Ionic liquid templated synthesis of cobalt-substituted mesoporous aluminophosphates: A novel heterogeneous catalyst for selective oxidation of cyclohexane to cyclohexanol

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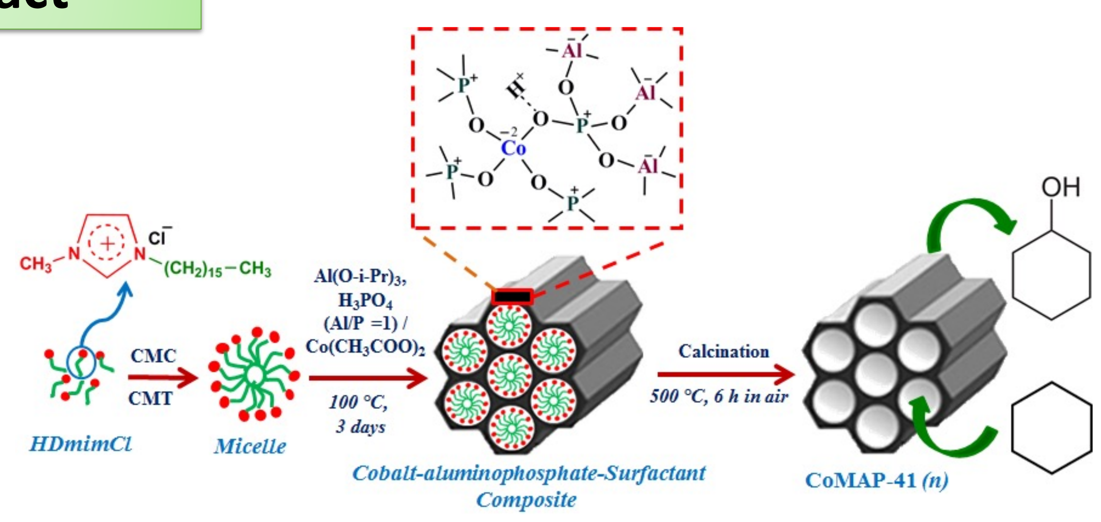
Abstract



Scheme 1. The synthetic approach and the reactivity of CoMAP-41.

- Ordered mesoporous aluminophosphate (MAP-41) and its cobalt-substituted analogue (CoMAP-41) were synthesised using an ionic liquid structure-directing agent.
- Various characterisations confirmed the presence of divalent cobalt in the tetrahedral framework of the matrix.
- CoMAP-41 (*n*) materials impart good thermal and hydrothermal stability.
- 95 % conversion and 96 % cyclohexanol selectivity were obtained from CoMAP-41 (*n*) using hydrogen peroxide as an oxidant.

Objective

- To develop and characterise ordered mesoporous aluminophosphate and its cobalt-substituted analogue using ionic liquids as structure-directing agents.
- To evaluate the catalytic performance in the selective oxidation of cyclohexane to cyclohexanol with hydrogen peroxide.

Introduction

- Selective oxidation of cyclohexane to cyclohexanol under mild conditions using environmentally friendly oxidants like H_2O_2 is gaining interest.
- Cyclohexanol is widely used industrially as a plasticiser and stabiliser in producing paints, varnishes, and lacquers and in synthesising nylon-10.
- Developing stable mesoporous AlPOs is challenging, requiring new surfactants and synthesis methods.
- The long-chain ionic liquid HDmimCl was used as a surfactant to synthesise ordered mesoporous silicates and aluminosilicates, resulting in improved textural properties compared to conventional surfactants.

Table 1. Structural and textural properties of CoMAP-41.

Catalyst	n_{Al}/n_P[a]	$n_{[Al+P]}/n_{Co}$[a] Gel	$n_{[Al+P]}/n_{Co}$[a] Product	a_0 (nm)	S_{BET} (m^2g^{-1})	D_{BJH} (nm)	h_W[b] (nm)
MAP-41	1.31	∝	∝	4.08	850	2.9	1.29
CoMAP-41	1.30	100	77	4.10	810	2.8	1.30
	1.27	50	42	4.23	650	2.9	1.33
	1.26	25	24	4.50	625	3.1	1.40

[a]Determined by XRF; [b]Wall thickness = $a_0 - D_{BJH}$.

