

Chromium substitution in a large-pore high-silica zeolite BEA: synthesis, characterisation and catalytic activity

S. Yuvaraj,* M. Palanichamy and V. Krishnasamy

Department of Chemistry, Anna University, Madras - 600 025, India

The incorporation of Cr^{III} into the framework of a high-silica large-pore zeolite- β is confirmed and its usefulness in the oxidation of phenol, toluene, cyclohexane and benzene investigated.

Synthesis of oxidative catalysts, *i.e.* materials containing redox metals such as Ti,¹ Fe,² Cr,³ V,⁴ *etc.*, is of current interest in zeolite science as they are active and selective in the mild oxidation of organic compounds. Substitution of Ti,⁵ Ga,⁶ B,^{4,7} V⁴ and Fe² has already been reported over zeolite BEA and unambiguously characterised substitution at tetrahedral framework sites. Regarding chromium substitution, as far as the literature is concerned, only a few articles have appeared in the open literature describing substitution in AlPO-5,⁸ AlPO-11,^{3a} MFI,⁹ and more recently, in mesoporous MCM-41¹⁰ structures. Chapus *et al.*,^{9a} Sugimoto *et al.*^{9b} and Pastore *et al.*^{3b} claimed partial substitution by chromium ions in the MFI structure. Here, we report chromium substitution in a large-pore high-silica zeolite BEA, and its catalytic behaviour towards the oxidation of phenol, toluene, cyclohexane and benzene.

Synthesis mixtures were prepared using tetraethylorthosilicate (98%, Merck), tetraethylammonium hydroxide (TEAOH, 40% aq. solution, Fluka), sodium aluminate (56% Al₂O₃, 37% Na₂O, Thomson, India) and chromium nitrate nonahydrate (99%, Fluka).

CrAl- β was prepared from the gel composition SiO₂:0.037 Al₂O₃:0.435 (TEA)₂O:0.037 Na₂O: x Cr₂O₃:17.2 H₂O where $10^{-3}x = 7.9, 3.7, 2.9, 2.2$ or 1.5 . The synthesis procedure was as follows: part of TEAOH was diluted with the required amount of water, to which sodium aluminate and tetraethylorthosilicate were added at room temperature with stirring. A solution of chromium nitrate and the remaining TEAOH was added for the completion of TEOS hydrolysis. The mixture was stirred for 1 h at room temp. and 5 h at 338 K to distill off the ethanol formed. Finally the resultant light green gel was poured into a 100 ml stainless-steel autoclave and heated at 408 ± 1 K in an oven for 12 days. After cooling the autoclaves, samples were centrifuged, washed, dried at 383 K and calcined at 748 K.

XRD (Rigaku, Ni-filtered, Cu-K α radiation) and surface area measurements ($470 \text{ m}^2 \text{ g}^{-1}$ for the calcined sample; BET with N₂ sorption system) showed that the synthesised materials are highly crystalline. The chemical composition of the calcined solid was obtained from ICP-AES (ARL 3410 equipped with a minitorch) and by a wet chemical method as SiO₂:0.028 Al₂O₃:0.019 Na₂O: x Cr₂O₃; $10^{-3}x = 3.2, 2.7, 2.2, 1.8$ or 1.3 . The sample with $x = 3.2 \times 10^{-3}$ was taken as the representative material in spectral measurements. The light yellow calcined sample ($x = 3.2 \times 10^{-3}$) was washed with 1 M acetic acid in order to remove extraframework soluble chromium oxides,^{9a} after which x decreased to 1.92×10^{-3} for the cream coloured solid. Therefore, it is concluded that the unleached chromium is present within the framework. This was further confirmed by the 955 cm^{-1} band of the calcined sample in the FTIR spectrum^{9a} (Bruker IFS 66v, KBr pellet technique). The 955 cm^{-1} band was retained in the washed sample. This confirms that some chromium ions are in substitutional sites. From TGA studies, (Mettler TA 4000 series) desorption of 0.99 mmol of

TEAOH (473–643 K) and 0.34 mmol of TEA⁺ (643–773 K) was observed. The peak in the range 643–773 K is due to the desorption of TEA⁺ interacting with the metal incorporated within the framework.^{5b} DRS spectra (Pye-Unichem SP-8 100 UV-VIS spectrometer) of the as-synthesised sample [Fig. 1(a)] showed two distinctive broad Cr³⁺ octahedral absorption bands at 659 and 457 nm assigned to the ⁴T₂ $\rightarrow$ ⁴T₅ and ⁴T₂ $\rightarrow$ ⁴T₄[F] transitions respectively.^{3b,11} The calcined sample [Fig. 1(b)] showed two charge-transfer O $\rightarrow$ Cr⁶⁺ bands at 378 and 275 nm, but no peaks were observed in the DRS of the washed sample.

