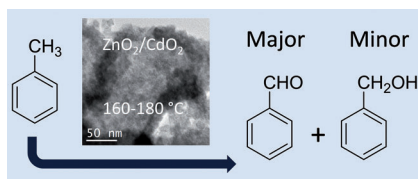


FULL PAPERS

A select few: CdO_2 and ZnO_2 nanoparticles decompose to yield oxygen and metal oxide below 200°C . Their use for the selective oxidation of the toluene CH_3 group to yield mainly benzaldehyde in a catalyst-free reaction is demonstrated (see figure).



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**Oxidation of Toluene and Other
Examples of C–H Bond Activation by
 CdO_2 and ZnO_2 Nanoparticles**



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Oxidation of Toluene and Other Examples of C–H Bond Activation by CdO₂ and ZnO₂ Nanoparticles

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Nanoparticles of CdO₂ and ZnO₂ are shown to oxidize toluene primarily to benzaldehyde in the 160–180 °C range, around which temperature the nanoparticles decompose to give the oxides. The product selectivity and other features of the reaction are explained taking into account the various byproducts

formed in the reaction. These metal peroxides also activate the C–H bonds of cyclohexane. It is possible to bring down the reaction temperature by partially substituting the Zn in ZnO₂ with Ni.

Introduction

Activation of the C–H bond has been getting increasing attention in the last few years.^[1–4] Alkyl aromatic compounds, such as toluene, constitute an important family of compounds and a reaction of importance in this context is the oxidation of toluene to benzaldehyde and benzyl alcohol.^[5–12] Commercially, benzaldehyde is produced either as a byproduct during the conversion of toluene to benzoic acid by aerial oxidation or at times, by the halogenation of toluene followed by saponification.^[13] The main concern in these reactions is the control of the product distribution, which is nontrivial. Recently, a number of strategies have been explored that employ molecular oxygen or other oxidizing agents.^[14–17] Heterogeneous catalysis, which is advantageous owing to the ease of separation of the catalysts, has also been employed for this purpose. Thus, Raja et al.^[18] designed single-site heterogeneous catalysts for the solvent-free oxidation of toluene using aluminophosphates. Hutchings and co-workers^[5] have recently reported an excellent method for the oxidation of toluene by molecular oxygen under high pressure and at approximately 165 °C, in the presence of catalytic Au–Pd alloy nanoparticles. This method is solvent-free, does not require post-reaction solvent separation, and yields benzyl benzoate in excess of 85%. The use of H₂O₂ and organic peroxides as sources of oxygen for the oxidation of toluene has also been reported.^[16,19] Another important reaction involving C–H activation is the oxidation of cyclohexane to cyclohexanol and cyclohexanone.^[20,21]

Herein, we report the oxidation of toluene by metal peroxides mainly to benzaldehyde, with a small fraction of benzyl al-

cohol. We made use of nanoparticles of CdO₂ and ZnO₂ for the purpose because they decompose at relatively lower temperatures, well below the decomposition temperatures of stable metal peroxides, such as MgO₂ and BaO₂,^[22–25] to give oxygen and the metal oxide. Furthermore, surfaces of metal peroxides are known to contain reactive species, such as peroxy or hydroperoxy radicals, with the potential to initiate radical chain reactions and to activate C–H bonds.^[26,27] Cleavage of the peroxy bonds even at low temperatures, as reported in the case of hydrogen peroxide, leads to reactive singlet oxygen species.^[28] Besides demonstrating the facile oxidation of toluene by solid CdO₂ and ZnO₂ nanoparticles in the 160–180 °C range, which primarily yields benzaldehyde, we show that the Zn–O surface influences product selectivity. We performed preliminary studies on the oxidation of cyclohexane by the peroxide nanoparticles to examine their general use in C–H bond activation. In addition to being solvent-free, the metal peroxide route seems to have certain advantages.

