

p-Cresol autoxidation using CoAPO-5 prepared by microwave heating of the precursor gel: comparison with homogeneous and biphasic reaction schemes using cobalt salt or complex catalysts

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Abstract

p-Cresol autoxidation to *p*-hydroxybenzaldehyde was performed at 60 °C and atmospheric pressure, using three methods: (1) quasi-heterogeneous reaction using CoAPO-5 catalyst; (2) homogeneous reaction using CoBr₂ salt; and (3) biphasic organic–aqueous interfacial reaction using cobalt complexes together with a surfactant. Cobalt was proven to be the most active/selective for the *p*-hydroxybenzaldehyde synthesis among the transition metal salts tested. Highly crystalline and uniform CoAPO-5 was prepared using microwave heating in 40 min from the precursor gels and characterized using XRD, SEM, and UV–VIS spectroscopy. *p*-Cresol conversion and selectivity to *p*-hydroxybenzaldehyde increase with the cobalt contents and improved as the Co/*p*-cresol (mg/g) ratio increases to ca. 1.0. The oxygen selectivity was 82–85% for CoAPO-5, which is slightly higher than obtained with CoBr₂. The highly alkaline solution employed for the reaction, however, resulted in serious metal leaching. The biphasic reaction attempted for *p*-cresol autoxidation resulted in poor performance due to the limits in solvent selection. The performance of *p*-cresol autoxidation reaction was strongly governed by the solvent and followed the order methanol > ethanol > butanol, all miscible with water. Hardly any reaction took place in non-polar solvents such as chloroform or toluene, or in 2-ethyl-1-hexanol. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *p*-Cresol autoxidation; *p*-Hydroxybenzaldehyde; CoBr₂; CoAPO-5; Biphasic reaction

1. Introduction

p-Hydroxybenzaldehyde is an important chemical intermediate for the preparation of pharmaceutical, agricultural or fragrance chemicals. According to the patent by Sumitomo Co. [1], *p*-hydroxybenzaldehyde can be prepared by *p*-cresol oxidation using a CoCl₂ homogeneous catalyst in methanol solvent in the presence of a rather high concentration of NaOH (>7 M). The NaOH is essential to suppress the side reactions

taking place at the benzene ring and OH group. At 1 atm and 60 °C, 92% *p*-cresol conversion with 75% selectivity to *p*-hydroxybenzaldehyde was reported, whilst *p*-hydroxybenzyl alcohol and its ether were the major side products (see Fig. 1). Cobalt salts used in autoxidation are generally believed to function as catalysts via reversible change in oxidation states between Co²⁺ and Co³⁺ [2].

Cobalt-containing aluminophosphate molecular sieves have been the subjects of many studies, owing to their interesting redox properties [3]. It has been reported that cobalt in CoAPO-5 and CoAPO-11 framework can change its oxidation states between +2 and +3 reversibly [4], whilst some authors

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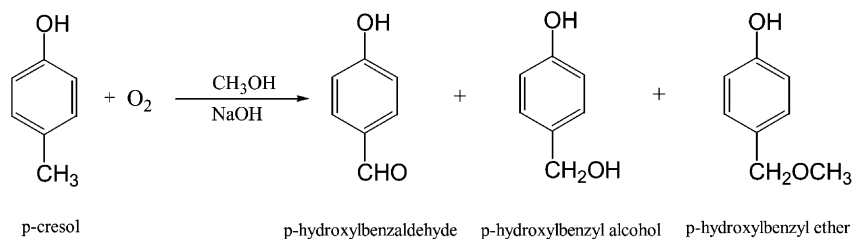


Fig. 1. *p*-Cresol autoxidation catalyzed by cobalt salts in basic condition.

expressed the opinion that framework cobalt exists only as Co(II) and undergoes distortion in the tetrahedral environment upon calcination [5]. Despite the controversy regarding the oxidation states of cobalt in ALPO structures, it is well accepted now that CoAPO molecular sieves act as carrier for oxygen [6]. In fact, *p*-cresol oxidation in liquid phase was reported using CoAPO-5 and CoAPO-11 as heterogeneous catalysts earlier [7]. CoCuAlCO₃ hydroxalcite-like compounds [8] and Co–salen complex immobilized on zeolite Y [9] were also attempted as heterogeneous catalysts for *p*-cresol oxidation.