The EPR (Varian spectrometer) spectrum [Fig. 2(a)] of the as-synthesised sample showed a broad peak centred at $g = 1.98$ containing multiple resonances and a peak-to-peak width of

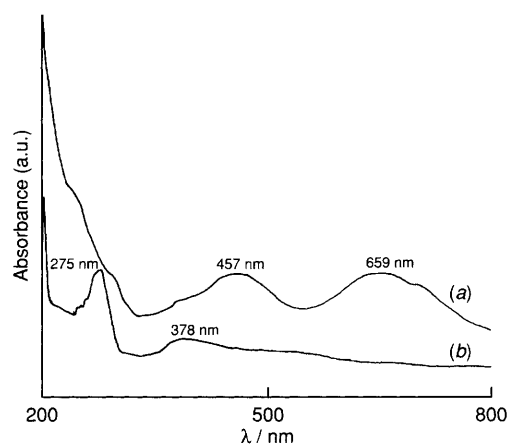


Fig. 1 Diffuse reflectance spectra of (a) as-synthesised and (b) calcined CrAl- β

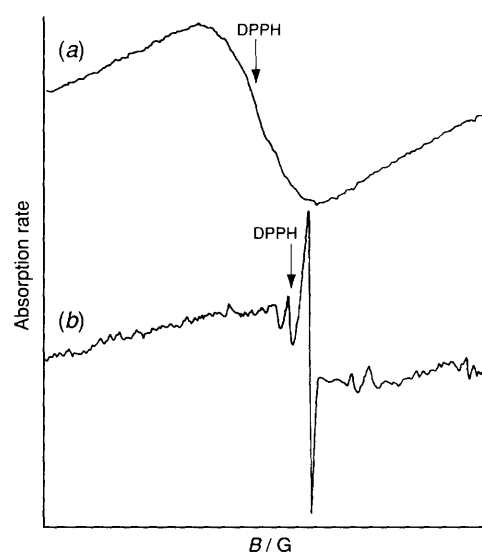


Fig. 2 EPR spectra of (a) as-synthesised and (b) calcined CrAl- β

Table 1 Liquid-phase oxidation with H₂O₂ by CrAl-β^a

Catalyst	Reactant	Conversion (mol%)	H ₂ O ₂ selectivity ^b (mol%)	Product	Product selectivity (mol%)
CrAl-β-C ^c	Phenol	27.9	52.6	Catechol	43.4
				Hydroquinone	54.8
				<i>p</i> -Benzoquinone	1.8
CrAl-β-W ^d	Phenol	18.4	66.2	Catechol	38.0
				Hydroquinone	60.3
				<i>p</i> -Benzoquinone	1.7
CrAl-β-C	Toluene	8.3	34.2	<i>o</i> -Cresol	42.1
				<i>p</i> -Cresol	56.5
				Benzaldehyde	1.4
CrAl-β-W	Toluene	5.6	45.7	<i>o</i> -Cresol	41.0
				<i>p</i> -Cresol	57.1
				Benzaldehyde	1.9
CrAl-β-C	Cyclohexane	7.8	47.3	Cyclohexanol	39.7
				Cyclohexanone	60.3
				Cyclohexanol	23.5
CrAl-β-W	Cyclohexane	5.1	59.1	Cyclohexanone	76.5
				Phenol	98.4
				Catechol	1.6
CrAl-β-C	Benzene	10.3	57.4	Phenol	98.4
				Catechol	1.6
CrAl-β-W	Benzene	7.2	72.2	Phenol	100.0
				Phenol	100.0

^a All samples were analysed on a GC (HP 5890, OV 17 column); *T* = 358 K except for benzene where *T* = 328 K, reactant/H₂O₂ = 3; reaction time = 6 h for phenol and 12 h for toluene, cyclohexane and benzene; catalyst = 0.2 g, 15 ml solvent; water for phenol, acetonitrile for toluene, butan-2-one for cyclohexane and acetone for benzene. ^b (Moles of product formed/moles of H₂O₂ in feed) × 100. ^c CrAl-β-C: calcined at 748 K (Si/Cr = 156). ^d CrAl-β-W: washed CrAl-β-C (1 M acetic acid) (Si/Cr = 260); see text.

