and sol–gel prepared catalysts. The state of the cobalt species in the samples has also been investigated by H₂-TPR and the profiles were given in Fig. 1. All the samples exhibit a high temperature (>670 °C) reduction peaks, which suggest that the cobalt species in the samples are probably in the Co(II) state and are strongly interacted with silica support [6b]. Fig. 2 shows the TEM images of different Co-SiO₂ catalysts. It is observed that imp-Co-SiO₂ sample contains larger Co particles on the surface and xg-Co-SiO₂ showed cobalt nanoparticles embedded in silica while ag-Co-SiO₂ showed the cobalt particles well dispersed throughout the silica matrix and are uniform with the size less than 2 nm.

We have first investigated the epoxidation of 4-methylstyrene using different cobalt catalysts in presence of air as an oxidant in DMF. The reaction proceeded well with these catalysts (Table 2, entries 1–3). Among the catalysts ag-Co-SiO₂ afforded high conversion and high selectivity to epoxide. Furthermore the Co-free SiO₂ catalyst has shown low conversion and selectiv-

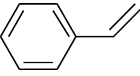
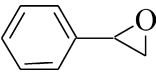
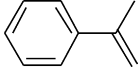
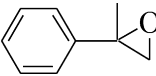
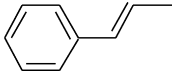
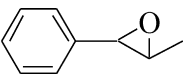
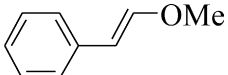
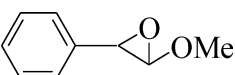
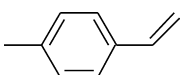
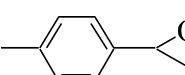
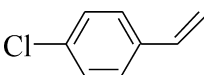
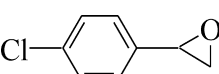
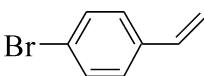
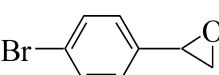
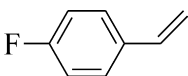
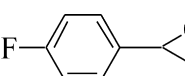
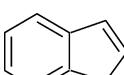
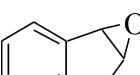
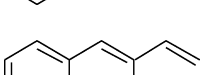
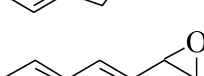
Table 2
Epoxidation 4-methylstyrene

Entry	Catalyst	Oxidants	Solvent	Conversion (%)	Epoxide selectivity (%)	Turnover number
1	imp-Co-SiO ₂	Air	DMF	72	77	19.5
2	xg Co-SiO ₂	Air	DMF	65	65	17.6
3	ag Co-SiO ₂	Air	DMF	92	89	24.8
4	Fumed Silica	Air	DMF	8	70	–
5	ag Co-SiO ₂	H ₂ O ₂ ^a	DMF	2	–	0.5
6	ag Co-SiO ₂	NaClO ^a	DMF	15	–	4.1
7	ag Co-SiO ₂	TBHP ^a	DMF	55	27	14.9
8	ag Co-SiO ₂	Air	<i>tert</i> -Butyl alcohol	0	–	–
9	ag Co-SiO ₂	Air	Chlorobenzene	8	–	2.16
10	ag Co-SiO ₂	Air	DMSO	78	6	21.1

Reaction conditions: substrate (1.0 mmol), solvent (5 mL) and flow rate of air 3.0 mL/min at 100 °C for 6 h.

^a Oxidant: 10 mmol.

Table 3
Epoxidation of different olefins using ag-Co-SiO₂ catalyst

Entry	Substrate	Product	Conversion ^a (%)	Epoxide selectivity ^a (%)
1			52	81
2			96	92
3			91	95
4			65	60
5			92, 90 ^b	89, 86 ^b
6			92	76
7			98	77
8			23	85
9			38	98
10			52	90

Reaction condition: substrate (1.0 mmol), catalyst (0.025 g), solvent (5 mL) and flow rate of air 3.0 mL/min at 100 °C for 6 h.

^a Analysed by GC.

^b After third recycle.

ity (Table 2, entry 4). Different oxidants were tested for the same reaction with ag-Co-SiO₂. The conversions are low with H₂O₂ and NaClO (Table 2, entries 5–6). Although styrene conversion is high with TBHP, the styrene oxide selectivity was very low (Table 2, entry 7). This is due to the uncontrolled radical reaction. Various solvents were tested for the epoxidation of 4-methylstyrene using ag-Co-SiO₂ catalyst and air. Very low conversions were obtained with *tert*-butanol and chlorobenzene (Table 2, entries 8 and 9) while DMSO provided high conversions but the selectivity for styrene oxide was low (Table 2, entry 10). The uniqueness of DMF as the solvent can be explained by the formation of an active tetrahedral DMF-coordinated Co-complex [6].

As shown in Table 3, different alkenes were also epoxidized in good to excellent yields using ag-Co-SiO₂ catalyst. In most cases, the reaction proceeded well with high selectivity under mild conditions.

After completion of the reaction, the catalyst was separated by centrifugation and washed with DMF, acetone and dried in an

oven. The recovered ag-Co-SiO₂ catalyst was reused for three recycles with consistent activity (Table 3, entry 5). AAS results of the used ag-Co-SiO₂ catalyst indicate leaching of 1.75% of cobalt in the epoxidation of 4-methylstyrene after the fourth cycle. When a fresh reaction was conducted with the filtrate obtained at the end of the epoxidation reaction, no product formation was observed.

4. Conclusion

Different cobalt-silica nanocomposite catalysts were prepared, characterized, and evaluated for selective aerobic epoxidation of alkenes. The catalysts prepared by co-gelation of the complex Co³⁺[NH₂-(CH₂)₂-NH-(CH₂)₂-NH-(CH₂)₃-Si(OCH₃)₂] with TEOS in an ethanolic solution containing aqueous ammonia. The gels were then subjected to supercritical ethanol conditions to obtain aerogels and vacuum drying to obtain xerogels. Characterization of these catalysts confirm the presence of highly dispersed Co(II) in aerogel prepared catalyst.

All three catalysts were active in epoxidation of alkenes in presence of air and DMF solvent but high selectivity was obtained using aerogel prepared catalyst. We believe this directly results from the enhanced mass transport within an aerogel particle due to the unique three-dimensional, interconnected network of mesopores.

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