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Chromia Modified Sol-gel Titania as Catalysts for Wet Peroxide Oxidation of Phenol

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Abstract

Wet peroxide oxidation of phenol was carried out over chromia modified sol-gel titania. An added advantage of this method is the removal of phenol from waste water effluents. The influence of solvent, reaction temperature, reaction time, catalyst amount and the molar ratio of phenol to hydrogen peroxide were investigated intensively. An initial induction period is noticed in all the cases. A thorough study on the reaction variables suggests free radical mechanism of the reaction. Physico-chemical characterizations of the prepared systems were done using powder XRD, EDX, BET surface area-pore volume measurements and TG-DTG analysis.

Introduction

The development of ecologically friendly technologies is currently one of the most important goals in industrial chemistry research. This is especially true in the field of oxidation of organic compounds, where there is an urgent need to replace highly effective but wasteful and toxic stoichiometric oxidants. A possible solution to this problem consists in using technology based on catalytic oxygen transfer from "clean" oxygen donors, such as hydrogen peroxide (H_2O_2). Organic compounds such as phenols and phenolic derivatives are amongst the most common chemicals found in regular commercial manufacturing processes. On account of their poor biodegradability, these compounds form a major threat to the ecological balance. Wet peroxide oxidation with hydrogen peroxide can bring about removal of phenol from effluents. Water is the only bye product formed and the oxidant is inexpensive. Also, aqueous hydrogen peroxide is a stable reagent, provided it is handled and stored in the proper manner [1]. The selective oxidation of phenol to industrially useful diphenols forms a convenient route to their efficient disposal. Catechol and hydroquinone are two of the many phenolic derivatives of high value. They are widely used as photography chemicals, antioxidants and polymerization inhibitors and are also used in pesticides, flavoring agents, and in medicine [2].

Mineral acids [3-5], simple metal ions [6-7] and metal complexes [8] are the traditional catalysts for this reaction, but these homogeneous catalysts are difficult to be separated and recovered from the reaction mixture, which prevents their practical utilization in phenol hydroxylation. Therefore, heterogeneous catalysis over various metal oxides and complexes, such as metal oxides or supported ones [9-11], metal complex oxides [12-13], zeolite encapsulated metal complexes [14] and hydrotalcite like compounds [15-16] have been of great interest to many researchers for a long time. Ning Zhang *et al.* [17] investigated the catalytic performance of naturally occurring ferritin for the selective hydroxylation of phenol with hydrogen peroxide. Coordination polymers based on bridging methylene blue have potential catalytic activity for the liquid phase hydroxylation of phenol [18]. Iron containing pillared clays are found to be efficient catalysts for phenol hydroxylation reaction where the presence of redox centers in the layers or in the galleries of the materials, together with a Bronsted acid environment in the galleries of the pillared clays induces the hydroxylation of phenol reaching conversions close

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to 70% under microwave irradiation even at low reaction time [19].

Titania has gained much attention in catalysis research due to its applications as a catalyst or catalyst support for metal or metal oxide catalysts used in heterogeneous catalysis including photocatalysis of industrially and environmentally important reactions. It is well established that the efficiency of the supported chromia catalysts mainly depends on the dispersion of active phase, which in turn can be greatly influenced by the nature of the supported oxide and the method of preparation of the catalysts. Anatase form of titania is found to be catalytically more active than the rutile form [20] and so studies are focused on the enhancement of anatase phase stability by various means. The synthesis of metallic oxides by the sol-gel process is presently a widely accepted method for the preparation of such materials. The advantages of this low temperature process include better purity and homogeneity. In the present investigation, we report the preparation of chromia incorporated titania and its characterization by X-Ray diffraction, EDX analysis, TG-DTG analysis and surface area – pore volume measurements. Here we report the use of titania as well as chromia modified titania systems for the hydroxylation of phenol with an emphasize given to the important variables affecting the phenol conversion and product selectivity.