Nanoparticles of ZnO₂ and CdO₂ were prepared by the reaction of ZnO and CdO with excess H₂O₂ at 80 °C (1 h) and 100 °C (12 h), respectively. The peroxide particles so obtained are crystalline with diameters in the 5–10 nm range (see Supporting Information, Figure S1). Importantly, these reaction conditions are mild in comparison with many other known synthetic procedures.^[29,30] The BET surface areas of the ZnO₂ and CdO₂ particles were 54 and 46 m²g^{−1}, respectively. The decomposition temperatures of the peroxides were in the range 160–180 °C as revealed by thermogravimetric analysis (Figure 1). In a typical experiment to oxidize toluene, a predetermined amount of toluene and metal peroxide were sealed in a Teflon-lined autoclave and heated at the desired temperature for a fixed period of time in a preheated air oven. The product obtained was characterized by GC–MS and NMR spectroscopy.

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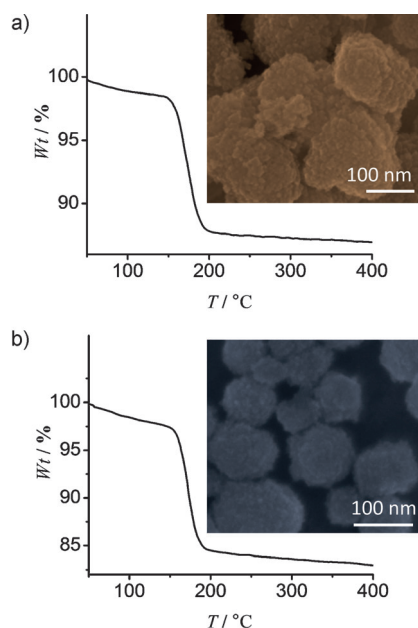


Figure 1. Thermogravimetric analysis data showing the decomposition profiles of nanoparticles of (a) CdO₂ and (b) ZnO₂. Insets show the SEM images of the particles.

Results and Discussion

The reaction of toluene with CdO₂ nanoparticles was performed over different periods at various temperatures up to 180 °C, at which the peroxide decomposition is complete leaving CdO behind. At 180 °C, the reaction was complete within 4 h and the entire peroxide was converted to the oxide. Under these reaction conditions, toluene oxidizes to yield predominantly benzaldehyde, along with some benzyl alcohol and a minute quantity of 3-methyldiphenylmethane or 1,2-diphenylethane (Table 1). We also observed the formation of benzyl hydroperoxide in the initial stages of the reaction. Benzoic acid and other oxidation products were not formed in the reaction. The reaction of the peroxide with toluene yields benzaldehyde and a water molecule. The yield of the oxidation products is estimated to be 70%, with a selectivity of 69% for benzaldehyde. An examination of the reaction profile of the CdO₂ during the first 4 h at 180 °C shows that the reaction proceeds gradually to yield increasing amounts of the reaction products (Figure 2a and Figure S2). However, selectivity towards benzaldehyde is somewhat higher during the initial period of reaction. The gradual conversion of toluene was found at other reaction temperatures as well. It took 12 h for completion of the reaction at 160 °C and the reaction was much slower at 140 °C, with the decomposition of the peroxide being incomplete even after 12 h. Figure 2b shows the selectivity and yields of the oxidation reactions at various temperatures after 4 h of reaction. Notably, selectivity towards benzaldehyde is higher at lower temperatures as well as in the initial stages of the reaction.

As Cd is toxic, we considered it desirable to use ZnO₂, which is environmentally benign. We performed the oxidation of tol-

Conditions	Yield [%] ^[b]		Selectivity [%]		
	T [°C]	t [h]	Benzaldehyde	Benzyl alcohol	Others
CdO₂					
180	4	70	69	26	5
	3 ^[c]	51	73	25	1
	2 ^[c]	43	72	24	4
	1 ^[c]	30	82	17	1
160	4 ^[c]	36	75	25	0
	12	57	71	28	1
ZnO₂					
180	4	58	80	16	4
	3 ^[c]	49	80	16	4
	2 ^[c]	41	84	12	4
	1 ^[c]	33	88	11	1
160	4 ^[c]	32	92	8	0
	12	68	76	21	3

[a] Oxidation of residual air in the reaction vessel was found to yield negligible quantities of benzaldehyde and other products. [b] The oxidation yields were estimated from GC-MS analysis and calculated with respect to peroxide. [c] The reaction was incomplete.

