Highly Selective Oxidation of Diphenylmethane to Benzophenone over Co/MCM-41

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Highly selective formation of benzophenone (99.1%) from diphenylmethane is reported for the first time using H_2O_2 (30%) as an oxidant and Co/MCM-41 as the catalyst.

Benzophenone (BP) is an important intermediate for perfumes, photoinitiators, and pharmaceuticals. A number of methods were reported for the synthesis of this compound.[1–3] Particularly, the classical Friedel–Crafts acylation reactions[4–8] and the use of high oxidation state transition metals for diaryl methyl derivatives oxidation (e.g. CrO_3, $KMnO_4$)[9–11] are two well-known synthesis methods. These methods always need critical conditions, such as, high temperature, high pressure, and long time. Thus, these processes are still expensive, polluting, and risky. Moreover, the selectivity of product is poor, and the separation of reactants and products from the reaction mixture is difficult. It is, therefore, of great practical interest to develop a more efficient, easily separable, reusable, and environment-friendly catalyst for the production of aromatic ketones. To develop an environment-friendly/green process for the production of aromatic ketones, it is necessary to have a nontoxic and reusable solid catalyst, which shows high activity and selectivity in the oxidation of diphenylmethane to benzophenone and has no significant problem of leaching of its components in the liquid reaction mixture. It was reported that MnO_4^{-1}-exchanged Mg–Al–hydrotalcite has high activity and selectivity and also has an excellent stability and reusability for the oxidation of diphenylmethane (DPM).[12] Recently, more and more attention has been paid to the replacement of the traditional oxidant such as Cr(VI) compounds, $KMnO_4$, HNO_3, and so on by hydrogen peroxide as a green oxidant. Accordingly, the key problem of relevant research is to look for efficient catalysts that can activate but not decompose hydrogen peroxide.[12]

The well-ordered mesoporous materials have a good use in catalysis for their unusual properties: monodispersed, single-pore distributed, huge pore volume and highly ordered mesoporous structure.[13] Many studies about these kinds of materials were widely reported recently especially for their character of ease of use and environment friendly. Cr–MCM-41 or 48 have been employed as catalysts for the oxidation of ethylbenzene to acetophenone with oxygen.[14] But so far there is no report on using mesoporous materials for oxidation of DPM. On the other hand, the cobalt modified material has a better oxidation catalysis property.[8] Here, we report that cobalt doped MCM-41 (Co/MCM-41) is a highly selective (99.1%) catalyst for the direct oxidation of DPM to BP. We also found that this process produces 2-hydroxybenzophenone (2-HOBP) though very low selectivity. This seems to be the first report on the production of 2-HOBP in this way.

Co–MCM-41 was synthesized with a process modified from Ref. 15. A brief description of the procedure is as follows: 5.0 g of CTAB was added to 66 mL of solution containing 1.0 g of sodium hydroxide. Then, 20 mL of ethyl silicate was added to the mixture slowly until the solution became a clear gel. Finally, the cobalt precursor ($Co(NO_3)_2{\cdot}6H_2O$) was added to the above gel and stirred for an hour. The resulting gel was transferred into a Teflon bottle and treated under autogenous pressure without stirring at 363 K for 7 days. The final solid product was filtrated, dried, and calcined at 823 K for 24 h. The oxidation reactions were carried out at the atmospheric pressure as follows: The catalyst (100 mg), DPM (99%, 1 g) and acetic acid glacial (HAc, AR, 10, 30, or 50 mL) were used as received without further purification and added successively into a temperature-controlled, round bottom, 3-necked-flask having a reflux condenser. The aqueous H_2O_2 (30%, approximate 1–2 mL) was added dropwise after the reaction mixture was heated to the set temperature. Reaction mixture was filtered under reduced pressure after the set time. The residue was washed with acetic acid and extracted with chloroform (AR). Anhydrous $MgSO_4$ (AR) was used to remove the water from the extracted organic phase. Then, the mixture was filtered under reduced pressure and washed again with chloroform. The obtained products were analyzed by GC-MS (HP6890) with a HP 19091T-416 capillary column. Reference substances were used for the identification of the products.

The N_2 adsorption/desorption isotherms and XRD spectra of Co–MCM-41 are shown in Figure 1. The isotherm and XRD pattens clearly indicate the mesoporous structure of prepared samples. This is also supported by the high BET surface areas (1041 m^2/g), pore volume (0.73), and average pore diameter (2.8 nm).