Experimental

Preparation of Chromia Modified Titania Catalyst Systems

The catalyst systems reported in the present study have been prepared through sol-gel route from metatitanic acid precursor. Titanyl sulphate is obtained by dissolving the precursor in concentrated sulphuric acid. Ammonia is added to this until complete precipitation of titanium hydroxide occurs. The sulphate freed precipitate is suspended in hot water and 10% HNO_3 was added drop wise until a stable sol is obtained at a pH of around 1.5. Appropriate amount of Chromium nitrate is added to the sol before gelation. The dried composite gel was calcined at 500°C to get the catalyst powder.

Catalyst Characterization

XRD patterns of the samples were recorded between 10 and 70° 2θ on a Rigaku D-max C X-ray diffractometer using Ni filtered Cu K_α radiation source (λ = 1.5406 Å). The BET surface area and pore volume measurements were carried out by nitrogen adsorption at 77 K using a Micromeritics Gemini-2360 surface area analyzer. The precalcined samples were outgassed for 4 hrs at 400°C in nitrogen atmosphere prior to the sorption measurement. Thermogravimetric analysis between room temperature and 800°C were carried out in nitrogen atmosphere with a ramp of 20° min^{-1} using a TGAQ V2.34 thermal analyzer (TA instrument make). EDX spectra of the samples were recorded in an EDX-JEM-35 instrument (JEOL Co. link system AN-1000 Si-Li detector).

Catalytic Reactions

Catalytic experiments were carried out in a 50 ml round bottom flask equipped with a reflux condenser, a magnetic stirrer and a temperature controllable oil bath. The catalyst to be studied was added to it and the reaction was considered to begin. For a typical run, 0.1 gm of the catalyst, 1mmol phenol, 5 mmol hydrogen peroxide as oxidant and 5 ml water as solvent were stirred vigorously at 60°C for 2 hrs. The reaction mixture was then stirred at controlled temperature. The reaction products were analyzed at stipulated time using a gas chromatograph. The products of the hydroxylation of phenol over the prepared catalysts were catechol, hydroquinone and *p*-benzoquinone owing to a successive oxidation of hydroquinone. Hydroquinone was obtained as the major product over the prepared systems.

Results and Discussion

Catalyst Characterization

The surface area and pore volume of the prepared systems are given in Table 1. The surface area of titania prepared in this route has a surface area of 79 m^2/g. A slight decrease in the surface area is observed when 2% of chromium is incorporated to titania. The incorporated chromium ions are occupying the pores of titania which is very clear from decrease in the pore volume values. XRD profiles of titania and chromia incorporated titania systems are shown in Fig. 1. After calcination at 500°C, the anatase phase appears as evidenced by its 101 peak (2θ = 25.5°) [21]. The anatase phase is stable in all the prepared systems. There is no peak corresponding to chromia, indicating efficient dispersion of the incorporated metal. The average crystallite size was determined using Scherrer equation [22]. The intensity of XRD peaks of anatase for chromia modified systems were lower than those of pure TiO_2. The crystallite size calculated is in accordance with the BET surface area and pore volume results. As the percentage of metal increases, there is a decrease in crystallite size corresponding to an increase in surface area. These observations are in support of the generally accepted view that metal incorporation inhibits the sintering of titania and stabilizes the surface area.

Table 1

Surface parameters of the prepared systems

Systems	Elemental composition from EDX, %		BET surface area, $m^2•g^{-1}$	Pore volume, $\times10^{-6} m^3•g^{-1}$	Crystallite size, $\times10^{-9}$ m
	TiO_2, atom %	Cr, atom %			
Ti	100	0	79	0.11	8.6
$TiCr_2$	97	3	71	0.09	11.6
$TiCr_6$	91	9	102	0.24	7.4
$TiCr_{10}$	87	13	112	0.23	6.0

