

Liquid phase oxidation of *p*-chlorotoluene to *p*-chlorobenzaldehyde over cobalt-doped mesoporous titania with a crystalline framework

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Abstract

Cobalt-doped mesoporous titania with a crystalline framework synthesized by surfactant templating method presented highly selective (99%) and reasonable conversion rate (49%) of catalytic oxidation of *para*-chlorotoluene to *para*-chlorobenzaldehyde in acetic acid using aqueous hydrogen peroxide as oxidant for the first time. Recycling of the catalyst indicates that the catalyst can be used a number of times without losing its activity to a greater extent. By contrast, cobalt-doped mesoporous titania without a crystalline structure and cobalt doped the commercial titania, Degussa P25 prepared by impregnation method with the similar concentration of cobalt were found inactive. The effects of catalyst concentration, reaction time, reaction temperature, and solvents on the performance of the catalyst were also investigated.

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1. Introduction

Highly selective oxidation *para*-chlorotoluene (PCT) to *para*-chlorobenzaldehyde (CBD) is an important reaction because CBD is a key intermediate in the synthesis of a variety of fine chemicals such as pharmaceutical drugs, dyes, optical brighteners, agricultural chemicals [1]. Traditionally, CBD was prepared by side-chain chlorination of PCT with subsequent hydrolysis of the benzyl chlorides formed [2]. It is also produced by the hydrogenation of *para*-chlorobenzonitrile [3]. In addition, several expensive and polluting processes with low conversion rate and selectivity are often employed when soluble acetates of transition metal catalysts are used in the industrial processes [4–7]. Since heterogeneous catalysts with significant advantages for recovery and stabilities are more desirable than the soluble catalysts, quite a few formulations have been investigated [8–10]. For example, using vanadium silicate molecular sieves as catalysts and under autogenous pressure, a selectivity of the order of >64.0% to CBD at 13.4 wt.% conversion of PCT with H₂O₂ was obtained [8,9]. However, it is still a major chal-

lenge to have a heterogeneous catalyst with >90% selectivity of CBD at >30% conversion of PCT in liquid phase.

Mesoporous titania materials are of considerable interest as they usually show higher surface areas and much more uniform and controllable pore size and pore morphologies compared with randomly organized forms of nanocrystalline titania [11–13]. Very recently, quite a few mesoporous TiO₂ with a crystalline framework were synthesized whereas the catalytic (except for photocatalytic) property of this material is seldom explored [13–19]. Moreover, nanosized iron oxide deposited into a mesoporous titania [20] and gold–vanadia catalysts supported on mesoporous titania [21] were used as catalysts for oxidation of cyclohexane and benzene, respectively. Recently, we synthesized cobalt-doped mesoporous TiO₂ with a crystalline framework (Co/MTiO₂) and demonstrated that it is an efficient catalyst for the oxidation of cyclohexane to cyclohexanol and cyclohexanone under mild conditions [22]. Therefore, it was suggested a good possibility to apply transition metal doped mesoporous titania with crystalline framework for the first time as a catalyst for the selective oxidation of PCT. Contrary to using mesoporous titania as just a support by impregnation method [20,21] in our study Co/MTiO₂ was prepared by cogellation method. On the other hand, cobalt-doped MCM-41 (Co-MCM-41) has been applied for a number of selective oxidation reactions, but

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its applications in the selective oxidation of PCT to CBD has not been exploited so far. Thus, Co-MCM-41 was also tested. Here, we report that Co/MTiO₂ prepared by templating method was highly selective with reasonable conversion rate of catalytic oxidation of PCT to CBD in acetic acid using aqueous H₂O₂ as oxidant for the first time.

2. Experimental methods

2.1. Synthesis of the catalysts

A detailed description of a process for synthesis of Co/MTiO₂ is available elsewhere [22]. The method for synthesis of Co-MCM-41 with Si/Co molar ratios of 40 was reported previously [23].

