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Metal Substituted Aluminophosphate Molecular Sieves as Phenol Hydroxylation Catalysts

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Abstract

Substitution of transition metals for either aluminum and /or phosphorus in the $AlPO_4$-11 framework is found to afford novel heterogeneous catalysts for liquid phase hydroxylation of phenol with hydrogen peroxide. $AlPO_4$-11 is more active than SAPO-11 and MgAPO-11 for phenol conversion to hydroquinone. The Bronsted acid sites of SAPO-11 and MgAPO-11 may promote the decomposition of hydrogen peroxide to water and oxygen, thus leading to lower phenol conversions. Substitution of divalent and trivalent metal cations, such as Fe, Co and Mn appears to significantly improve the conversion of phenol. The activity follows the order of FeAPO-11>FeMnAPO-11>CoAPO-11>MnAPO-11>>$ALPO_4$-11. FeAPO-11, FeMnAPO-11 and $AlPO_4$-11 give similar product selectivities of about 1:1 hydroquinone (HQ) to catechol (CT). MnAPO-11 and CoAPO-11 favor the production of catechol, particularly at low conversions. FeAPO-11 and TS-1 (titanium silicate with MFI topology) are comparable for the phenol conversions with TS-1 giving higher selectivities toward hydroquinone. The external surfaces of the catalysts palys a significant role in these oxidation reactions. MeAPO molecular sieves may be complementary to the metal silicalite catalysts for the catalytic oxidations in the manufacture of fine chemicals.

Key words: metal-aluminophosphates, MeAPOs, TS-1, hydrogen peroxide, phenol hydroxylation, hydroquinone, catechol

Introduction

In the continual effort to transform fine chemical production to more environmentally acceptable technologies, metal-containing aluminophosphate molecular sieves offers tremendous potential as catalysts for heterogenous oxidation in the production of these chemicals. This follows from the significant advancement in the field of heterogenous catalysis by molecular sieves, resulting from the synthesis of the titanium-containing silicate (TS-1) by Italian researchers.[1,2,3] This catalyst has proven to be very effective in a wide range of catalyic oxidation reactions of industrial importance, such as, epoxidation of alkenes, oxidation of alcohols, and hydrocarbons, caprolactam synthesis and hydroxylation of aromatics.

The success TS-1 established the precedence for other redox metal-containing molecular sieves to be used in such heterogenous catalytic reactions. One such group of materials is the metal substituted aluminophosphates (MeAPOs).[4] These materials were synthesized following their earlier counterparts, the pure aluminophosphates ($AlPO_4$).[5] They are formed from the isomorphous substitution of aluminium for di- or trivalent metals in the framework of aluminophosphate molecular sieves. Substitution of metal cations with redox properties such as Fe, Co and Mn may be expected to afford novel heterogenous catalysts for liquid phase oxidation reactions. The framework phosphorus in $AlPO_4$s can also be substituted with vanadium[6,7], another redox metal, to give vanadium-containing molecular sieves (VAPOs). Though tremendous progress has been achieved in their preparation, and though they have demonstrated promising "oxidizing potential", surprising little has been done in exploiting their catalytic potential in oxidation reactions.

Sheldon and coworkers found that CoAPO-11 and CoAPO-5 are both effective, stable, and recyclable solid catalysts in the facile oxidation (with O_2) of p-cresol to p-hydroxybenzaldehyde at 50°C, with conversion and selectivity both reaching 90%.[8,9] The superior performance of the catalysts over homogenous cobalt salt was attributed to the fact that unlike the cobalt salt, CoAPO cannot form μ -hydroxo bridged cobalt dimers. In other reports, Lin et al.[10] showed CoAPO-5 to be an active and moderate catalyst for the autoxidation of cyclohexane in acetic acid. At 30-40% conversion, selectivities to adipic acid was up to 45 %. The oxidation of saturated hydrocarbons involving CoAPO molecular sieves has also been demonstrated by Kraushaar-Czarnetzki et al.[11] The redox properties of the catalyst was related to the ability of the framework Co to change between the Co(II) and Co(III) oxidation states.

