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Selective Oxidation of 4-Tert-butyltoluene to 4-Tert-butylbenzaldehyde Over Co/MCM-41

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Abstract Selective oxidation of 4-tert-butyltoluene (TBT) to 4-tert-butylbenzaldehyde (TBBZ) and 4-methyl-acetophenone (MAP) is reported for the first time using aqueous hydrogen peroxide as oxidant and Co/MCM-41 as the catalyst under mild conditions for the first time. Co/MCM-41 presented reasonable selectivity (82%) of TBBZ with a conversion rate of 15% of TBT without any initiator. Under the suitable reaction conditions, Co/MCM-41 also presented reasonable selectivity (58%) of MAP with a conversion rate of 12% of the substrate. The catalysts can be reused once with almost the same activity.

Keywords Selective oxidation · 4-Tert-butyltoluene · 4-Tert-butylbenzaldehyde · 4-Methylacetophenone · Co/MCM-41

1 Introduction

4-tert-butylbenzaldehyde (TBBZ) is an important intermediate in production of Lilestral (BBA) or Lilial (Givaudan, Kingston, UK), which is an important fragrance compound used in large quantities in soap and cosmetic perfumes [1]. A number of methods were reported for the synthesis of this compound. Gerber et al. applied the cobalt(II) acetate–bromide catalyzed air oxidation system [2]. However, there was over oxidation to the benzoic acid which increased as the aldehyde accumulated. Bejan et al. have described electrochemical assisted air oxidation which increases the rate of the autoxidation reaction [3]. The end product of the oxidation is still the benzoic acid, but the aldehyde concentration can be maximized [4]. Jones et al. described the use of solid peroxygen sources, such as sodium perborate mono and tetra hydrate, or urea for selective oxidation of 4-tert-butyltoluene (TBT) to TBBZ catalyzed by cobalt acetate and bromide ion [5]. They found that sodium perborate monohydrate was more effective than aqueous hydrogen peroxide, and benzyl bromide was suggested as an important intermediate. Recently, Amin and Beattie reported the oxidation of TBT to TBBZ catalyzed by homogeneous catalyst-cobalt acetate and bromide in acetic acid using aqueous hydrogen peroxide as oxidant [6]. Contrary to that obtained by Jones et al. [5], they found that sodium perborate monohydrate was not more effective than aqueous hydrogen peroxide, and 4-tert-butylbromide was not an important intermediate. Moreover, Kostrab et al. reported the aerial oxidation of substituted aryl aromatic hydrocarbons using Co/Mn/Br^- catalyst system in water–dioxane medium [7]. Since the catalytic system employs homogeneous salts with significant disadvantages for separation, recovery, and stabilities, the above processes are still expensive, polluting, and risky. Therefore, heterogeneous catalysts with significant advantages for recovery and stabilities are more desirable. Chen et al. reported that in the vapor phase V–Cs–Cu–Tl/TiO_2·SiC catalysts were used in the partial oxidation of

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TBT to TBBZ [8]. Under the suitable reaction conditions, they were able to achieve a selectivity of 85 mol% with conversions of 12 mol% of the substrate. However, high temperature and high pressure were need. 4-Methylacetophenone (MAP) is used for blossom notes in mimosa and for the production of hawthorn type perfumes, especially in soap perfumes [9]. Conventionally, MAP is prepared from toluene and acetic anhydride or acetyl chloride [10, 11].

Well-ordered mesoporous materials are useful in catalysis for their unusual properties: monodispersed, single-pore distributed huge pore volume and highly ordered mesoporous structure [12–14]. Many studies about these kinds of materials were widely reported recently especially for their character of ease of use and environment friendly. For example, cobalt doped MCM-41(Co/MCM-41) has been used as efficient catalysts for the oxidation of diphenylmethane to benzophenone [13]. Ce/MCM-41 was used to catalyze cyclohexane to cyclohexanol [14]. But so far there is no report on using transition metal doped MCM-41 for the oxidation of TBT as we know. In this investigation, Fe/MCM-41, Co/MCM-41, and cobalt-doped mesoporous titania with anatase crystalline structure (Co/TiO_2) was used for the oxidation of TBT under mild condition. This seems to be the first production of TBBZ in this way.