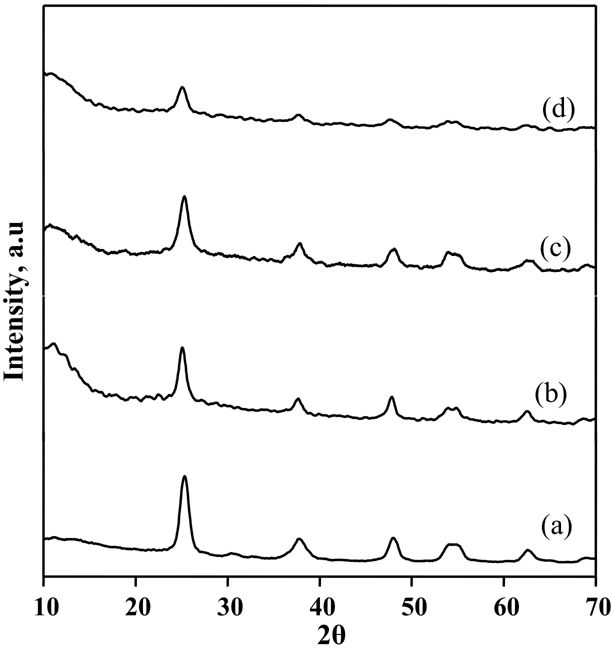

Fig. 1. X-ray diffraction profiles of (a) Ti, (b) $TiCr_2$, (c) $TiCr_6$ and (d) $TiCr_{10}$.

The elemental composition, as the atom percentage of the catalysts is also included in Table 1. From the EDX analysis, it is clear that the expected catalyst profile can be successfully achieved by the present preparation method since the amount of the metal in the samples were very close to the expected value. Thermogravimetric analysis of the samples heated under a flow of nitrogen can be seen in Fig. 2. The initial weight loss in the temperature range of 90-150°C is attributed to the removal of surface adsorbed water. Chromia modified systems exhibited a high thermal stability.

Influence of Catalyst

The reaction is done using phenol and hydrogen peroxide in water solvent in the absence of a catalyst (blank run) and in the presence of the catalyst

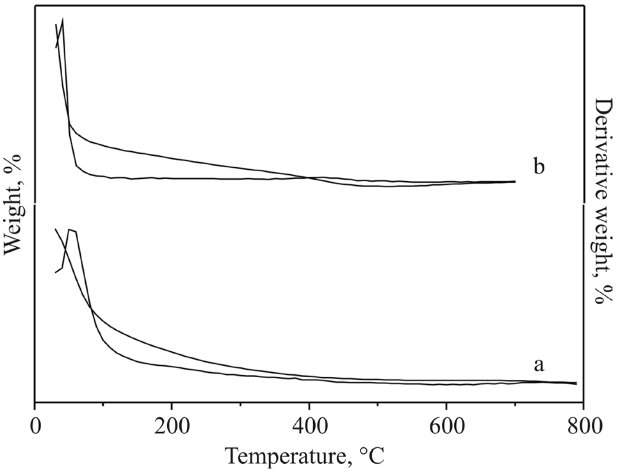

Fig. 2. TG/DTG profiles of (a) Ti and (b) $TiCr_6$.

(0.1 g $TiCr_6$) at 343 K. Catechol (*o*-diphenol), hydroquinone (*p*-diphenol) and benzoquinone were the major products of this reaction despite the different conditions and catalysts used. A percentage conversion of 1.4 and 50.2 after 2 hrs is obtained in the absence and presence of catalyst respectively. Low yield for the reaction in unanalyzed reaction is due to higher activation energy of the uncatalyzed reaction. Addition of the catalyst significantly reduced the activation energy and the reaction proceeded through a different mechanism, resulting in a higher percentage conversion.

Influence of Reaction Temperature

The activities and product selectivities in the temperature range of 50 to 80°C for phenol hydroxylation with H_2O_2 over $TiCr_6$ catalyst are presented in Table 2. Obviously phenol conversion increased when the reaction temperature increases from 50 to 60°C and when the temperature was above 60°C, there is a remarkable reduction in phenol conversion. At 50°C, phenol conversion was only 21.1% with a hydroquinone selectivity of 51.4%. When the temperature increased to 60°C, phenol conversion increased to 50.2% with hydroquinone selectivity of 61.0%. Considering both conversion and selectivity, the reaction temperature chosen for hydroxylation reaction was 60°C.

The decrease in phenol conversion with increase in reaction temperature is consistent with the exothermic nature of the reaction. The accelerated decomposition of H_2O_2 at elevated temperatures may also contribute to the drop off in the conversion. It has been reported that the activation energy for the decomposition of H_2O_2 is lower than that for the hydroxylation of phenol. Above 90°C, the amount of residual phenol in the reaction mixture was rather negligible. However, no peaks could be detected in the GC analysis corresponding to the products. This may be due to the over oxidation resulting in tarry products.