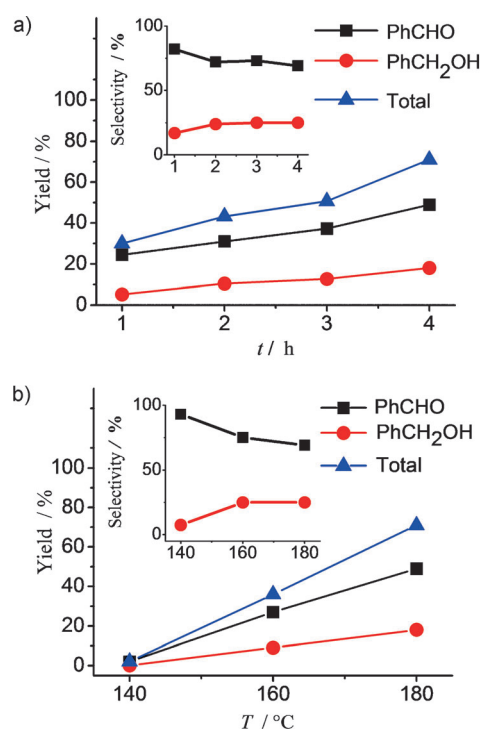


Figure 2. a) Total yield and the relative proportion of the major products of oxidation of toluene by CdO₂ (i.e., benzyl alcohol and benzaldehyde) at 180 °C for different reaction times. b) Total yield of the reaction product obtained at various reaction temperatures for a reaction time of 4 h. The insets show the selectivity of different reaction products.

uene with ZnO₂ nanoparticles, and found that not only the yield but also the product selectivity were at least as good as with CdO₂. On performing the reaction at 180 °C for 4 h, 58% of the peroxide was converted to the oxidation products

(Table 1), which consisted mainly of benzaldehyde (80%) and benzyl alcohol (16%). ZnO₂ was converted to ZnO and no benzoic acid was detected among the oxidation products. The yield could be increased at lower reaction temperature, albeit at a slower rate. For example, the decomposition of ZnO₂ was not complete in 4 h at 160 °C, and the yield was only 32%. The yield increased to 68% if the reaction was performed for 12 h, concurrent with the complete decomposition of the peroxide. The oxidation product contained 76% benzaldehyde, 21% benzyl alcohol, and trace amounts of other products. We compare the results obtained with ZnO₂ and CdO₂ nanoparticles in Figure 3a and b. Although CdO₂ nanoparticles would appear to be superior to ZnO₂ nanoparticles in terms of product yields after 4 h, ZnO₂ is perhaps as good as or better than CdO₂ at lower temperatures.

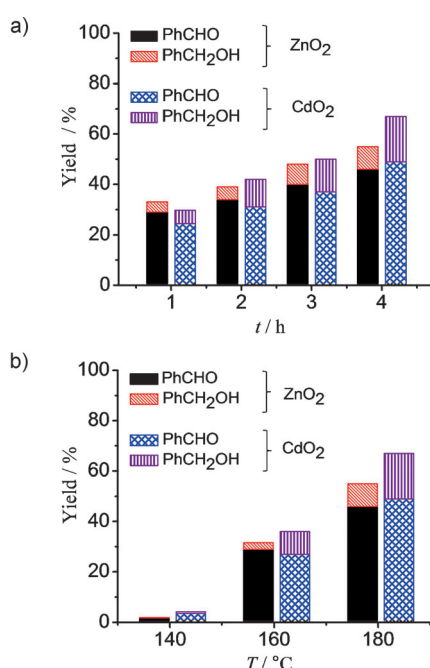


Figure 3. Total yields obtained from the oxidation of toluene by CdO₂ and ZnO₂ nanoparticles. Different colors within a bar represent relative amounts of benzaldehyde and benzyl alcohol. Yields obtained at (a) 180 °C for different reaction times and (b) various reaction temperatures for a reaction time of 4 h.