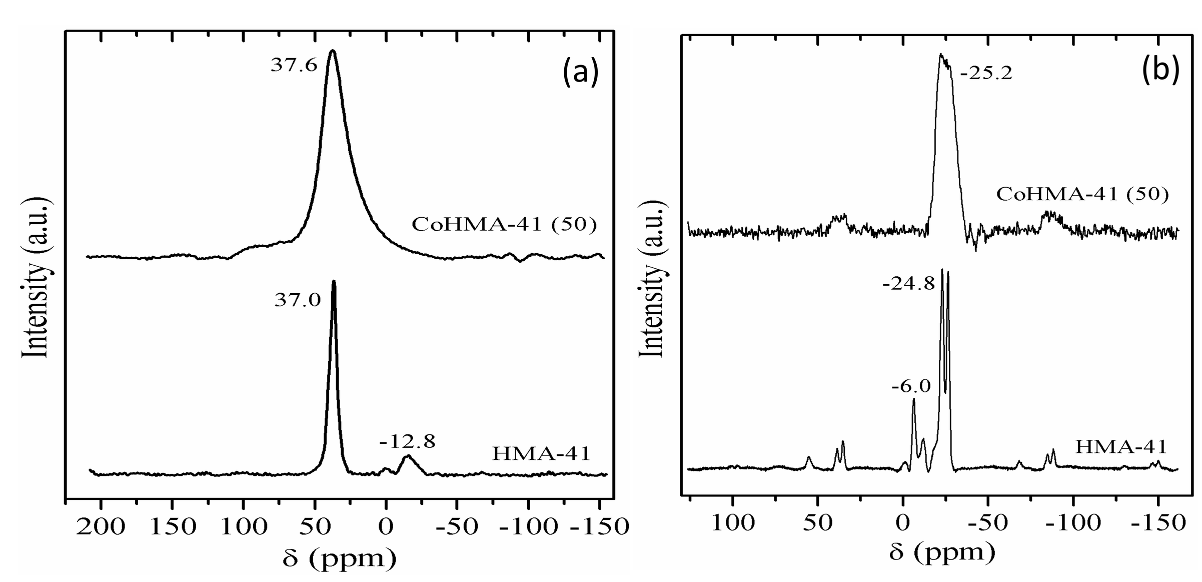


Figure 2. ^{27}Al MAS NMR (a) and ^{31}P MAS NMR spectra (b) of pristine and cobalt-substituted mesoporous aluminophosphates.