2 Experimental

Transition metals M (Co, Fe) doped MCM-41 with Si/M ratio of 40 were prepared as described in the literatures [13, 14]. A detailed description of a process for synthesis of Co/TiO_2 is available elsewhere [15]. UV-vis diffuse reflectance spectra were measured at room temperature in air on a SHIMADZU UV-2401PC photometer over the range from 200 to 800 nm.

The oxidation reactions were carried out at the atmospheric pressure as follows: the catalyst (100 mg), TBT (AR, 2 g), and 30 mL of solvent (acetic acid, acetonitrile, acetone, methanol, dichloromethane, and ethanol) 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 H_2O_2 (30%, ~4 mL) was added drop wise after the reaction mixture heated to the set temperature. Reaction mixture was filtered under reduced pressure after the set time (10 h). The residue was extracted with chloroform. Anhydrous $MgSO_4$ (AR) was used to remove more water from the extracted organic phase. Then the mixture was filtered under reduced pressure and washed again by diethyl ether. The obtained products were analyzed by 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

The oxidation of TBT to TBBZ with the aqueous H_2O_2 over different catalysts is summarized in Table 1. Interestingly, Co/TiO_2 which is highly efficient catalyst for the selective oxidations of cyclohexane [15] and *p*-chlorotoluene [12] exhibited very low activity for the oxidation of TBT. In contrast, cobalt doped mesoporous Co/MCM-41 demonstrated very high activity for the oxidation of TBT. The difference between Co/MCM-41 and Co/TiO_2 implies that mesoporous silica is more suitable than mesoporous titania although both of them were doped the same cobalt ions. On the other hand, since the BET surface areas of Co/MCM-41 (BET surface areas = 991 m^2/g) is much bigger than that of Co/TiO_2 (BET surface areas = 79.8 m^2/g), whereas the pore size of Co/TiO_2 (10.8 nm) is much bigger than that of Co/MCM-41 whose pore size is 3.6 nm, this may imply that surface area would play more important role. However, the situation must be more complicated than a surface area phenomenon. It has been reported that the high-surface area, the extent of dispersion, and local structure of the metal oxides are beneficial for catalytic activity [16]. For example, Co/MCM-41 with Si/Co ratio of 20 exhibited much lower conversion rate and selectivity than that with Si/Co ratio of 40. The lower efficiency of Co/MCM-41 with Si/Co ratio of 20 for the oxidation of TBT, has been attributed partly to the lower dispersion of cobalt ions after the loadings of cobalt ions was increased. For further comparisons, we have also studied

Table 1 Summary of the oxidation of TBT

Entry	Catalyst	Solvent	Conversion of TBT (%)	Selectivity of TBBZ (%)
1	Co/MCM-41	Acetonitrile	2	44
2	Co/MCM-41	Dichloromethane	3	29
3	Co/MCM-41	Acetone	8	29
4	Co/MCM-41	Methanol	3	0.6
5	Co/MCM-41	Ethanol	2	4
6	Co/MCM-41	Acetic acid	15	82
7[a]	Co/MCM-41	Acetic acid	9	70
8	Fe/MCM-41	Acetic acid	1	53
9	MCM-41	Acetic acid	8	15
10	Co/TiO_2	Acetic acid	5	75

Reaction conditions: reaction temperature is the boiling point of solvents, except for acetic acid at 363 K; catalyst = 100 mg; reaction time = 4 h; 30 mL of solvent

[a] Si/Co ratio is 20

the oxidation of TBT using MCM-41 without the incorporation of Co as a catalyst under the same conditions with those used for Co/MCM-41. As expected, MCM-41 exhibited very low activity. Furthermore, even incorporating other metal ions, such as, Fe/MCM-41 prepared using the same procedure as Co/MCM-41, exhibited significantly lower activity than Co/MCM-41.