p-Cresol oxidation can, in principle, also be conducted in a biphasic organic–aqueous interfacial mode [10] in which an aqueous solution and a relatively innocuous organic liquid immiscible with the aqueous phase are used to dissolve the catalyst and reactant, respectively. Here, a surface-active complexing agent or ligand can be used to draw the catalyst to the organic–aqueous interface where it effects the desired reaction. An emulsifier is used to promote phase dispersion and to increase the contact area for the reaction. The catalyst complex can be easily recovered in a compact emulsion layer positioned between the organic and aqueous phases upon standing. Potential benefits of the organic–aqueous biphasic reaction scheme have been demonstrated in autoxidation [11], oxidative coupling [12], and carbonylation [13] reactions.

In this work, autoxidation of *p*-cresol to *p*-hydroxy benzaldehyde was conducted at 60 °C, atmospheric pressure using three methods: (1) assumed heterogeneous reaction using CoAPO-5 catalyst; (2) homogeneous reaction using CoBr₂ salt catalyst; and (3) biphasic organic–aqueous interfacial reaction using Co complex catalyst in the presence of a surface-active ligand, to make a comparison between different

reaction modes. It is noteworthy that CoAPO-5 was prepared by microwave heating of the substrate gel mixture with a substantial reduction in synthesis time [14] in comparison with the conventional hydrothermal synthesis; we report here its crystallization kinetics and characterization.

2. Experimental

2.1. CoAPO-5 preparation and characterization

The synthesis gels for CoAPO-5 were prepared following the patent procedure of Wilson and Flanigen [15]. A 10.5 g of H₃PO₄ (85%, Oriental Chemical Industries) was added under vigorous stirring to a solution of 6.0 g pseudo-boehmite (Pural SB, 75.1 wt.%, Condea Chemie) and 25 g of distilled water. A solution of Co(NO₃)₂·6H₂O (97%, Duksan Pharmaceutical Co.) in 14.3 g of distilled water was added to the gel, and then 6.92 g of triethylamine (99%, Aldrich) was added slowly. Final substrate composition was as follows: 1.5Et₃N: (1 – *x*/2) Al₂O₃:1.0P₂O₅:*x*CoO:50H₂O, 0.01 < *x* < 0.06. The hydrothermal synthesis was carried out in a convection oven over a period of 48 h at 200 °C in a teflon-lined SS autoclave. Alternatively, 20 g of the gel was placed in a polytetrafluoroethylene (PTFE) autoclave, sealed, and placed in the microwave oven. The microwave equipment employed was a CEM MDS-2100 model equipped with a fiber optic temperature and pressure controller as well as an adjustable power output (maximum 950 W at 2450 MHz). The synthesis batch was quickly heated (2–4 °C/s, 950 W) to 180–190 °C within 3 min and was kept at this temperature for 1 h under reduced power (400 W). The solid products obtained were separated by filtration, washed several

times using distilled water, dried at 100 °C overnight, and finally calcined at 500 °C for 6 h. The crystallinity of the samples prepared was measured by X-ray diffraction using Ni-filtered Cu K α radiation (Philips, PW-1700), and the morphology of the samples was examined by SEM (Hitachi, X-650). UV–VIS diffuse reflectance spectroscopy was performed on a Varian CARY 3E double beam spectrometer and dehydrated MgO as a reference in the range of 190–750 nm.