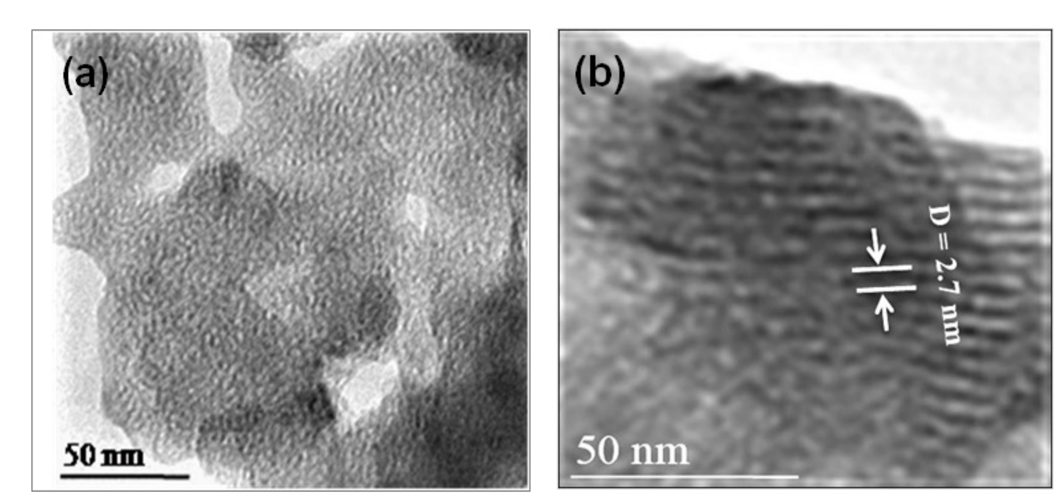
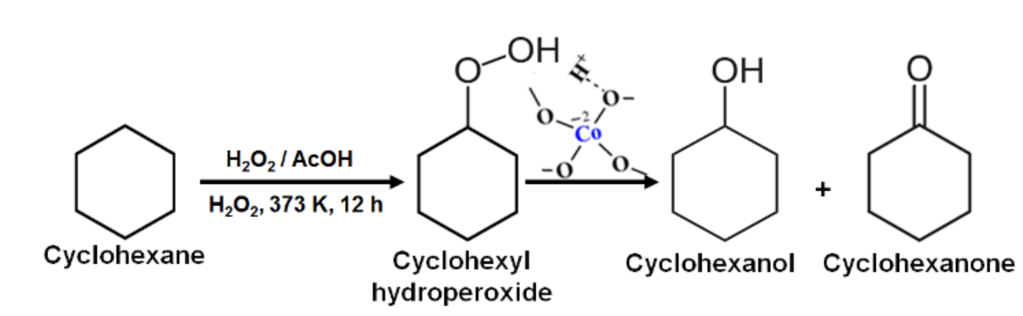


Figure 3. TEM images of CoMAP-41(50).



Scheme 2. Oxidation of cyclohexane over CoMAP-41.

Table 2. Oxidation of cyclohexane using CoMAP-41 and H_2O_2.

Catalyst[b]	Cyclohexane conversion[c] (%)	Selectivity[c] (%) -Ol	Selectivity[c] (%) -One	Selectivity[c] (%) Others[d]
No catalyst	8.4	80.0	2.2	17.8
MAP-41(∝)	8.7	77.6	3.4	19.0
CoMAP-41(100)	80.5	96.2	1.6	2.2
CoMAP-41(50)	95.4 [90.2]	95.8 [93.6]	2.7 [3.5]	1.5 [2.9]
CoMAP-41(25)	98.5	90.4	5.8	3.8

Reaction condition: Cyclohexane : oxidant = 1:1, catalyst = 50 mg, solvent/acetic acid = 10 mL, initiator/MEK = 5 mmol, 373 K and 12 h.
[b]Numbers in parentheses are the nominal [Al + P]/Co ratios.
[c]Numbers in the square bracket are the data for the recycled sample.
[d]Mainly cyclohexyl acetate.

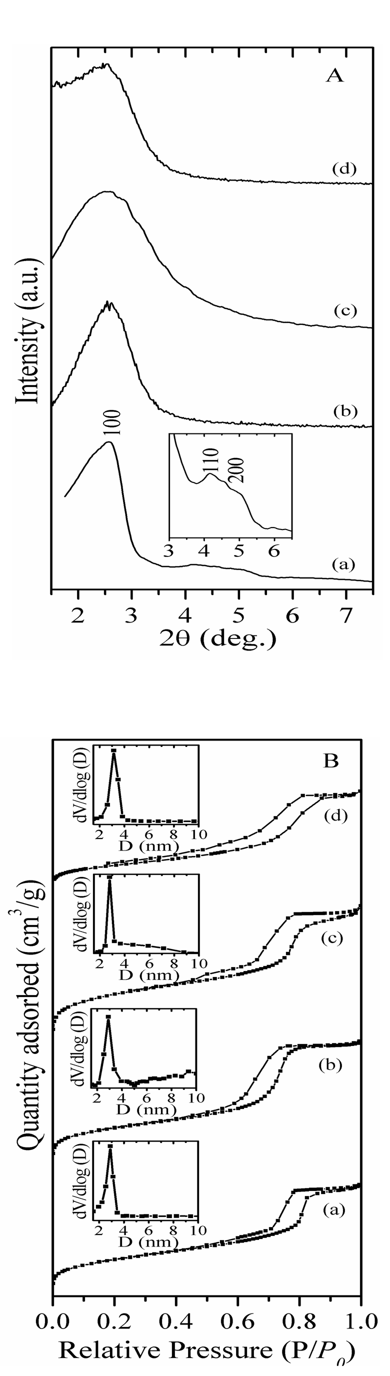


Figure 3. XRD patterns (A), and N_2 sorption isotherms and pore size distribution (B):
(a) MAP-41(∝); (b) CoMAP-41(100); (c) CoMAP-41(50); (d) CoMAP-41(25).