Sheldon and coworkers investigated also, the catalytic behavior of a variety of redox MeAPOs in liquid phase oxidations with O_2 and tetrabutylhydroperoxide (TBHP), examples of which include: the oxidation of alkanes, alkylaromatic, alcohols and the epoxidation or oxidative cleavage of olefins with TBHP. They reported for example, that CAPO-5 is as excellent, recyclable, solid catalyst for the oxidation of secondary alcohols to the corresponding ketones using TBHP or O_2 as the terminal oxidant.[12] Chen et al. reported that CAPO-5 was an active, stable and selective catalyst in the decomposition of cyclohexyl hydroperoxide towards cyclohexanone, benzylic oxidations and the (auto)-oxidation of secondary alcohols with TBHP and O_2.[13] VAPO-5 and VAPO-11 were both demonstrated by other researchers, to catalyze oxidations, such as epoxidation of allylic alcohols analagous to homogenous vanadium salts[7,14] and benzylic oxidations with TBHP and oxygen.[7]

In this paper wish to show that the MeAPO are active catalysts for the hyroxylation of phenol with hydrogen peroxide.

Experimental

Synthesis of MeAPOs: Synthetic procedures were according to those of Flanigen and co-workers.[4] Phosphoric acid (Fisher,85 %) was the source of phosphorus. Metal acetates (Fisher) were sources of Co, Mn and Mg, while ferric sulfate (Aldrich) was source of Fe. Aluminum source was either aluminum isopropoxide (Aldrich) or Catapal B (Vista Chemical Co.) and the source of silicon was Ludox HS 40 (Dupont). Organic amines (R) were obtained form Aldrich. These were as follows: diethylethanolamine for MgAPO-5 and CoAPO-5, di-n-propylamine for MgAPO-11and CoAPO-50, diisopropylamine for CoAPO-11 and FeAPO-11, tripropylamnie for MAPO-36. With the exception of AlPO-11, SAPO-11 and FeAPO-11, the general molar composition of the reaction mixtures were: R:0.167MeO:0.917Al_2O_3:P_2O_5: 0.33AcOH:5.5 C_3H_7OH:50H_2O:50 H_2O. For FeAPO-11, the iron content of the reaction mixture was varied according to Table 4. The synthesis mixtures were heated in Teflon-lined autoclaves at temperature between 150°C and 200°C and times between 24 hours and 168 hours, following which, the autoclaves were water quenched, the solid product filtered, washed with distilled water and dried in air overnight. All samples were chararacterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and chemical analysis by ICP or AA to monitor crystallinity, particle size, crystal morphology and chemical composition. XRD patterns, which were recorded on a Philips X'PERT Difractometer using Cu k_α radiation and nickel filters, showed each sample to be of high crystallinity. A sample of TS-1 was obtained from Ueitkon, (Switzerland).

Catalytic testing: Hydroxylation reactions were performed in a stirred 250 mL round bottom flask fitted with a water cooled condenser. Reactions were done under atmospheric pressure , and temperatures were between ambient and 353 K. Typically, 0.2 g of calcined molecular sieve powder, 45 ml of water, a known weight of phenol (Aldrich) and a known quantity of 30% hydrogen peroxide (Fisher) was added to the reaction flask. The reaction was heated to desired temperature and the progress of the reaction was monitored as a function of time. Reaction products were analyzed by means of gas chromatography.