2.2. *p*-Cresol autoxidation reaction

A reaction mixture consisting of *p*-cresol (9 g, 83.4 mmol), sodium hydroxide (10.08 g, 252 mmol) and methanol (27 ml) was placed in a 250 ml three neck flask reactor connected to a condenser. The reactor was placed in the constant temperature water bath and purged with oxygen for about 10 min and allowed to equilibrate to the set temperature of 60 °C. After introducing CoAPO-5 (500 mg), reaction was initiated with vigorous mechanical stirring (1200 rpm) in constant oxygen pressure of 1 atm for 6 h. Oxygen consumed was monitored using a constant pressure gas burette to which the reactor is hooked up. The experimental apparatus used in this work is similar to that employed in our earlier study [11]. After reaction was completed, methanol was distilled off, and dilute hydrochloric acid was added to the reaction mixture for neutralization and the residue was extracted with ethyl acetate. The product was analyzed using a Shimadzu GC-14A gas chromatograph equipped with a CPB-20 capillary column and a FID. Homogeneous reaction was performed in an identical manner using CoBr₂ (182 mg) as catalyst in methanol. For biphasic organic/aqueous reaction, an organic solvent with dissolved *p*-cresol and distilled water containing NaOH (10.08 g) at a fixed volume ratio of 1:1 were placed into a reactor. Surfactant and a suitable ligand were introduced, purged for 10 min with oxygen, and cobalt source was added. After repeating oxygen purge, reaction is commenced by mechanical stirring. Upon completion of reaction, the content of the reactor was poured to a separating funnel. The catalyst complex was found mostly in a compact emulsion layer between the organic and aqueous phases. The easy of catalyst recovery arises from the surface activity of the catalyst complex aided by surfactant and the

ability of the biphasic reaction mixture to phase-separate upon standing. Product analysis of the organic layer was conducted as mentioned above.

3. Results and discussion

3.1. Microwave synthesis of CoAPO-5

CoAPO-5 was prepared using two different hydrothermal synthesis methods of conventional oven heating and microwave heating using a gel with identical composition of 1.5Et₃N: (1 - x)/2 Al₂O₃:1.0P₂O₅: x CoO:50H₂O, 0.01 < x < 0.06. ALPO₄-5 without cobalt in the framework was also prepared for comparison. Fig. 2 shows the XRD patterns of CoAPO-5 prepared by microwave heating of the synthesis gel mixture, which essentially showed identical diffraction patterns to AlPO₄-5 with AFI structure. As shown in the crystallization kinetics curves of CoAPO-5 in Fig. 3, a highly crystalline CoAPO-5 was obtained in microwave heating at 180–190 °C in 40 min, an order of magnitude faster

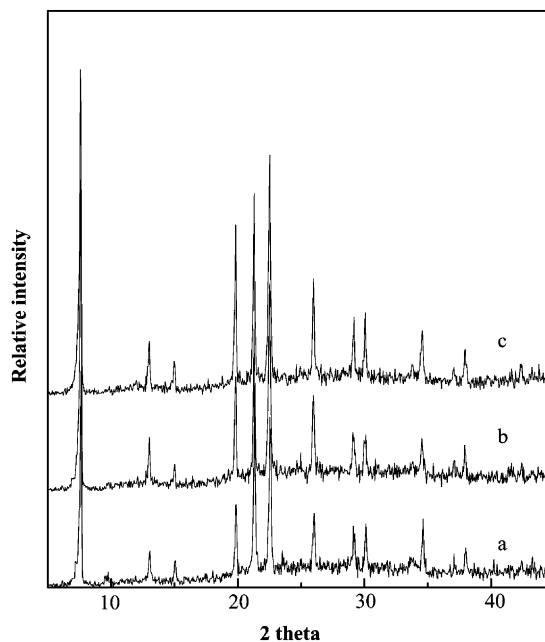


Fig. 2. XRD patterns of CoAPO-5 synthesized at 463 K under microwave heating: (a) 10 min; (b) 40 min; and (c) 60 min.