2.2. Characterization

The SEM micrographs of the calcined samples were obtained in an AMRAY 1000B. Transmission electron micrographs (TEM) of the Co/MTiO₂ samples recorded on a JEM-2010 Microscope with 100 kV of acceleration to probe the mesoporosity of the Co/MTiO₂ samples.

FT-IR measurements were performed on a Thermo Nicolet AVATAR FT-IR 360 instrument. Potassium bromide pellets containing 0.5% of the catalyst were used in FT-IR experiments and 125 scans were accumulated for each spectrum in transmission, at a spectral resolution of 4 cm⁻¹. The spectrum of dry KBr was taken for background subtraction.

2.3. Oxidation of PCT

The oxidation reactions of PCT were carried out at the atmospheric pressure as follows: the catalyst (0.20 g), PCT (5 ml) and 50 ml of solvent were used as received without further purification and added successively into a temperature-controlled, round bottom, three-necked-flask having a reflux condenser. The aqueous H₂O₂ (30%, approximate 10 ml) was added dropwise after the reaction mixture heated to the set temperature. Reaction mixture was filtered under reduced pressure after the set time. The residue was extracted with chloroform. Anhydrous MgSO₄ (AR) was used to remove more water from the extracted organic phase. Then, the mixture was filtered under reduced pressure and washed again by chloroform. The obtained products were analyzed by gas chromatography using a Thermo 3000 column (10% on Celite545, 1 m, thermal conductivity detector) and GC-MS (Finnigan GC800 TP/MS Voyager) using DB-5MS capillary column. Reference substances were used for the identification of the products.

3. Results and discussion

Using above preparing process, Co/MTiO₂ was grey yellow in color. In Ref. [22] it has been clearly indicated that the mesoporous structure of prepared material. The pore volume, average pore diameter and specific area were measured to be 0.22 cm³ g⁻¹, 10.8 nm, and 79.8 m² g⁻¹, respectively. It was

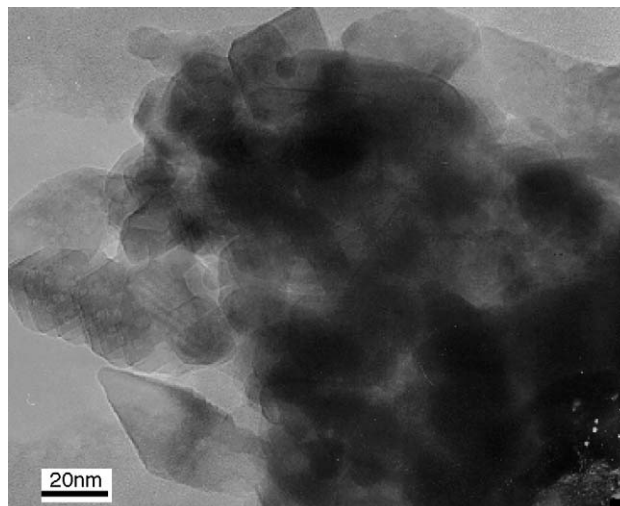


Fig. 1. TEM image of Co/MTiO₂.

also suggested that the cobalt-doped mesoporous titania have anatase crystalline phase and no peaks corresponding to cobalt oxides and cobalt titanate were observed by XRD measurement [22]. This indicates that our cobalt oxides were highly dispersed on the surface of the TiO₂, or were incorporated into the TiO₂ framework.

The crystallinity of anatase phase in the mesoporous wall is also observed from the HRTEM image of Co/MTiO₂ shown in Fig. 1. It can be seen that the formation of highly crystalline TiO₂ aggregates composed of three-dimensional disordered primary nanoparticles. The average size of the TiO₂ nanoparticles is approximately 20 nm, which is consistent with the crystallite size estimated from XRD analysis. Therefore, each particle observed by TEM analysis should be a single crystal.

Fig. 2 shows the morphology of Co/MTiO₂ samples by SEM. The Co/MTiO₂ powders show highly aggregated and non-uniform structure, resulting in the higher pore volume of the large inter-aggregated pores. The observation by SEM is in agreement with one by TEM.