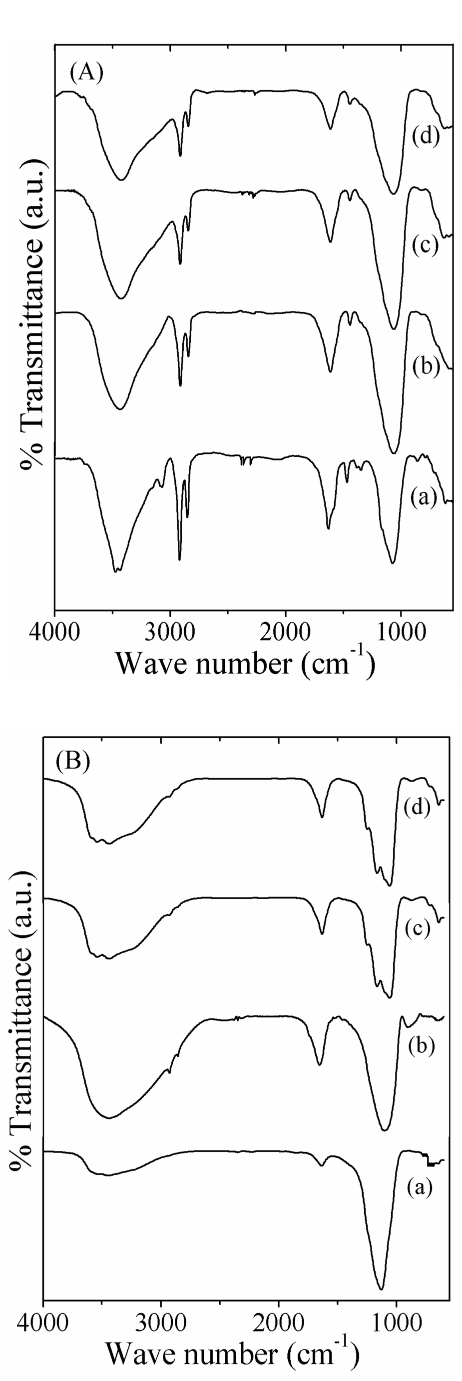


Figure 4. FT-IR spectra of synthesised (A) and calcined (B) catalysts:
(a) MAP-41(∝); (b) CoMAP-41(100); (c) CoMAP-41(50); (d) CoMAP-41(25).