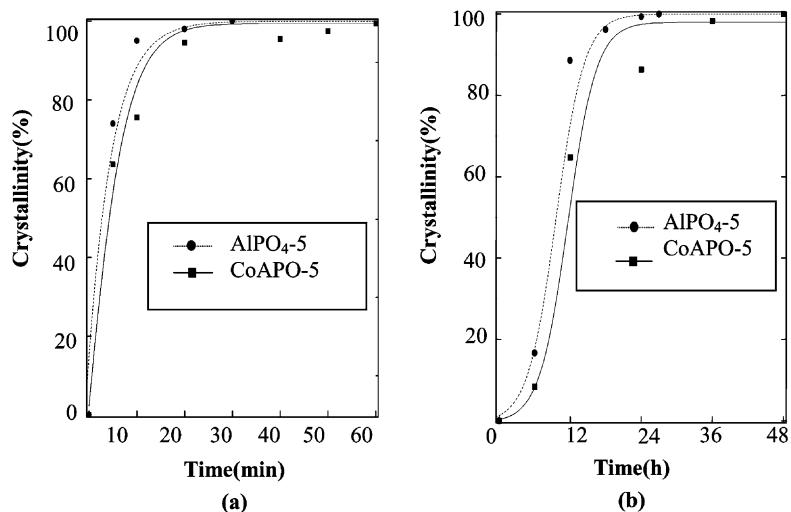


Fig. 3. Crystallization kinetics for CoAPO-5 prepared: (a) microwave heating; and (b) conventional oven heating.

than in conventional oven heating which took ca 36 h to obtain a comparable crystallinity. As is usually observed for the hydrothermal synthesis of zeolitic materials with isomorphously substituted hetero-atoms, the presence of cobalt retarded the crystallization of the AFI structure to some extent and CoAPO-5 crystallized slower than ALPO₄-5. Crystals were cylindrical with hexagonal shaped cross section and smaller (ca. 7.2 μm length after 40 min synthesis) and more uniformly distributed with microwave heating

than those obtained with conventional oven heating (ca. 14 μm in 48 h).

Incorporation of cobalt into the ALPO₄-5 framework was confirmed from the UV–VIS spectra shown in Fig. 4 for CoAPO-5 prepared by microwave heating. As expected, virtually identical spectra were obtained as with the samples from conventional oven heating. As-synthesized CoAPO-5 was blue in color and its UV–VIS spectra shows triplet peaks at 500–700 nm which is usually assigned to the characteristic

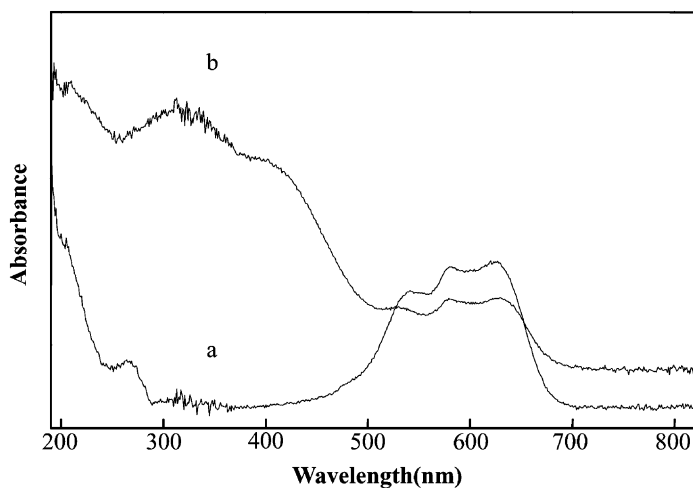


Fig. 4. UV–VIS diffuse reflectance spectra of CoAPO-5 by microwave heating: (a) as-synthesized; and (b) after calcined.

$^4A_2 \rightarrow ^4T_1(P)$ transition of high-spin Co(II) in tetrahedral coordination. Upon calcination, the sample turned green and the triplet peak diminished accompanied by the emergence of new peaks at 300–500 nm, which have been interpreted as a consequence of Co(II) oxidation to Co(III) [4,16]. It was also suggested that framework cobalt species exist as Co(II) ions only and the color changes during calcinations indicate only a distortion of the tetrahedral environment [5,17].