Influence of H_2O_2 to Phenol Ratio

The amount of oxidant used is an essential parameter for oxidation reactions. Table 3 summarizes the influence of molar ratio of hydrogen peroxide to phenol in phenol hydroxylation over $TiCr_6$ catalyst. The oxidant present even in trace quantities can bring about appreciable oxidation of phenols to diphenols. A larger molar ratio of hydrogen peroxide to phenol in the catalysis led to higher efficiency of utilization for H_2O_2. The phenol conversion first increases with the increase in the ratio to a certain extent and thereafter an increase in the H_2O_2 to phenol ratio causes a drastic reduction in the percentage conversion. The drastic reduction may be related to the over oxidation of phenol to tarry products at high peroxide concentration. The product selectivity is also influenced by the H_2O_2 to phenol molar ratio. At an optimum molar ratio of 5:1, the percentage selectivity is highest with a good product distribution.

Influence of Catalyst Weight

The catalyst amount required for maximum conversion of phenol was found out in the specified reaction conditions. The activities in phenol hydroxylation over $TiCr_6$ catalyst with different catalyst amounts are presented in Table 4. Hydroxylation occurs very slowly in the absence of a catalyst. Phenol conversion increased with a catalyst amount up to 0.1 g and then a further increase in catalyst amount decreases the phenol conversion. Addition of large amount of the catalyst to the reaction mixture had a negative effect in the prepared systems. This is because a larger amount of the catalyst hastened

Table 2

Influence of reaction temperature on phenol hydroxylation

(Amount of catalyst – 0.1g $TiCr_6$, Phenol:H_2O_2 = 1:5, Duration – 2 hrs)

Temperature, °C	Conversion, %	Selectivity, %		
		Catechol	Hydroquinone	Quinone
50	21.1	24.8	51.4	31.8
60	50.2	31.2	61.0	2.3
70	31.6	30.5	54.9	10.3
80	18.5	28.8	45.8	20.3

the decomposition of hydrogen peroxide. Optimum amount of the catalyst was fixed at 0.1 g.

Influence of Solvent

Selection of appropriate solvent is an essential requisite for any reaction. The right solvent was selected by examining the activity in different solvents of varying polarity. Table 5 presents the effect of solvent influence in phenol hydroxylation over $TiCr_6$ catalyst. When acetone is used as a solvent, the hydroxylation occur at a slower rate even at temperatures up to 70°C. Interestingly a change from organic solvents to water led to a significant increase in phenol conversion, indicating that water is the best solvent over the prepared systems. Water is safe, cheap and environmentally friendly solvent. However the amount of water strongly affected the phenol conversion and the product selectivity. At 60°C, the catalytic activity was in the order water > methanol > acetonitrile > acetone. The high activity in the aqueous medium can be recognized with strong adsorption of phenol on the catalyst in this solvent, which is driven by non ideality of water phenol system. At the same mole fraction, the calculated activity coefficient of phenol is much higher in water than in other solvents. When using organic solvents, their oxidation can be a competitive reaction system [23].

Table 3

Influence of H_2O_2 to phenol molar ratio on phenol hydroxylation

(Amount of catalyst – 0.1g $TiCr_6$, Temperature – 60°C, Duration – 2 hrs)

H_2O_2 to phenol ratio	Conversion, %	Selectivity, %		
		Catechol	Hydroquinone	Quinone
3:1	17.5	12.6	41.8	33.3
4:1	26.9	26.0	57.2	16.3
5:1	50.2	31.2	61.0	2.3
6:1	21.2	11.9	41.1	25.0
7:1	17.5	17.9	39.7	31.0

Table 4

Influence of catalyst weight on phenol hydroxylation

($TiCr_6$ catalyst, Temperature – 60°C, Phenol:H_2O_2 = 1:5, Duration – 2 hrs)