500 G. All these resonances are associated with framework Cr³⁺ irrespective of coordination^{3b} (octahedral or tetrahedral). After calcination the sample showed a sharp signal [Fig. 2(b)] which is attributed to Cr⁵⁺,^{9a} while the washed sample showed no signal.

²⁹Si MAS NMR (Bruker DSX 300 spectrometer at 6.4 KHz) showed a peak at δ −110.5 (4Si) with a shoulder at δ −105 possibly due to (3Si, Al) or (3Si, Cr) sites;^{9a,10} ²⁷Al MAS NMR showed only one tetrahedral peak at δ −56.

Further evidence for the isomorphous substitution of chromium in zeolite BEA came from the catalytic oxidation/hydroxylation of phenol, toluene, cyclohexane and benzene with H₂O₂ (30% Merck) and the results obtained are given in Table 1. All reactions were carried out in a stirred reactor (600 rpm). Good to excellent selectivities towards hydroquinone, cyclohexanone and phenol were observed. From Table 1, hydrogen peroxide selectivity was good and even superior in some cases for washed samples than for calcined samples. Toluene exhibited very good ring hydroxylation activity as against the more common side-chain oxidation to benzaldehyde whereas other reactants such as phenol and cyclohexane showed better selectivities towards oxygenated products.

The catalysts retained their activity and selectivity for oxidation/hydroxylation over three cycles and possessed good recyclability. ICP–AES confirmed that no leaching of chromium occurred during the reactions.

Further research on the status of chromium in the zeolite BEA by EXAFS and cyclic voltammetry is in progress.

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References

- 1 N. Ulagappan and V. Krishnasamy, *J. Chem. Soc., Chem. Commun.*, 1995, 373.
- 2 R. Kumar, A. Thangaraj, R. N. Bhat and P. Ratnasamy, *Zeolites*, 1990, **10**, 85.
- 3 (a) M. Eswaramoorthy, N. John Jebarathinam, N. Ulagappan and V. Krishnasamy, *Catal. Lett.*, 1996, **38**, 255; (b) H. O. Pastore, E. Stein, C. U. Davanzo, E. J. S. Vichi, O. Nakamura, M. Baesso, E. Silva and H. Vargas, *J. Chem. Soc., Chem. Commun.*, 1990, 772.
- 4 T. Sen, M. Chatterjee and S. Sivasankar, *J. Chem. Soc., Chem. Commun.*, 1995, 207.
- 5 (a) M. A. Camblor, A. Corma, A. Martinez and J. Perez Pariente, *J. Chem. Soc., Chem. Commun.*, 1992, 589; (b) M. A. Camblor, A. Corma and J. Perez-Pariente, *Zeolites*, 1993, **13**, 82; (c) J. S. Reddy and A. Sayari, *J. Chem. Soc., Chem. Commun.*, 1995, 23.
- 6 M. A. Camblor, J. Perez-Pariente and V. Fornes, *Zeolites*, 1992, **12**, 280.
- 7 R. D. Ruiten, K. Pamin, A. P. M. Kentgens, J. C. Jansen and H. Vanbekkum, *Zeolites*, 1993, **13**, 611.
- 8 J. D. Chen, J. Dakka, E. Neelaman and R. A. Sheldon, *J. Chem. Soc., Chem. Commun.*, 1993, 1379; B. M. Weckhuysen and R. A. Schoonheydt, *Zeolites*, 1994, **14**, 360.
- 9 (a) T. Chapus, A. Tuel, Y. Ben Taarit and C. Naccache, *Zeolites*, 1994, **14**, 349; (b) M. Sugimoto, H. Katsuno, K. Takatsu and N. Kawata, *Appl. Catal. A: Gen.*, 1992, **80**, 13.
- 10 N. Ulagappan and C. N. R. Rao, *Chem. Commun.*, 1996, 1047.
- 11 J. S. T. Mambrim, E. J. S. Vichi, H. O. Pastore, C. U. Davanzo, H. Vargas, E. Silva and O. Nakamura, *J. Chem. Soc., Chem. Commun.*, 1991, 922.

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