3.2. *p*-Cresol autoxidation in homogeneous and heterogeneous reaction modes

The standard set of reaction conditions for *p*-cresol autoxidation is listed in Table 1. First of all, several transition metal salts of Co, Cu, Cr, and Mn, which are commonly employed for oxidation reactions, were tested for their catalytic activity/selectivity in homogeneous *p*-cresol autoxidation. The oxygen uptake profiles are shown in Fig. 5, and the product distribution in Table 2. The total volume of

Table 1
Standard reaction condition for *p*-cresol autoxidation

Parameter	Specification	
	Homogeneous/ heterogeneous reaction	Biphasic reaction
<i>p</i> -Cresol	83.4 mmol	83.4 mmol
NaOH	252 mmol	252 mmol
Organic phase	Methanol 27 ml	2-Ethyl-1-hexanol, 30 ml
Aqueous phase	–	Water, 30 ml
Temperature	60 °C	60 °C
Reaction time	6 h	6 h
Stirring speed	1200 rpm	1200 rpm
O ₂ -pressure	1 atm	1 atm
Catalyst	CoBr ₂ , 0.834 mmol CoAPO-5, 500 mg	CoBr ₂ , 0.834 mmol
Ligand	–	DMEDA ^a , 0.04 M
Surfactant	–	DSS ^b , 0.004 M

^a *N,N'*-dimethylethylenediamine.

^b Dodecyl sodium sulfate.

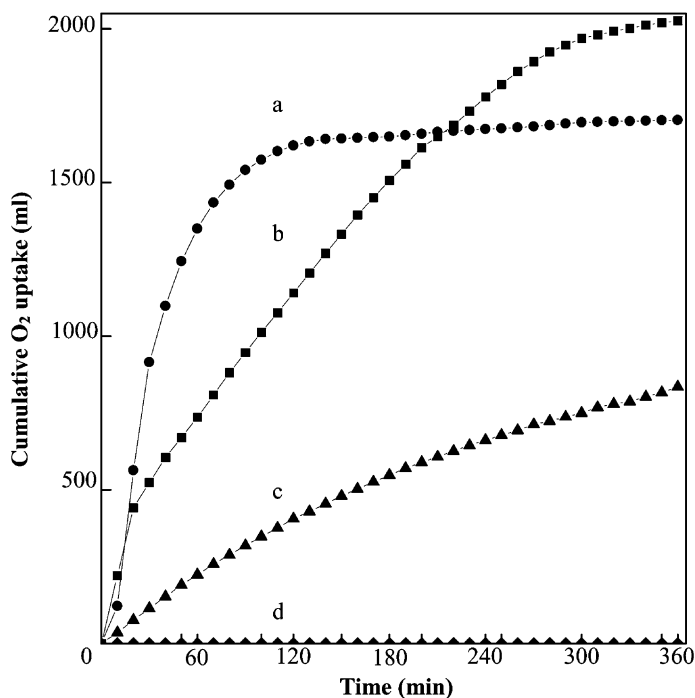


Fig. 5. Cumulative O₂ uptake profile of autoxidation of *p*-cresol using homogeneous catalysts: (a) CuCl; (b) CoBr₂; (c) CrCl₂; and (d) (OAc)₂Mn·4H₂O.

Table 2
O₂ selectivity, *p*-cresol conversion and selectivity to *p*-HBA

Catalysts	O ₂ selectivity (%)	<i>p</i> -Cresol conversion (%)	Product selectivity (%)			
			<i>p</i> -HBA ^a	<i>p</i> -HBAlc ^b	<i>p</i> -HBME ^c	Others
CoBr ₂	79.5	86.2	73.4	14.3	10.3	2.0
CuCl	8.9	8.1	5.2	47.3	36.8	10.7
CrCl ₂	70.9	31.7	49.3	32.8	9.4	8.5
CoAPO-5 ^d	83.9	82.6	73.5	15.1	9.6	1.8
CoAPO-5 ^e	85.4	64.0	63.3	18.4	15.7	2.6
CoAPO-5 ^f	82.6	45.4	62.6	19.7	14.8	2.9
CoAPO-5 ^g	82.1	81.3	74.4	14.1	9.4	2.1
CoAPO-5 ^h	80.9	66.1	62.0	19.1	16.5	2.4
CoAPO-5 ⁱ	82.5	49.1	60.7	20.6	15.5	3.2

^a *p*-Hydroxybenzaldehyde.

^b *p*-Hydroxybenzyl alcohol.

^c *p*-Hydroxybenzyl methyl ether.

^d Co/(Al + Co) = 0.06 (conventional heating).

^e Co/(Al + Co) = 0.04 (conventional heating).