As the decomposition temperatures of the peroxides are comparable to the reaction temperatures, the peroxides might simply decompose to yield oxygen, which reacts with toluene. However, our results show the reaction pathway to be different. Metal peroxides are known radical initiators,^[31] so it is believed that their decomposition produces radicals for the oxidation of toluene, with the subsequent radical reaction occurring in the solution phase. Investigations on organic peroxide-induced toluene oxidation on metal catalysts have recently shown the involvement of reactive oxygenated species with the catalyst surface,^[18] thus indicating a need for surface tailoring. As different metal peroxides may contain different reactive

oxygen species, it is expected that they would lead to different reaction products.^[27] In the present study, we found that the two metal peroxides with the same decomposition temperatures exhibit different product selectivities, thereby indicating the role of the reagent surface in the reactions (Table 1).

Our study of the aerial oxidation of toluene at the same reaction temperatures, in the absence of metal peroxides, yielded benzyl alcohol as the main reaction product (see Figure 4, Table 2). Sun et al.^[17] have shown that the decomposition of

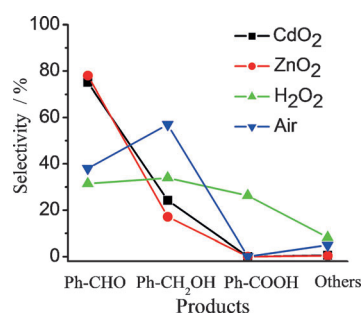
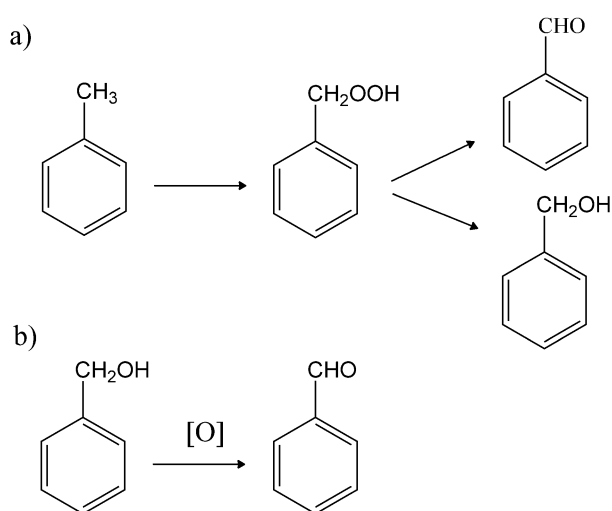


Figure 4. Selectivity towards different oxidation products with the use of CdO₂, ZnO₂, H₂O₂, and air as oxidants under comparable experimental conditions.

Table 2. Comparison of oxidation products of toluene by CdO₂, ZnO₂, H₂O₂, and air obtained under comparable experimental conditions. Unlike the selectivity observed in different reactions, the comparison of the yields is not straightforward as yield depends on the actual mechanism of the reaction.

Reagent	Conditions		Selectivity [%]			
	T [°C]	t [h]	Benzaldehyde	Benzyl alcohol	Benzoic acid	Others
CdO ₂	180	4	69	26	0	5
ZnO ₂	180	4	80	16	0	4
H ₂ O ₂	180	4	31	34	26	8
air	180	4	38	57	0	5

benzyl hydroperoxide yields benzaldehyde and water. In our experiments, toluene appears to transform to benzaldehyde via the benzyl hydroperoxide intermediate (Scheme 1a). We have estimated the amount of benzyl hydroperoxide formed at various times occurring from the start of the reaction. As Figure 5 shows, it increases initially and then decreases gradually, as the yield of the stable reaction products increases. We estimated the amount of water present in various reaction mixtures to be proportional to that of the benzaldehyde. Benzyl alcohol can also form by the decomposition of benzyl hydroperoxide at high temperatures in the presence of hydrogen-rich solvents, such as xylene or toluene.^[32] In our reactions too, the amount of benzyl alcohol increases with increase in the reaction temperature, consistent with Scheme 1. Alternatively, further oxidation of benzyl alcohol can lead to benzaldehyde (Scheme 1b).^[6] We believe that this can only be a minor competing pathway, since more aldehyde is formed initially.



