

## Chromium Silicalite-2 (CrS-2): an Efficient Catalyst for the Chemoselective Epoxidation of Alkenes with TBHP†

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Chromium-containing medium-pore molecular sieve (Si/Cr > 140) having MEL (CrS-2) topology efficiently catalyses the chemoselective epoxidation of various olefins to the corresponding epoxides using 70% *tert*-butyl hydroperoxide (TBHP) as an oxidant.

The epoxidation of alkenes constitutes one of the most useful reactions in organic synthesis because the epoxide group is readily opened to produce a 1,2-functionality in a stereospecific manner.<sup>1</sup> Traditionally, the direct conversion of an alkene into an oxirane can be achieved by organic peracids.<sup>2</sup> However, alkyl hydroperoxides, especially *tert*-butyl hydroperoxide (TBHP), in the presence of Mo, V, W or Ti complexes as catalysts, have assumed in recent times, considerable importance as agents for the preparation of oxiranes from alkenes.<sup>3</sup> Moreover, chromyl nitrate in stoichiometric amounts under homogeneous conditions has been shown to epoxidize electron-rich alkenes, although in an unselective manner and in lowered yields.<sup>4</sup> The use of heterogeneous catalysts in the liquid phase, on the other hand, offers several advantages compared with their homogeneous counterparts *e.g.* ease of recovery and recycling and enhanced stability.

A recent development in the chemistry of zeolites is the incorporation of transition metals possessing redox charac-

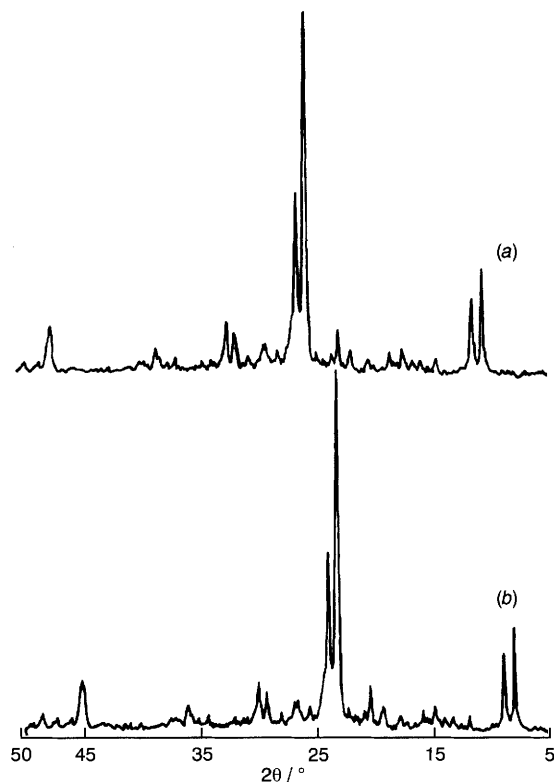


Fig. 1 X-Ray powder diffraction profiles of (a) silica polymorph of ZSM-11 and (b) Cr-ZSM-11; data collected on a Rigaku Max III VC instrument using Ni-filtered Cu-K $\alpha$  radiation

teristics into the framework of molecular sieves which can give rise to catalysts with shape selective oxidation properties. Of late, redox zeolites like titanium and vanadium silicates with MFI and MEL topologies have been shown to possess unique catalytic properties in oxidation reactions with H<sub>2</sub>O<sub>2</sub>.<sup>5</sup> Most recently, the incorporation of chromium into the silicalite-1 (CrS-1) and aluminophosphate (CrAlPO-5) systems has been achieved.<sup>6</sup> Moreover, it is pertinent to note that both the CrO<sub>3</sub>-TBHP system under homogeneous conditions<sup>7</sup> or the CrAlPO-5-TBHP system under heterogeneous conditions<sup>8</sup> selectively oxidize allylic alcohols to the corresponding carbonyl compounds. We wish to report, for the first time, our preliminary results on the synthesis and characterization of Cr-ZSM-11 (CrS-2) and its unique catalytic properties in the chemoselective epoxidation of alkenes with 70% TBHP as oxidant (Scheme 1).

The hydrothermal synthesis of chromium silicates was carried out using gels of the following composition: SiO<sub>2</sub>: *x* Cr<sub>2</sub>O<sub>3</sub>: 0.4 NBu<sub>4</sub>OH: 30 H<sub>2</sub>O where *x* = 0.005, 0.009 or 0.012 with tetrabutylammonium hydroxide employed as the organic template. In a typical synthesis, NBu<sub>4</sub>OH (Aldrich, 20% methanolic solution) was added slowly to an ice-cold solution of tetraethyl orthosilicate (22 g) (Aldrich 99.9%) under vigorous stirring. The mixture was stirred at room temp. for 2 h and then Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (1 g) (Aldrich, 99%) in water (10 ml) was added dropwise. This mixture was stirred at 343 K for 1 h and then the remaining water was added. The resultant clear homogeneous reaction mixture (pH = 11.80) was charged into a stainless steel autoclave and heated at 443 K for 90 h under static conditions to induce crystallization. After crystallization, the light green product was filtered, washed with deionized water, dried at 383 K and calcined at 773 K under air or nitrogen. The yield of the product was between 70 and 80 mass%. Three such chromium silicates with Si:Cr input ratios