^f Co/(Al + Co) = 0.01 (conventional heating).

^g Co/(Al + Co) = 0.06 (microwave heating).

^h Co/(Al + Co) = 0.04 (microwave heating).

ⁱ Co/(Al + Co) = 0.01 (microwave heating).

oxygen consumed after 6 h reaction decreased in the order CoBr₂ (2026 ml) > CuCl (1703 ml) > CrCl₂ (836 ml) with oxygen selectivity (*p*-cresol converted/total oxygen consumed) of CoBr₂ (79.5%) > CrCl₂ (70.9%) > CuCl (8.9%). Oxygen not involved in *p*-cresol oxidation was consumed in methanol solvent oxidation in the strongly alkaline environment [7]. (OAc)₂Mn·4H₂O was totally inactive. CoBr₂ showed far superior *p*-cresol conversion (86.2%) and selectivity (73.4%) to *p*-hydroxybenzaldehyde. By-products were *p*-hydroxybenzyl alcohol (14.3%), *p*-hydroxybenzyl methyl ether (10.3%) and a small amount of polymeric material (2%). Thus it is clearly established that cobalt is the appropriate transition metal for the *p*-hydroxybenzaldehyde synthesis among the transition metal salts tested. Cu contained in cobalt based hydrotalcite compounds was claimed as a promoter in *p*-cresol autoxidation [8].

Cobalt(II) in relatively high concentration can be easily inserted into aluminophosphate molecular sieves in tetrahedral coordination and redox properties of CoAPO-5 has been actively investigated [18–20]. In this study, CoAPO-5 molecular sieves were prepared by varying the cobalt content in the synthesis gel (Co/(Al + Co) = 0.01–0.06), using a microwave heating method. As shown in Table 2, 0.5 g of CoAPO-5

prepared from a gel with Co/(Al + Co) = 0.06 showed comparable catalytic performance to 0.834 mmol CoBr₂ in the homogeneous reaction. When applying 1.0 g of the same CoAPO-5, no further improvement was observed. *p*-Cresol conversion and selectivity to *p*-hydroxybenzaldehyde increase with the cobalt content up to Co/(Al + Co) = 0.06, while the oxygen selectivity remains 82–85% for CoAPO-5, which is somewhat higher than that obtained with CoBr₂. The catalytic performances summarized in Table 2 demonstrate that CoAPO-5 prepared by microwave heating was virtually identical to those prepared in conventional oven heating. These results indicate that microwave heating is a useful means to prepare transition metal containing molecular sieves in very short synthesis time with no detrimental effects on catalytic performances. For catalysts with excess cobalt contents, some hydroxide precipitation was observed in the highly alkaline reaction medium. Peeters et al. investigated *p*-cresol autoxidation using CoAPO-5 and CoAPO-11 and raised the problem of catalyst stability [7]. Accordingly, ICP analysis on the hot filtrate after reaction was conducted and the results are shown in Table 3. As can be seen substantial leaching of cobalt from the CoAPO-5 was detected and the higher the initial content of cobalt in the

Table 3
ICP analysis of filtered liquid after reaction

Catalyst	Cobalt/ <i>p</i> -cresol (mg/g) (initial) ^a	Percentage of metal dissolved (wt.% by ICP)
CoAPO-5 ^b	0.17	4
CoAPO-5 ^c	0.61	7
CoAPO-5 ^d	0.91	11

^a The initial ratio of cobalt (in the CoAPO-5) to *p*-cresol (reaction mixture).

^b Co/(Al + Co) = 0.01 (conventional heating).

^c Co/(Al + Co) = 0.04 (conventional heating).