Scheme 1. Possible reaction schemes involved in the oxidation of toluene.

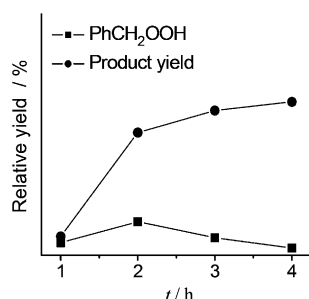


Figure 5. Total yield and the amount of benzyl hydroperoxide present in the reaction mixture of toluene and ZnO₂ at 180 °C at various time intervals.

Little is known about the interaction of metal peroxides with organic molecules. On the other hand, H₂O₂ and organic peroxides, which are used for C–H activation reactions, give OH[•] and OOH[•] radicals on decomposition.^[16] These radicals can extract a proton from toluene to produce PhCH₂[•] radicals. We have observed the formation of 3-methyldiphenylmethane or one of its isomers as a reaction byproduct (≈ 1–5% of benzaldehyde, Figure S3), which indicates the formation of benzyl radicals in our experiments as well.^[33,34] PhCH₂[•] can readily combine or extract an oxygen molecule and a proton to produce PhCH₂OOH. Studies on metal peroxides have shown that they help to form chain-initiating radicals^[26] as they contain trapped OH[•] and O²⁻ on the crystal surfaces.^[35] Our experiments on the oxidation of toluene with equal amounts of H₂O₂ yielded nearly equal proportions of benzaldehyde, benzyl alcohol, and benzoic acid (Figure 4, Table 2), thus indicating a different course of reaction. Decomposition of PhCH₂OOH can be catalyzed by metals. Scott^[36] and Wang et al.^[19] have proposed that the peroxy oxygen atoms of benzyl hydroperoxide bind to catalytic metal ions before decomposition. It is possible that PhCH₂OOH is somehow associated with the solid reagents in our reactions, thereby giving rise to different product selectivities. To check the role of the Zn–O surface, we performed toluene oxidation reactions by H₂O₂ in the presence of ZnO. Unlike the equal

proportions of alcohol and aldehyde obtained in its absence, we observed approximately 70% aldehyde and approximately 30% alcohol, which indicated that the metal peroxide has a role in product selectivity.

Activation of the C–H bond in toluene by the metal peroxides seems to have certain advantages over other methods. Thus, unlike many of the oxidation protocols involving biphasic reactions or solvents,^[14,37–40] the reaction reported herein is somewhat akin to solvent-free reactions. The reaction temperature is in the acceptable range of 160–180 °C in the case of ZnO₂ and CdO₂ nanoparticles. We can bring the reaction temperature down further by partial substitution of Zn with Ni in ZnO₂. Thus, with Zn_{0.8}Ni_{0.2}O₂ (energy-dispersive X-ray spectrum in Figure S4), we obtain 80% benzaldehyde and 20% benzyl alcohol at 140 °C with a total reaction yield of about 49% against a minimal 3–4% with pure ZnO₂ at this temperature.

The reaction time of 4 h at approximately 160 °C is considerably shorter than that in many of the existing methods, which require 1–3 days.^[5,15,39,41] In the absence of any catalysts,^[5] catalyst poisoning^[7] and regeneration are avoided. Besides, CdO₂ and ZnO₂ are not dangerous, unlike organic peroxides,^[42] and are readily prepared. The monoxides can also be reconverted to the respective peroxides by treatment with H₂O₂. To the best of our knowledge, this is the first report on C–H activation by the use of metal peroxides as the oxygen source.