In order to find out the reasons for the differences among MCM-41, Co/MCM-41, Fe/MCM-41, and Co/TiO_2, their diffuse reflectance UV-vis spectra were measured and shown in Fig. 1. Because UV-vis spectroscopy was known to be a very sensitive probe for the identification and characterization of metal ion coordination and its existence in the framework and/or in the extra-framework position of metal containing zeolites [17]. Obviously, without transition metal, MCM-41 exhibits a negligible band above 220 nm. However, once MCM-41 has incorporated iron and cobalt, there is significant absorption over both the UV and visible range. Particularly, Co/MCM-41 exhibited a broad visible absorption band over 400 and 750 nm. While the absorption at 400 nm indicated the presence of Co^{3+}, the absorption around 600 nm can be attributed to the presence of both Co^{2+} and Co^{3+} [16, 18].

Fe/MCM-41 mainly exhibited a peak at *ca.* 265 nm, which was similar to that for ferrisilicate containing tetrahedrally coordinated iron species [19]. This band could be assigned to the $d\pi$–$p\pi$ charge transfer between the Fe and O atoms in the framework of Fe–O–Si in the zeolite [20]. A band with the maxima near 320 nm for Co/TiO_2 is attributed to the $O^{2-} \rightarrow Ti^{4+}$ [21]. Incorporation of cobalt resulted in a shoulder near 400 nm. It is evident that the absorption over 400 and 750 nm is different among these samples. In particular, even doped the same cobalt, Co/TiO_2–SiO_2 exhibited very weak absorption whereas Co/MCM-41 exhibited a significant peak in this range. Therefore, this suggests that the presence of both Co^{2+} and Co^{3+} would be beneficial for the oxidation of TBT.

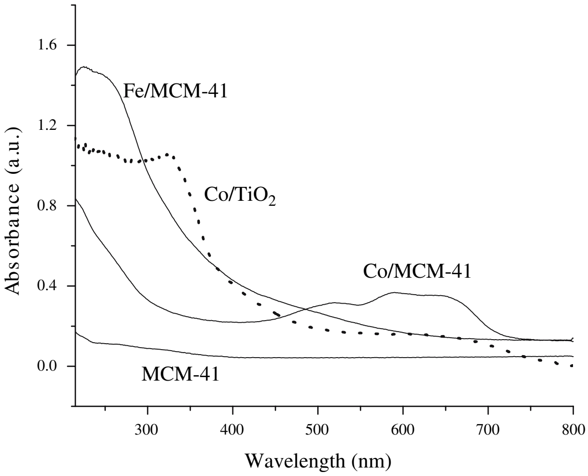


Fig. 1 Comparison of UV-vis diffuse reflectance spectra of MCM, Co/MCM-41, Fe/MCM-41, and Co/TiO_2

Therefore, in the following we concentrate on the study of the influence of various parameters on the activities of Co/MCM-41. Using Co/MCM-41 as catalyst, in acetic acid, TBBZ was obtained as the major product, TBBA, 4-tert-butylphenol and 4-tert-butyl benzyl alcohol are also detected. Interestingly, MAP that was not reported in previous studies for the oxidation of TBT was also observed. The formation of both TBBZ and MAP indicates that both methyl group and tert-butyl group of TBT can be oxidized.

The nature of solvents was known to have a major influence on reaction kinetics and product selectivity in the oxidation of TBT. Apparently, Co/MCM-41 catalyst has the best performance in acetic acid. The conversion of TBT and the selectivity of TBBZ is 15 and 82%, respectively. It shows that a significantly lower conversion was obtained in the case of methanol, acetone, acetonitrile, and dichloromethane. This may be due to the possible partial decomposition of hydrogen peroxide because the decomposition of hydrogen peroxide is faster in these solvents than in acetic acid [21]. The high efficiency of Co/MCM-41 may be explained by the following reasons: firstly, cobalt ions were incorporated in the framework positions of MCM-41 during synthesis [22]. Co presented in the framework structure of Co/MCM-41 can impart dual catalytic activity to the catalyst and can form labile oxygen vacancies and the relatively high mobility of bulk oxygen species [23–25]. Second, Co-doped mesoporous materials still have monodispersed, single-pore distributed, huge pore volume and highly ordered mesoporous structures which are excellent activity for catalysis [12]. Third, a complex with peroxy acetic acid was possibly formed in the pores of Co/MCM-41 which is relatively more hydrophobic and stable than hydrogen peroxide. Thus, acetic acid does not only act as a solvent, but also serves as a good oxidizing agent. In short, the synergistic affects among doped cobalt, mesoporous framework of MCM-41, acetic acid, and hydrogen peroxide make Co-MCM-41 an effective catalyst for the oxidation of TBT under mild conditions.