^d Co/(Al + Co) = 0.06 (conventional heating).

catalyst, the more serious was the metal leaching. Thus the excellent catalytic performances of CoAPO-5 in *p*-cresol autoxidation will be mainly due to homogeneous catalysis. This conclusion is also reached [7]. Stability remains a serious problem for this catalyst. Cobalt–salen complex anchored to zeolite Y was recently claimed to be a stable and active heterogeneous catalyst for *p*-cresol reaction [9], but this conclusion was based on the limited UV–VIS spectroscopy data. We tested the cobalt–salen complex dissolved in the reaction medium and found only slightly improved conversion compared to CoBr₂. Cobalt–amine complex anchored onto the mesoporous silica MCM-41 was also prepared by us using the literature procedure [21] but, when applied to *p*-cresol autoxidation, substantial leaching was observed with inferior catalytic performance. Hydrotalcite containing cobalt was also

reported to be active in *p*-cresol autoxidation; despite the claimed stability, consecutive catalytic runs produced a conversion decrease from 84 to 60% [8].

3.3. *p*-Cresol autoxidation in biphasic reaction modes

Stability problem of cobalt-containing solid catalysts induced us to attempt an organic–aqueous biphasic reaction scheme, in which properly chosen surface-active ligand and a surfactant draw the catalyst to the interface where it effects the desired reaction. The biphasic system can provide convenient recovery of the catalyst, which exists as compact emulsion layer in the middle between the aqueous and organic phases. Since an organic phase immiscible to water is a prerequisite to implement the biphasic scheme, toluene, chloroform, and 2-ethyl-1-hexanol were tested as solvents for *p*-cresol. CoBr₂ was used as a cobalt source and various amphiphilic amine and phosphite ligand which were proved effective in earlier oxidation studies [11,12] were tested. The ligand to cobalt ratio was fixed at 2/1, and the organic/aqueous volume ratio to 1/1. Table 4 shows the results. Only with amine ligands such as DMEDA, TEPA, and TMEDA 3–5% *p*-cresol conversion was obtained with *p*-hydroxybenzyl alcohol being the major product, the rest being completely ineffective. Changing the ligand to catalyst ratio did not result in an improvement. As shown in Fig. 6, only ca. 200 ml oxygen consumption was measured in the biphasic scheme compared

Table 4
Ligand and solvent screening in the biphasic autoxidation of *p*-cresol

Ligand	Solvent	<i>p</i> -Cresol conversion (%)	Product selectivity (%)			
			<i>p</i> -HBA	<i>p</i> -HBA _{lc}	<i>p</i> -HBME	Others
DMEDA ^a	2-Ethyl-1-hexanol	4.0	8.0	52.6	29.0	10.4
DMEDA	Chloroform	Negligible	–	–	–	–
DMEDA	Toluene	Negligible	–	–	–	–
TEPA ^b	2-Ethyl-1-hexanol	3.0	2.0	66.1	19.1	12.8
TEPA	Chloroform	Negligible	–	–	–	–
TEPA	Toluene	Negligible	–	–	–	–
TMEDA ^c	2-Ethyl-1-hexanol	3.0	2.0	59.4	19.7	18.9
Ethylene diamine	2-Ethyl-1-hexanol	Negligible	–	–	–	–
Triethyl phosphite	2-Ethyl-1-hexanol	Negligible	–	–	–	–
Triphenyl phosphite	2-Ethyl-1-hexanol	Negligible	–	–	–	–

^a *N,N'*-dimethylethylenediamine.

^b Tetraethylenepentamine.

^c *N,N,N',N'*-tetramethylethylenediamine.