Oxidation reaction of DPM with the aqueous H_2O_2 using Co/MCM-41 is summarized in Table 1. In this reaction, BP was obtained as the major product, 2-benzylphenol and 4-benzylphenol were also detected but not 3-hydroxy-benzophenone

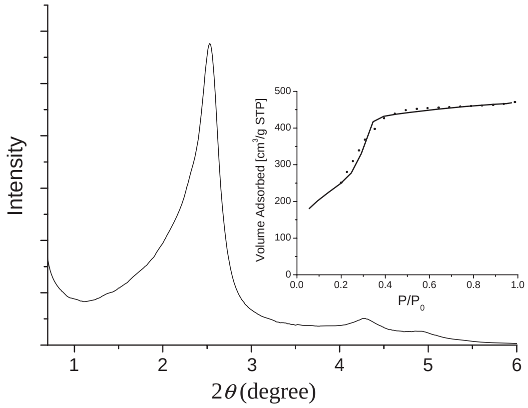


Figure 1. The XRD spectra N_2 and adsorption/desorption isotherms (Inset) of Co–MCM-41.

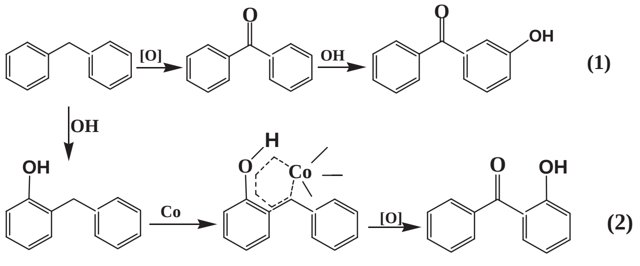
Table 1. Results of the oxidation of diphenylmethane[a]

Entry	Temperature /K	Reaction time/h	Conversion of DPM/%	Selectivity of BP/%
1	373	4	4.1	90.7
2	373	8	36.6	94.0
3	373	12	22.2	97.8
4	313	10	3.5	57.4
5	323	10	4.8	73.0
6	333	10	8.0	78.8
7	343	10	7.2	80.2
8	353	10	8.7	86.0
9	363	10	27.2	60.8
10[b]	363	11	15.8	78.1
11[c]	363	11	14.6	73.7
12[b]	373	11	23.3	99.1

[a]Reaction conditions: 1–2 mL 30% H_2O_2, 0.1 g Co/MCM-41. [b]30 mL HAc. [c]50 mL HAc; all others 10 mL HAc.

(3-HOBP) nor 4-hydroxybenzophenone (4-HOBP). Interestingly, 2-HOBP that was not reported in previous studies for the oxidation of DPM was also observed. Firstly, the effect of reaction time on the activities was investigated at 373 K that is close to the boiling point of acetic acid glacial. It was found that the conversion of DPM decreased, while the selectivity of BP increased a little, when reaction time increased from 8 to 12 h. Thus, the optimum reaction time would be between 8–12 h. These findings are not clearly understood yet, and further experiments are underway. Secondly, at 10 or 11 h, the effect of reaction temperature on the activities was studied. It is seen from Table 1 that the conversion of DPM increased with increase in reaction temperature and passed through a maximum at 363 K. But the highest selectivity was obtained at 373 K. At 373 K the selectivity of BP can be over 90% even when the reaction time and the amount of solvent are different. Thirdly, the effect of the solvent amount on the activities was examined at 363 K. It is clear that the selectivity of BP was significantly improved when the volume of HAC increased from 10 to 30 mL whereas the conversion of DPM decreased significantly. However, further increasing the amount of HAc to 50 mL does not change the activity significantly. Finally, we found that at 373 K, in 30 mL of HAc the highest selectivity of BP was 99.1% after 11 h reaction. At the optimum reaction condition, the efficiency of reacted H_2O_2 for the formation of BP was detected to be 13.7% with 98.2% total consumption of H_2O_2 by iodometric titration method. The low efficiency of reacted H_2O_2 may indicate that the H_2O_2 oxidized not only DPM, but also other complexes, such as a framework silica–peracetic acid complex, when HAc was used as solvent.[16,17]

The detection of 2-HOBP instead of 3-HOBP and 4-HOBP in the products indicates that the intermediate to form 2-HOBP was 2-benzylphenol (*o*-cresol, α-phenyl-) which was also detected in the products (path 2). If it were BP (path 1), there would have been 3-HOBP in the products, because the activity site of BP was *m*-site. It is also more reasonable that the aromatics were oxidized to benzylphenols first then further oxidized to aromatic ketones.[18] Therefore, the possible mechanism of the reaction about 2-HOBP is illustrated via the path 2 in Scheme 1.



Scheme 1. Possible mechanism of the product of 2-hydroxybenzophenone.

In summary, Co–MCM-41 appears to be an efficient catalyst for the synthesis of BP. A higher selectivity (99.1%) can be obtained at 373 K by using acetic acid as solvent.

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