The ability of metal peroxides to activate the C–H bond is further demonstrated by the study of the oxidation of cyclohexane. We examined the oxidation of cyclohexane and *n*-hexane by ZnO₂ at 160 °C for 12 h by using identical reaction procedures to the case of toluene. Cyclohexane oxidation occurs with an efficiency of 60% to yield 80% cyclohexanol and 20% cyclohexanone, along with minute quantities of other products. We also attempted to increase the yield by tailoring the reaction conditions. A much smaller yield was obtained if the reaction was performed at 180 °C for 4 h. On using solvents such as acetonitrile or acetic acid, as often used in H₂O₂-based oxidation reactions, the reaction mixture turned black and a number of additional byproducts were obtained. On the other hand, *n*-hexane oxidation appears to introduce a carbonyl group at various positions on the alkane chain.

Conclusion

Nanoparticles of Cd and Zn peroxides act as good oxidizing agents for toluene yielding desirable products. The method described herein has several advantages, including the relatively low operating temperature and absence of catalysts. The ability of the metal peroxides to activate the C–H bond is also demonstrated by the oxidation of cyclohexane. Notably, the peroxides can be regenerated from the oxide products and the reaction temperature can be brought down by substitution of Zn in ZnO₂ with nickel.

Experimental Section

CdO₂ and ZnO₂ nanoparticles were synthesized by the treatment of the corresponding monoxides with H₂O₂. Typically, ZnO (2 g) in

H₂O (20 mL) was reacted with 30% H₂O₂ (10 mL) at 80 °C for 1 h. Conversion of CdO to CdO₂ was slower and took place when 30% H₂O₂ (10 mL) was added dropwise to the CdO dispersion over a period of 12 h under the same conditions. At the end of the reaction, the as-synthesized nanoparticles were collected by centrifugation at 4000 rpm for 5 min. The XRD patterns of the powders obtained confirmed the purity of CdO₂ (JSPDS: 78-1125, *a* = 5.386 Å)^[24] and ZnO₂ (JCPDS: 78-1124, *a* = 4.902 Å)^[23] nanoparticles.

Nickel-incorporated ZnO₂ was obtained by modifying a standard procedure.^[43] Zinc acetate (8 mmol) and nickel acetate (2 mmol) were dissolved in water (40 mL) and H₂O₂ (30%, 10 mL) was added. A concd KOH solution was added dropwise, instantly yielding a light greenish-white precipitate. The XRD pattern of the sample matched that of pure ZnO₂. We estimated the Ni content in the sample to be 17–19% from energy-dispersive X-ray spectroscopic analysis.

The toluene oxidation reactions were performed in Teflon-lined autoclaves. In a typical experiment, the desired amounts of toluene (139 mmol) and the metal peroxide (3 mmol) were sealed in a 20 mL autoclave and kept inside a preheated oven at 180 °C for 4 h. The autoclave was allowed to cool naturally after the reaction. The reaction products were readily separated from the oxides by sonication. Oxidation reactions with H₂O₂ were performed in the presence of an equivalent amount of H₂O₂ under identical conditions. Aerial oxidation was performed by taking advantage of the fact that in a larger autoclave, a small amount of toluene filling left a large volume of air usable for oxidation. Oxidation of cyclohexane and *n*-hexane were performed at 160 °C, keeping all other conditions the same as in the case of toluene.

In all the oxidation reactions of toluene that we performed, there was a possibility of aerial oxidation because the reaction vessel was partly filled with air, in addition to the dissolved oxygen. Therefore, to estimate the blank baseline yield, we carefully analyzed the oxidation products that arose owing to the presence of oxygen in the reaction vessel. This was deemed important as recent studies have shown that such oxidation can take place at a temperature as low as 160 °C.^[5,37] The amount of product so obtained was extremely small (about 5%) in comparison with the peroxide reaction, and yielded similar amounts of benzaldehyde, benzyl alcohol, and benzyl toluene. Therefore, the effect of dissolved and aerial oxygen enclosed in the reaction vessel was neglected.

The purity of the peroxides and the decomposition products (after the toluene oxidation reaction) was established by powder XRD (Bruker D8 diffractometer, $\lambda = 1.5406 \text{ \AA}$). The identification and quantitative estimation of the toluene oxidation product were performed with NMR (Bruker AV-400) and GC–MS (Shimadzu GC-2010) techniques.

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Keywords: C–H activation · cadmium peroxide · nanoparticles · oxidation · zinc peroxide

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