Fig. 3 presents FTIR spectra of Co/MTiO₂. It is believed that the broad peaks at 3409 and 1632 cm⁻¹ can be attributed to the

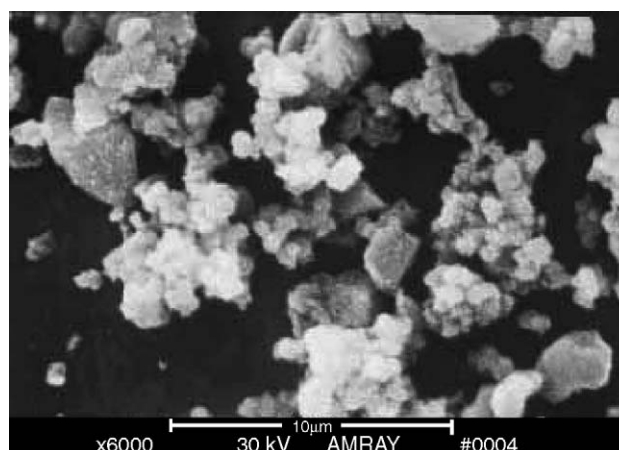
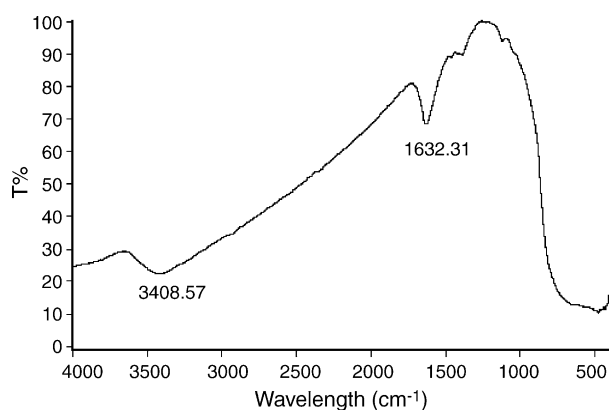


Fig. 2. SEM image of Co/MTiO₂.

Fig. 3. FT-IR spectrum of Co/MTiO₂.

surface-adsorbed water and hydroxyl groups [24–26]. The broad peaks in the range of 400–1000 cm⁻¹ are contribution from the anatase phase [24–27] which is consistent with the observation of XRD. No bands associated with residual dodecylamine are observed.

Oxidation reaction of PCT with the aqueous H₂O₂ using Co-MCM-41 and Co/MTiO₂ are depicted in Table 1. The catalysts are compared under similar conditions and found that only CBD and very small amount of *para*-chlorobenzoic acid (CBA) were detected, the other products, such as, 3-methyl-6-chlorophenol, 2-methyl-5-chlorophenol, hydroxyl chlorobenzyl alcohols, and hydroxyl chlorobenzaldehydes detected in Refs. [8,9] in which vanadium silicate was used as catalyst were not found in our systems. It is clear that these cobalt-doped catalysts exhibited very high selectivity for the oxidation of PCT to CBD.

Although Co-MCM-41 has much bigger surface area, 975 m²/g, it is much less active compared with Co/MTiO₂. This may imply that pore size would play more important role since the pore size of Co/MTiO₂ (10.8 nm) is much bigger than Co-MCM-41 whose pore size is 3.6 nm. And these results have revealed that Co/MTiO₂ has better performance.

Interestingly, the commercial titania, Degussa P25 impregnated with cobalt nitrate solution by maintaining the concentration of cobalt similar to Co/MTiO₂ did not exhibit any meaningful activity. This could be partly due to the lower dispersion of cobalt ions because most of cobalt ions would be dispersed on the surface of TiO₂ rather than in the framework of TiO₂

by impregnation. Other factors such as number of active sites, mixed anatase and rutile particles, lower amount of OH surface groups, decrease of crystallinity or existence of separated cobalt or mixed phases can also modify the efficiency [28]. More specifically, cobalt-doped mesoporous TiO₂ without a crystalline framework prepared by solvent extracting method to remove template other than by calcination was also found inactive and cobalt was easily leached. The observations that without crystallinity resulted in the loss of catalytic efficiency indicate that the crystallinity of the catalyst would be crucial for the oxidation of PCT.