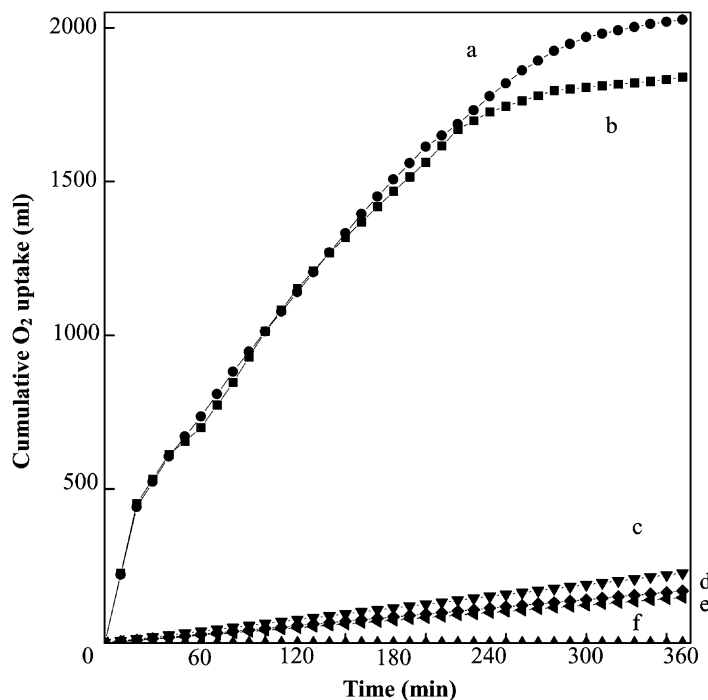


Fig. 6. Cumulative O₂ uptake profile of homogeneous, heterogeneous and biphasic reactions using a cobalt catalyst with different ligands: (a) homogeneous phase reaction using CoBr₂; (b) quasi-heterogeneous phase reaction using CoAPO-5; (c) biphasic reaction mode with DMEDA; (d) biphasic reaction mode with TEPA; (e) biphasic reaction mode with TMEDA; (f) biphasic reaction mode with ethylenediamine, triethyl phosphite or triphenyl phosphite (reaction conditions are the same as those specified in Table 1).

with ca. 2000 ml consumed in the homogeneous or quasi-heterogeneous systems. Since the most fundamental difference introduced in the biphasic reaction is the change in solvent, it was decided to investigate the solvent effect in *p*-cresol oxidation. According to the conversion/product selectivity shown in Table 5, overall performance for *p*-cresol oxidation in different

solvents followed the order methanol > ethanol > butanol in homologous series. On the other hand, little reaction took place in non-polar solvents such as chloroform or toluene, and in the long chain alcohol, 2-ethyl-1-hexanol. Therefore, it is clear that *p*-cresol oxidation is critically dependent on the selection of solvent. Methanol with high conversion (86.2%) and

Table 5
Solvents effect in *p*-cresol autoxidation using CoBr₂ (homogeneous)^a

Solvent	O ₂ selectivity (%)	<i>p</i> -Cresol conversion (%)	Product selectivity (%)			
			<i>p</i> -HBA	<i>p</i> -HBAlc	<i>p</i> -HBME	Others
Methanol	79.5	86.2	73.4	14.3	10.3	2.0
Ethanol	60.3	57.3	53.6	29.4	11.4	5.6
Butanol	62.9	54.9	50.3	25.7	15.9	8.1
2-Ethyl-1-hexanol	Negligible	–	–	–	–	–
Chloroform	Negligible	–	–	–	–	–
Toluene	Negligible	–	–	–	–	–

^a Reaction conditions are the same as those specified in Table 1, except for the solvent.

high *p*-hydroxybenzaldehyde selectivity (73.4%) appears to be the solvent of choice for *p*-cresol oxidation reaction, which prevents the application of organic-water biphasic reaction scheme in this case.

4. Conclusions

Autoxidation of *p*-cresol to *p*-hydroxybenzaldehyde was conducted at 60 °C, atmospheric pressure using (1) quasi-heterogeneous reaction using CoAPO-5 catalyst; (2) homogeneous reaction using CoBr₂ salt; and (3) biphasic organic–aqueous interfacial reaction using Co complex catalysts together with a surfactant. At the outset, it was clearly established that Co is the most active and selective catalytic species among the transition metal salts tested. High quality CoAPO-5 molecular sieve could be prepared very efficiently using microwave heating method with no detrimental side effects in catalytic performance for *p*-cresol autoxidation. However, strongly basic reaction medium for the reaction resulted in serious metal leaching from CoAPO-5, which leads to the conclusion that mainly homogeneous catalysis is involved. *p*-Cresol autoxidation reaction was found to be strongly governed by the solvent used and the overall performance followed the order methanol > ethanol > butanol, all miscible with water. Little reaction took place in non-polar solvents such as chloroform or toluene, and in the long chain alcohol, 2-ethyl-1-hexanol. Consequently, attempted organic–aqueous biphasic *p*-cresol autoxidation resulted in poor performance due to the water-immiscible organic solvent employed.

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