Catalyst weight, g	Conversion, %	Selectivity, %		
		Catechol	Hydroquinone	Quinone
0.05	19.8	17.3	7.1	75.6
0.10	50.2	31.2	61.0	2.3
0.15	45.6	22.1	31.2	40.8
0.2	34.79	16.5	25.1	58.4

Table 5

Influence of solvent on phenol hydroxylation

(0.1 g $TiCr_6$ catalyst, Temperature – 60°C, Phenol:H_2O_2 = 1:5, Duration – 2 hrs)

Solvent	Conversion, %	Selectivity, %		
		Catechol	Hydroquinone	Quinone
Acetone	1.2	42.4	45.8	12.1
Water	50.2	31.2	61.0	2.3
Methanol	38.3	7.9	39.7	41.0
Acetonitrile	24.8	30.5	44.9	20.3

Influence of Time

The effect of time on wet peroxide oxidation of phenol was studied over a range of 210 minutes. Figure 3 shows the time profiles of catalytic performances of pure titania and $TiCr_6$. Notably a relatively short reaction time resulted in incomplete conversion of phenol as well as undesirable product selectivity and the conversion increased with reaction time. There was an induction period of about 90 minutes where the systems gave marginal phenol conversions. After 90 minutes, a sharp rise was observed in the yield of diphenols. Suitably, a long reaction time was beneficial for the conversion of phenol, but its deep oxidation of hydroquinone into benzoquinone and of benzoquinone into tar could not be avoided after longer times. Therefore the reaction time of 120 minutes was suitable for phenol hydroxylation over the prepared systems.

Influence of Chromium Content

An attempt to investigate the influence of metal content on the catalytic activity is quite reasonable (Table 6). The proximity of the hydroxylating agent and of the substrate molecule on or near the active catalyst site is essential for driving the reaction. In water, both phenol and hydrogen peroxide dissolve simultaneously and approach the active center, thereby generating hydroxy radicals, which is proposed to be the active species involved in the hydroxylation reaction. Moreover such an electrophile is produced easily and stabilized in water than in organic solvents. Possibly, the lack of hydroxylated nature for the other organic solvents may be responsible for the non-occurrence of this reaction. Furthermore when this reaction is carried out using different oxidants other than hydrogen peroxide, namely oxygen, air and tert-butyl hydroperoxide, none of them hydroxylated phenol to a significant extent under similar reaction conditions, possibly due to the lack of generation of the active oxidant species and the solubility problems associated with the reactant and the oxidant.

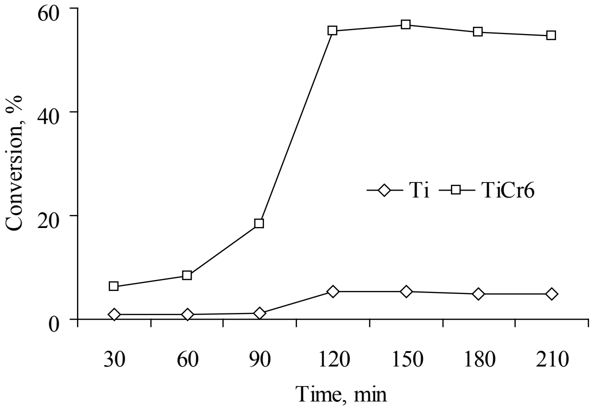

Fig. 3. Effect of time on stream on the percentage phenol conversion.

A heterogeneous-homogeneous reaction mechanism has been proposed for the liquid phase oxidation over solid catalysts. The appearance of an induction period and the exponential increase in the percentage conversion with time in the present study support the involvement of a free radical mechanism. The high susceptibility of the aromatic ring of phenols towards oxidation can be attributed to the possible generation of the delocalised aryloxy radical *via.* the removal of a hydrogen atom. The generation of phenoxy radicals may occur on the catalyst surface. At the same instant, catalyst surface can also trigger the homolytic cleavage of the hydrogen peroxide. The formation of catechol and hydroquinone is believed to occur *via.* the attack of $OH^{\bullet}$ on the benzene ring. The formation of phenoxy radicals occurs at the catalyst surface after which the propagation of the reaction can occur either in the liquid phase or

Table 6

Catalytic activity and product selectivity over the prepared systems
(0.1 g catalyst, Temperature – 60°C, Phenol:H_2O_2 = 1:5, Duration – 2 hrs)

Systems	Conversion, %	Selectivity, %		
		Catechol	Hydroquinone	Quinone
Ti	5.4	26.6	42.4	31.1
$TiCr_2$	43.6	33.9	43.6	13.4
$TiCr_6$	50.2	31.2	61.0	12.3
$TiCr_{10}$	53.5	21.4	56.9	16.4

on the catalyst surface. The proposed mechanism for this reaction is sketched in Fig. 4. The intermediates formed in the propagation step can lead to side reactions, forming polymerized products.