On the other hand, we have also studied the oxidation of PCT using MTiO₂ without the incorporation of Co as a catalyst under the same conditions with those used for Co/MTiO₂. As expected, MTiO₂ did not exhibit any significant activity. Furthermore, if the amount of incorporating cobalt ions was decreased to only one-third of that we used, the conversion rate would drop to only about 2% but with a selectivity of 95%.

Due to the good performance of Co/MTiO₂, in the following we concentrate on the study of the influence of various parameters on the PCT conversion and selectivity of CBD over Co/MTiO₂.

We initiated a solvent screen to explore the effect of different solvents on the conversion of PCT and summarized in Table 2. It was found that Co/MTiO₂ catalyst had the best performance in acetic acid. In other solvents except for acetonitrile the catalyst did not exhibit any significant activities. Since only cobalt-doped mesoporous titania with crystalline framework can work efficiently, without cobalt and crystalline structure the material cannot work at all, it is suggested that the high catalytic activities of Co/MTiO₂ may be explained by the following reasons: firstly, those cobalt ions incorporated in the crystalline framework positions of Co/MTiO₂ during synthesis can impart dual catalytic activity to the catalyst and can form labile oxygen vacancies and the relatively high mobility of bulk oxygen species [29–31]. Secondly, Co-doped mesoporous materials still have monodispersed, single-pore distributed, huge pore volume and highly ordered mesoporous structures [22] which are excellent activity for catalysis. Thirdly, it has been reported that acetic acid does not only act as a solvent, but also serves as a good oxidizing agent because of the formation of the framework titanium-peracetic acid complex when it reacts with hydrogen peroxide in the presence of titanium-

Table 1
Comparison of catalytic activities of different catalysts for the oxidation of PCT to CBD

Catalysts	Conversion of PCT (%)	TON	Selectivity to CBD (%)	Selectivity to CBA (%)
Co-MCM-41	3	30	100	0
Co/MTiO ₂ (run 1)	49	168	99	1
First recycle (run 2)	44	152	99	1
Second recycle (run 3)	44	151	99	1
Third recycle (run 4)	44	152	99	1

Note: reaction conditions: 5 ml PCT; 0.20 g catalyst; 10 h reaction time; 10 ml H₂O₂ (30%); 50 ml acetic acid as solvent; 353 K for reaction temperature. TON, turnover number (millimole of oxidized products per millimole of cobalt in the catalyst).

Table 2
Influence of solvent on oxidation of PCD to CBD

Temperature (K)	Solvent (ml)	Conversion of PCT (%)	Selectivity to CBD (%)	Selectivity to CBA (%)
343	Solvent-free	0.1	43	57
338 ^a	Methanol (50)	0.2	22	78
353 ^a	Acetonitrile (50)	0.9	79	21
329 ^a	Acetone (50)	0	0	0
335 ^a	Chloroform (50)	<0.1	100	0
343	Acetic acid (50)	24	99	1

Note: reaction conditions: 5 ml PCT, 0.20 g catalyst, 10 h reaction time, and 10 ml H₂O₂ (30%).

^a The boiling point of solvent.

containing zeolites for the liquid phase oxidation of cyclohexane [32].

Similarly, the enhancement of oxidation PCT to CBD by using acetic acid as solvent also indicates that in our system, acetic acid and crystalline titanium framework did also play important roles. If peracetic acid instead of hydrogen peroxide was used in the solution, the selectivity of CBD and conversion of PCT decreased to 78% and 19%, respectively, whereas the selectivity of CBA was increased 22%. Therefore, a possible framework titanium-peracetic acid complex in our system would be different from the pure peracetic acid. This again suggests that the synergistic effects among doped cobalt ions, mesoporous framework of MTiO_2 , acetic acid and hydrogen peroxide make Co/MTiO_2 an effective catalyst for the oxidation of PCT under mild conditions.