Figure 1 illustrates the conversion of TBT and the selectivity for the products as a function of the reaction temperature using Co/MCM-41 as the catalyst. It is clear that the conversion of TBT was found to increase slightly with increase in reaction temperature. The changes of selectivity with temperature are complicated: an initial steep decrease in the selectivity of TBBZ and TBBA was observed when the temperature was increased up to 343 K. Very interestingly, a further increase in the reaction temperature resulted in the steep increase of the selectivity of TBBZ whereas the selectivity of TBBA

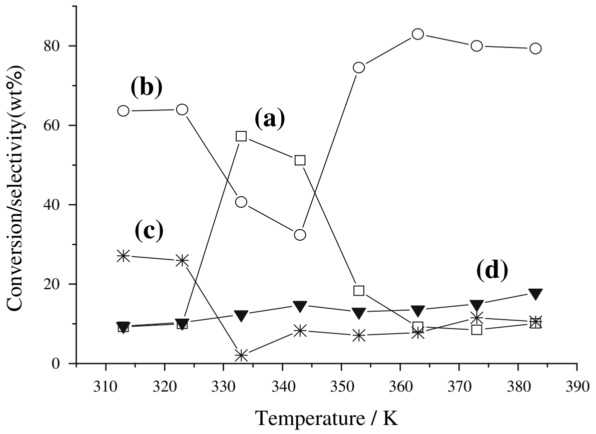


Fig. 2 Effect of reaction temperature on the catalytic activity of Co/MCM-41. (**a**) Selectivity of MAP; (**b**) selectivity of TBBZ; (**c**) selectivity of TBBA; (**d**) conversion of TBT

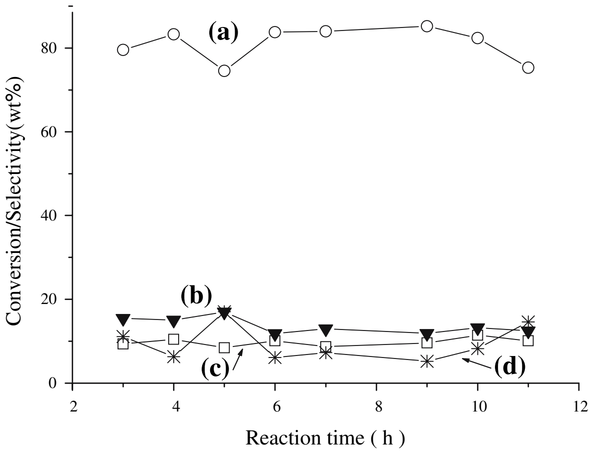


Fig. 3 Effect of reaction time on the conversion and selectivity over Co/MCM-41. (**a**) Selectivity of TBBZ; (**b**) conversion of TBT; (**c**) selectivity of MAP; (**d**) selectivity of TBBA (*reaction conditions*: substrate/oxidant, 0.77; reaction temperature, 363 K; catalyst, 100 mg; solvent, acetic acid)

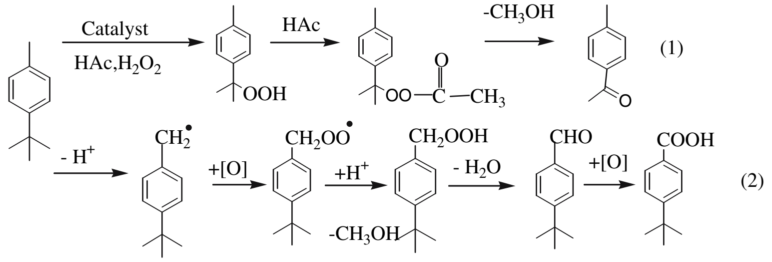
leveled off. In contrast, an initial steep increase of the selectivity of MAP before 343 K. Further increase temperatures lead to steep decrease. Since more MAP was produced than TBBZ between 330 and 345 K and the highest selectivity of TBBA was obtained at 363 K, 363 K would be optimum temperature for producing TBBZ. However, at 333 K the maximum selectivity of MAP with 58% and a conversion arte of 12% of TBT were obtained. This indicates that the production of MAP can be improved under suitable reaction temperature by using Co/MCM-41 as a catalyst.