Pure titania gave very low conversion under the specified conditions and chromium incorporated systems are highly effective in hydroxylating phenol. But no strict correlation is obtained between the catalytic activity and the catalyst properties. In all the systems, the percentage phenol conversion increases with the metal loading. This supports the active involvement of the incorporated metal in the reaction. A combined influence of various factors like the surface area, crystallite size, redox properties and the electron accepting properties may be the driving force for the reaction.

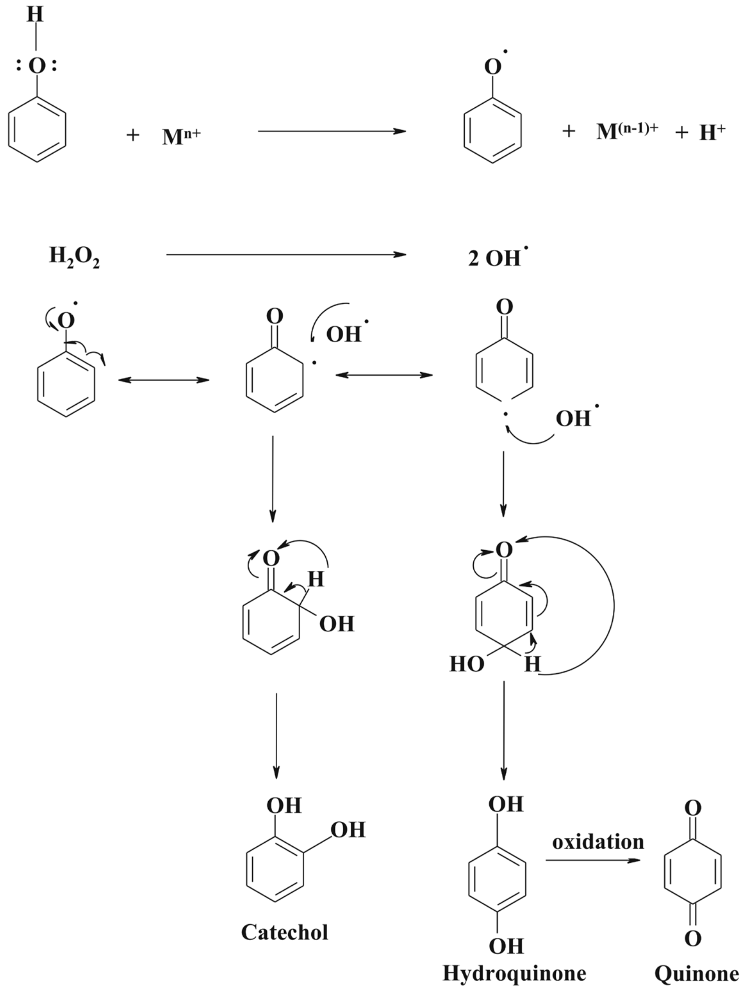

Fig. 4. Plausible mechanism for the hydroxylation of phenol with hydrogen peroxide.

Conclusions

Chromia modified titania systems were prepared through sol-gel route and its catalytic data showed their effectiveness towards phenol hydroxylation. The reaction seems to have a complex dependence on the nature and amount of the incorporated metal. The efficiency of the catalysts is closely related to the proper choice of the solvent, reaction temperature, reaction time, catalyst amount and the molar ratio of phenol to hydrogen peroxide. The performance of the prepared catalytic systems points to its potential use in the degradation of phenolic wastes. The enhanced anatase phase stability of the modified systems is an important consequence of chromia incorporation.

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