Results and Discussion

Table 1 shows the performance of CoAPOs of various topologies for the hydroxylation of phenol. The order of activity observed was CoAPO-11 >> CoAPO-50 > CoAPO-36 = CoAPO-5. The much higher activity observed for CoAPO-11 is not readily explained by a pore size effect. CoAPO-11 is a medium pore material with free pore diameter of 6.3 nm x 3.9 nm while the later three materials, CoAPO-50, -11 and -36 are large pore MeAPOs with free pore diameters of 0.61 nm, 0.75 nm and 0.80 nm respectively. Diffusion of the reactants in the smaller pores of CoAPO-11 due to reactant selectivity, is more likely to be slower than in the larger pore materials. This could rationally result in a lower percentage coversion of phenol. On the contrary, for the catalytic reaction, CoAPO-11 was used in the uncalcined form, with little or no pore access, resulting from the entrapment of the organic amine, while the other materials were fully calcined. This therefore strongly indicates that active sites on the external surfaces of the catalysts play a significant role in the phenol conversion reaction. The lower activities observed for the other materials, may be a result of deterioration in the their physicochemical properties following calcination. Changes such as reduced crystallinity, development of acidity and loss of catalytically active framework metal cations are all possible. Clearly, further characterization studies needs to be done, and this is the subject of another study.[15] CoAPO-36 and -50 both showed higher selectivity than CoAPO-11, for hydroquinone formation.

The relatively high activity demonstrated by CoAPO-11 prompted further catalytic investigation of the $AlPO_4$-11 structure type. Table 2 shows a comparison of the catalytic performance in the conversion of phenol for a range of MeAPO-11. $AlPO_4$-11 showed a higher activity and selectivity than both SAPO-11 and MgAPO-11 for hydroquinone formation. This may be related to the competing hydrogen peroxide decomposition reaction, brought about by the high concentration of Bronsted acidities in both SAPO-11 and MeAPO-11 compared to $ALPO_4$-11, resulting in a lower conversion of phenol for the later two molecular sieve. This problem of the role acidity in oxidation reactions has been previously highlighted in the use of Ti (IV) - silicates containing Al(III) or Fe (III) in the epoxidation of propylene.[3] The acidity associated with the trivalent elements, resulted in a much lower conversion to the epoxide, compared with the pure Ti-silicate (TS-1). FeAPO-11 and TS-1 are comparable for the phenol conversions with TS-1 giving higher selectivities toward hydroquinone.

As with the case of Co, substitution of framework aluminum by other transition metal cations, such as Fe, and Mn appears to significantly improve the conversion of phenol (Table 2 and 3). The activity follow the order of FeAPO-11 > FeMnAPO-11 > CoAPO-11 > MnAPO-11 >> $AlPO_4$-11. FeAPO-11, FeMnAPO-11, and $AlPO_4$-11 give similar product selectivities of about 1:1 hydroquinone to catechol whereas MnAPO-11 and CoAPO-11 favor the production of catechol, particularly at low conversions. Like the case of uncalcined CoAPO-11 discussed earlier, uncalcined FeMnAPO-11 also show high conversions and selectivities for the conversion of phenol to hydroquinone and here again the significance of external surface reaction is indicated.

Optimization of reaction conditions were carried out for FeAPO-11. Table 4 shows that with increasing amount of iron in the FeAPO-11 synthesis mixture, a disproportionately small increase in phenol conversion was observed, from 10.8 % in the original sample to 12.1 % for a sample containing a 10 fold increase in iron concentration, with selectivity to hyroquinone reduced. Phenol conversion was also shown to increase with increase in reaction time for 1, 3, and 5 hours. The progress of the reaction as a function of time was monitored at increasing concentration of hydrogen peroxide. Table 5 showed that by increasing the amount of peroxide from 2 g to 8 g, a steady increase in the phenol conversion was observed form 8 % to 38.4 %. Conversely the selectivity towards hydroquinone was reduced.

Further studies are being conducted on the physicochemical properties of these catalysts to provide a better understanding of their performance in this oxidation reaction.

Conclusion

MeAPOs have demonstrated significant catalytic acitivities for the liquid phase hydroxylation of phenol with hydrogen peroxide. Substituion of divalent and trivalent metal cations, such as Fe, Co, and Mn appears to significantly improve the levels of conversion, while the presence of Bronsted acid sites may cause hydrogen peroxide decomposition. The external surface of these catalysts appears to play a significant role in their catalytic activity. FeAPO-11 and TS-1 are comparable for the phenol coversions with TS-1 giving higher selectivities. MeAPO molecular sieves may be complementary to the metal silicalite catalysts for the catalytic oxidations in the manufacture of fine chemicals.