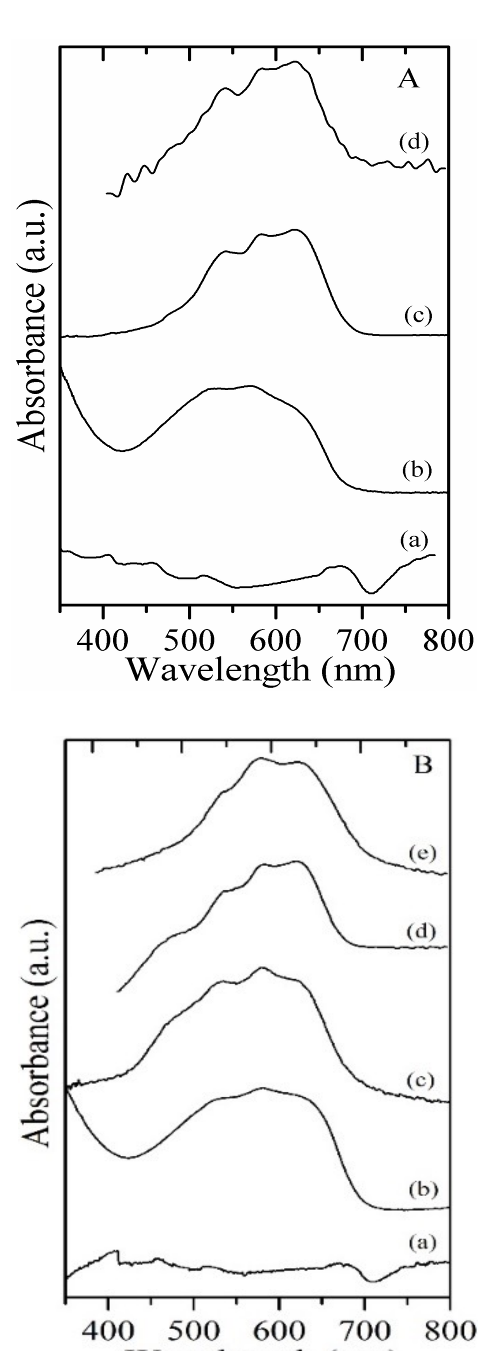


Figure 5. DRUV-VIS spectra of synthesised (A) and calcined (B) samples:
(a) MAP-41(∝); (b) CoMAP-41 (100); (c) CoMAP-41 (50); (d) CoMAP-41 (25); (e) Recycled CoMAP-41 (50).

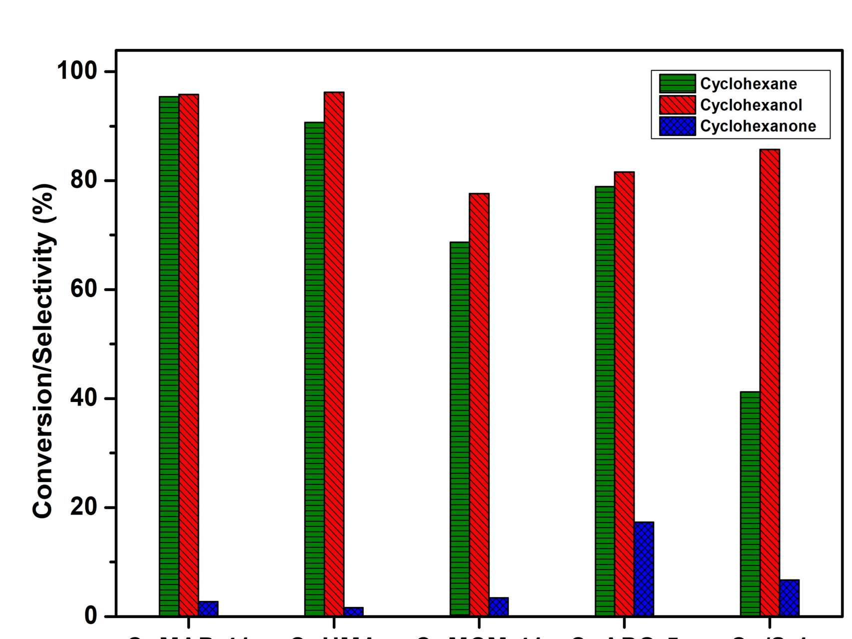


Figure 6. Comparison of various cobalt-containing catalysts for the oxidation reaction of cyclohexane.

Conclusion

- The catalyst MAP-41 and CoMAP-41 (*n*) were synthesised using the ionic liquid HDmimCl as a structure directing agent.
- The pore wall thickness of the MAP material is generally greater than that of the corresponding HMA-41 and MCM-41 structures synthesised using CTACl.
- The thicker pore walls typically enhance the mechanical, thermal, and chemical stability of the materials, highlighting the advantages CoMAP-41.
- The CoMAP-41(50) catalyst showed high catalytic activity with a yield of cyclohexanol as high as 90%.
- The catalyst is recyclable with minimal or no loss in activity for up to 4 cycles.

Reference

M. A. Kumar, N. Nagarjun, H. Manyar, P. Selvam, ChemCatChem, 2024, 16, 8, e202301729.