The effect of reaction time on TBT reaction over Co/MCM-41 was also investigated and depicted in Fig. 2. It is seen that the selectivity of TBBZ fluctuated between 75 and 85% while the highest conversion of TBT and the highest selectivity of TBBA were both obtained at 5 h because with the increase of reaction time, most of H_2O_2 was decomposed and leading to the decrease of the conversion of TBT. Considering the effect of reaction time on both conversion of TBT and selectivity of TBBZ, 4 h would be an appropriate time for the oxidation of TBT. Interestingly, the selectivity of MAP changed little with the increase of the reaction time.

The effect of catalyst concentration on TBT reaction over Co/MCM-41 is shown in Fig. 3. There is little change in the selectivity of TBBZ with increase in catalyst concentration. The conversion of TBT fluctuated between about 11 and 17%. The highest conversion and selectivity was obtained when the amount of the catalyst was 60 mg, so 60 mg was the optimum amount of the catalyst. These results indicated that in the system catalyzed by Co/MCM-41 only small amount of catalyst is active in the oxidation of TBT at higher amount of catalyst, this also indicated that the amount of Co/MCM-41 catalyst is possibly limited by H_2O_2.

A possible mechanism to form the three major products is depicted in Scheme 1. Initially, one proton was released from the methyl group of TBT and followed the formation of superoxide. The thermal decomposition of this superoxide may yield TBBZ and methanol. Then, TBBA would be formed by the consecutive oxidation of TBBZ (path 2). The superoxide may also react with acetic acid to yield MAP (path 1). Based on this mechanism, as observed in Fig. 1, at higher temperature, more H_2O_2 would decompose, and less MAP (path 1) would be produced whereas more TBBZ would be produced. Moreover, the mechanism also indicated that the amount of Co/MCM-41 catalyst is possibly limited by H_2O_2 as discussed in Fig. 3.

Scheme 1 A possible mechanism for producing MAP, TBBZ, and TBBA



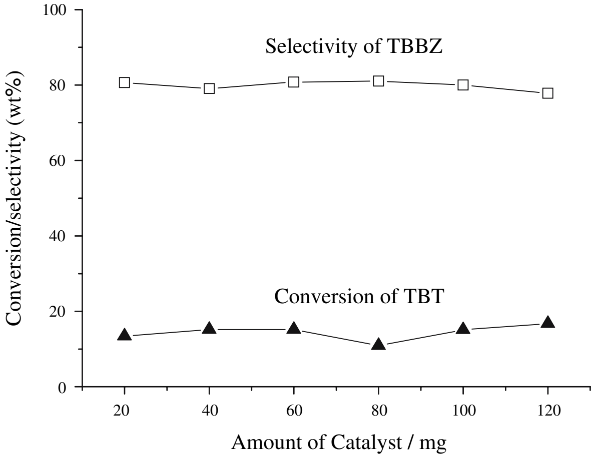


Fig. 4 Effect of catalyst concentration on the conversion of TBT and selectivity of TBBZ over Co/MCM-41

Finally, the Co/MCM-41 catalyst was also recycled to check its stability based on the following process: after the initial reaction, the catalyst was separated from the reaction mixture and was washed with acetone and dried at 363 K, followed by the activation at 673 K for 2 h. The reaction was then carried out on the recycled activated catalyst under the optimum conditions. It was found that the conversion of TBT was still nearly 15% and the selectivity of the target products decreased little. All these observations suggest that Co/MCM-41 is a stable and highly efficient catalyst for the TBT oxidation (Fig. 4).

4 Conclusions

In summary, Co/MCM-41 appears to be an efficient catalyst for the TBT oxidation. A high selectivity of TBBZ (82%) can be obtained at 363 K by using acetic acid as solvent. Under the suitable reaction conditions, Co/MCM-41 also presented reasonable selectivity (58%) of MAP with a conversion rate of 12% of the substrate. The catalyst can be reused once without losing the activity.

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