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Table1: Hydroxylation of phenol over CoAPOs

Catalyst	*Phenol conv. %	CT sel. %	HQ sel. %
CoAPO-5	6.0	62.7	37.3
CoAPO-11	25.5	56.0	44.0
CoAPO-36	6.5	36.2	63.8
CoAPO-50	9.2	39.6	60.4

* 0.2g catalyst, 2g (21 mmole) phenol, 2 g (18 mmole) 30% hydrogen peroxide, 45 mL water @ 80°C, 15h

Table 2: Hydroxylation of phenol over $AlPO_4$-11

Catalyst	*Phenol conv. %	CT sel. %	HQ sel. %
FeAPO-11**	26.2	51.1	48.9
ALPO-11	11.5	44.1	55.8
SAPO-11	7.2	52.2	47.8
MgAPO-11	7.3	75.8	24.2

** calcined @ 550°C for 8 hrs in N_2, 4-hrs in air

* 0.2g catalyst, 2g (21 mmole) phenol, 2 g (18 mmole) 30% hydrogen peroxide, 45 mL water @ 80°C, 15h.

Table 3: Summary of hydroxylation of phenol over MeAPO-11

Catalyst	Time (h)	Phenol conv. %	CT sel (%)	HQ sel (%)
CoAPO-11[a)]	3	12.2	63.8	36.2
CoAPO-11[a)]	5	23.1	55.4	44.6
CoAPO-11[a)]	15	25.5	56.0	44.0
Mn-APO-11[b)]	3	5.6	70.7	29.3
Mn-APO-11[b)]	5	9.4	65.6	34.4
Mn-APO-11[b)]	15	14.7	58.1	41.9
FeMnAPO-11[a)]	3	16.2	48.8	51.2
FeMnAPO-11[a)]	5	24.4	48.9	51.1
FeMnAPO-11[a)]	15	19.2	54.3	45.7
FeAPO-11[c)]	3	25.0	52.1	47.9
FeAPO-11[c)]	5	24.4	48.9	51.1
FeAPO-11[c)]	15	26.2	51.1	48.9
TS-1	1	24.5	27.0	73.0
TS-1	3	27.1	30.7	69.3
TS-1	5	29.0	31.3	68.7

a) As synthesized
b) Calcined @ 550°C for 20 hrs
c) Calcined @ 550°C for 8 hrs in N_2, 4 hrs in air

Table 5: The effect of iron content of FeAPO-11 on phenol hydroxylation

Catalyst	Al/Fe in synthesis mixture	Reaction time (h)	*Phenol conv. %	SEL CT	SEL HQ
CI121494C	216.5	1	8.2	39.2	60.8
		3	12.4	39.9	60.1
		5	15.1	42.2	57.8
CI120194C	38.4	1	10.2	38.1	61.9
		3	11.9	39.8	60.2
		5	16.3	44.2	55.9
CI120694C	19.3	1	10.8	39.3	60.7
		3	11.9	38.6	61.4
		5	17.5	47.2	52.8

* 0.2g catalyst, 2g (21 mmole) phenol, 2 g (18 mmole) 30% hydrogen peroxide, 45 mL water @ 80°C, 5h.

Table 6: **The effect of hydrogen peroxide concentration on hydroxylation of phenol with FeAPO-11**

H_2O_2 wt. (g)	Reation time (h)	*Phenol conv. %	CT SEL. %	HQ SEL. %
2	1	0.00	0.00	0.00
	3	0.00	0.00	0.00
	5	8.17	35.2	64.8
4	1	0.00	0.00	0.00
	3	21.7	48.4	51.6
	5	22.7	48.2	51.8
6	1	0.00	0.00	0.00
	3	30.9	50.7	49.3
	5	31.1	50.1	50.0
8	1	0.00	0.00	0.00
	3	37.2	50.8	49.2
	5	38.4	52.0	48.1

* 0.2g catalyst, 2g (21 mmole) phenol, 45 mL water @ 80°C.