Fig. 4 displays the effect of catalyst concentration on the conversion of PCT and selectivity of CBD over Co/MTiO_2 at 10 h by using acetic acid as solvent. An initial steep increase in the conversion of PCT and a slightly increase in selectivity of CBD were observed when the amount of the catalyst was increased up to 0.20 g. Beyond this amount, the conversion of PCT and selectivity of CBD leveled off in the reaction mixture. Therefore, 0.20 g would be the optimum catalyst amount used for the selectively producing CBD. These results indicate that in the system catalyzed by Co/MTiO_2 only small amount of catalyst is active in the oxidation of PCT at higher amount of catalyst. This also indicates that the amount of Co/MTiO_2 catalyst is possibly limited by H_2O_2 . This could be also attributed to the possible catalytic decomposition of H_2O_2 by Co/MTiO_2 and the competent interaction of metal oxo-species in Co/MTiO_2 sample with alkylperoxy species and PCT [31,33, 34].

The effect of reaction time on PCT reaction over Co/MTiO_2 was also investigated and depicted in Fig. 5. It is seen that the rate of PCT conversion increases with increase in reaction time up to 10 h while the selectivity of CBD changes little during this reaction time. The reaction time is longer than 10 h, the conversion of PCT leveled off whereas selectivity of CBD decreased a little which suggests that more CBA would be produced due to

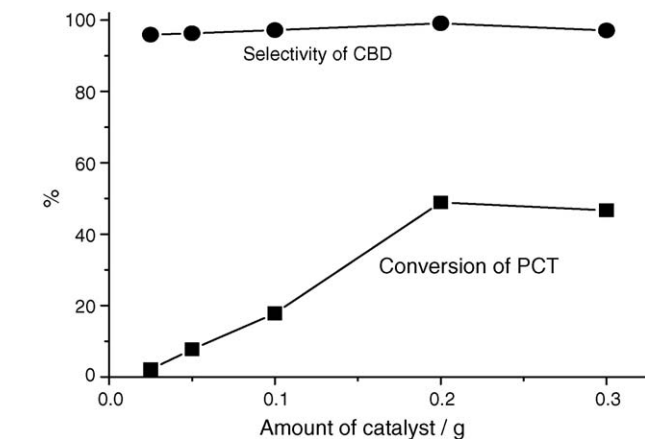


Fig. 4. Effect of catalyst concentration on the conversion and selectivity over Co/MTiO_2 (reaction conditions: reaction temperature, 353 K; reaction time, 10 h).

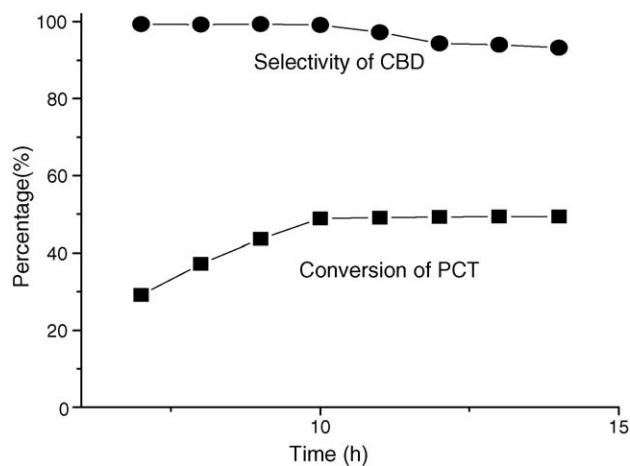


Fig. 5. Effect of reaction time on the conversion and selectivities over Co/MTiO_2 (reaction conditions: 50 ml acetic acid; 5 ml PCT; 10 ml H_2O_2 (30%); reaction temperature, 353 K; catalyst, 0.20 g).

the further reaction of CBD which was observed. Thus, 10 h is suitable reaction time.