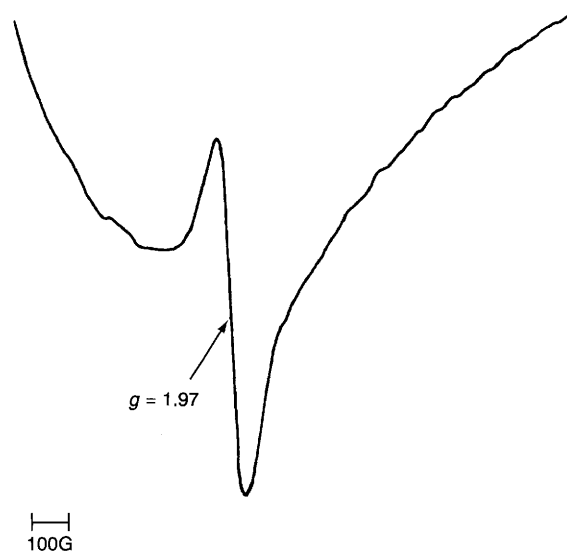


Fig. 2 ESR spectrum of calcined Cr-ZSM-11 (recorded on a Bruker ER 200D spectrometer at room temperature)

of 40, 80 and 150:1 were prepared and characterized by X-ray powder diffraction (XRD), IR and ESR spectral techniques.

The XRD pattern of the three Cr-MEL samples matched well with that of the chromium-free polymorph (Fig. 1). The sorption properties of the calcined Cr-ZSM-11 samples for *n*-hexane and cyclohexane at  $p/p_0 = 0.5$  are characteristic of microporous material. The scanning electron micrograph of CrS-2 shows uniform crystals of particle size 2–2.5  $\mu\text{m}$ . The IR spectrum of CrS-2 exhibits an absorption band at 963  $\text{cm}^{-1}$  corresponding to the stretching mode of Si–O–Cr and also bands at 460, 550 and 790  $\text{cm}^{-1}$  indicative of MEL framework structures.<sup>9</sup> Fig. 2 shows the ESR spectrum of the calcined CrS-2 sample recorded at 293 K. The *g* value of 1.97 is in the range reported for a variety of other stable or transient oxochromium(v) complexes.<sup>4</sup> Finally, the output in the zeolite was determined by wet chemical analysis and the output ratio was found to be 140, 185 and 300:1 for input Si:Cr ratios of 40, 80 and 150:1 respectively.

**Table 1** Epoxidation of cyclohexene with TBHP over zeolites<sup>a</sup>

Entry	Zeolite	Epoxide, yield <sup>b</sup> (%)	Unreacted cyclohexene <sup>c</sup> (%)
1	No catalyst	—	100
2	CrS-2	86.5	2.3
3	TS-2 <sup>d</sup>	20.8	66.0
4	VS-2 <sup>e</sup>	57.6	25.3

<sup>a</sup> Reaction conditions: cyclohexene (5 mmol); cat: 10% mass (Si/Cr = 140); 70% TBHP (5 mmol); Solvent, MeOH; 333 K. <sup>b</sup> Determined by GLC; HP-5880 silicon gum capillary column. <sup>c</sup> Unreacted cyclohexene + unidentified products. <sup>d</sup> TS-2, Si/Ti = 29. <sup>e</sup> VS-2, Si/V = 96.

**Table 2** Epoxidation of various substrates over CrS-2: (Si/Cr = 140)

Entry	Substrate	<i>t</i> /h	<i>T</i> /°C	Product <sup>a</sup>	Yield <sup>b</sup> (%)
1	Allyl alcohol	4	65	2,3-Epoxyallyl alcohol	82
2	Cinnamyl alcohol	6	25	2,3-Epoxy-cinnamyl alcohol	80
3	Geraniol <sup>c</sup>	5	65	2,3-Epoxygeraniol	95
4	Cyclohexene	6	65	1,2-Epoxy-cyclohexane	70
5	Acrylonitrile	5	65	2,3-Epoxy-acrylonitrile	60
6	Mesityl oxide	6	65	3,4-Epoxy-mesityl oxide	31

<sup>a</sup> Characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. <sup>b</sup> Isolated yield; the remainder is essentially starting material. <sup>c</sup> The zeolite catalyst was recovered and reused three times with virtually no loss of activity.

In a typical reaction procedure in catalysis evaluation, a mixture of cinnamyl alcohol (1.34 g, 10 mmol), CrS-2 (134 mg, 10% mass) and 70% TBHP (1.5 ml, 11 mmol) in MeOH (15 ml) was stirred at 25 °C for 6 h. After the reaction was complete (TLC), the catalyst was filtered off and the product purified by flash chromatography to afford 2,3-epoxycinnamyl alcohol (1.2 g, 80%). The results of the epoxidation of cyclohexene over various zeolites (Table 1) indicate that CrS-2 exhibits significantly higher activity and selectivity than TS-2 or VS-2. It is found that the choice of solvent (MeOH) for CrS-2 catalysed epoxidation of geraniol with TBHP is critical as the reaction fails when carried out in solvents such as chloroform and acetone.

Table 2 lists the results of the various types of olefins that have been successfully epoxidized with the CrS-2–TBHP system. A novel feature of this catalyst is its unusual regio- and chemo-selectivity towards allylic C=C double bonds over the isolated C=C bonds or hydroxy groups (entries 1–3). It is also remarkable that even electrophilic olefins can be epoxidized by the present catalyst system (entries 5 and 6). It is proposed that the oxochromium(v) species present in the zeolite framework is responsible for epoxidation and work is in progress to gain further insight into the mechanistic aspects of this process.

In conclusion, CrS-2 is a stable, recyclable solid catalyst for the chemoselective liquid-phase oxidation of alkenes into the corresponding epoxides using 70% TBHP as the oxidant.

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## Footnote

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