The dependence of the conversion of PCT on the reaction temperature was investigated in the temperature range 343–373 K using over Co/MTiO_2 (Fig. 6). The conversion of PCT was found to increase with increase in reaction temperature and passed through a maximum at 353 K. A further increase in the reaction temperature resulted in the decrease in the conversion rate of PCT and selectivity of CBD, probably owing to a quicker decomposition of H_2O_2 at higher temperature. In addition, as mentioned previously, if peracetic acid instead of hydrogen peroxide was used in the solution, the selectivity of CBD and conversion of PCT decreased to 78% and 19%, respectively, whereas the selectivity of CBA was increased 22%. Therefore, at higher temperature, it is reasonable that the reaction of H_2O_2 with acetic acid will be also faster and it is speculated that more peracetic acid but less of the possible framework titanium-peracetic acid complex would be produced since peracetic acid is relatively more stable than H_2O_2 . Moreover, the possible framework titanium-peracetic acid complex would also

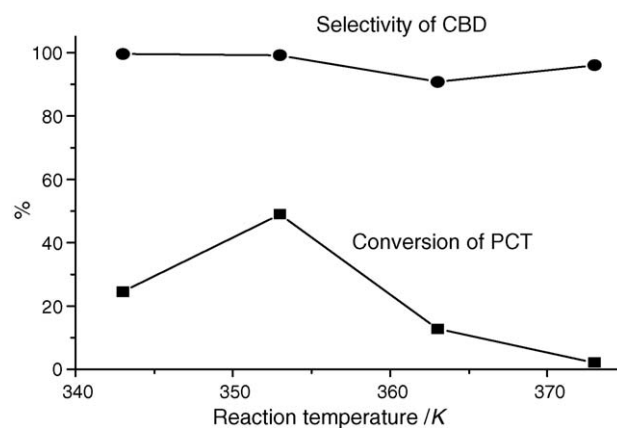


Fig. 6. Effect of reaction temperature on the conversion and selectivity over Co/MTiO_2 (reaction conditions: 50 ml acetic acid; 5 ml PCT; 10 ml H_2O_2 (30%); reaction temperature, 353 K; catalyst, 0.20 g; reaction time, 10 h).

decompose more quickly at higher temperature. These may be the main reasons for the decrease of conversion rate of PCT. At higher temperature, the slightly decrease of selectivity of CBD and the increase of selectivity of CBA is attributed to the further reaction of CBD.

Finally, to check the stability and recycling ability as well as leaching of cobalt ions from Co/MTiO₂ under reaction conditions, recycling experiments were carried out using acetic acid as solvent. The typical recycling procedure was as follows: after the initial reaction, the catalyst was separated from the reaction mixture and washed with acetone and dried at 363 K, followed by the activation at 673 K for 4 h. The reaction was then carried out on the activated recycled catalyst at 353 K under the optimum condition. The results are also summarized in Table 1. It was found that Co/MTiO₂ shows an immediate a little decrease of the activity after the first reaction cycle, and a 44% conversion of PCT and 99% selectivity of CBD were still obtained. However, after successive cycling (runs 2–4) of the catalyst, a minor change of catalytic activity was noticed. In order to check the structure of the catalyst after each reaction, XRD patterns were recorded and indicated that the catalyst retains the anatase structure. The present study indicates that the catalyst can be recycled a number of times without losing its activity to a greater extent.

4. Conclusions

In conclusion, cobalt-doped mesoporous titania with a crystalline framework synthesized by surfactant templating method presented highly selective (99%) and reasonable conversion rate (49%) of catalytic oxidation of PCT to CBD in acetic acid using aqueous hydrogen peroxide as oxidant for the first time. Recycling of the catalyst indicates that the catalyst can be used a number of times without losing its activity to a greater extent. By contrast, cobalt-doped mesoporous titania without a crystalline structure and cobalt doped the commercial titania, Degussa P25 prepared by impregnation method with the similar concentration of cobalt were found inactive. The synergistic effects among doping of cobalt, a crystalline framework of mesoporous TiO₂, acetic acid, and hydrogen peroxide make Co/MTiO₂ an effective catalyst for the oxidation of PCT to CBD under mild condition. Its applications in the selective oxidation of other similar compounds are underway.

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