

Microwave-accelerated solvent-free aerobic oxidation of benzyl alcohol over efficient and reusable manganese oxides

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Received 8 March 2007; received in revised form 15 April 2007; accepted 17 April 2007

Available online 1 May 2007

Abstract

A new facile and cost-effective process involving the solvent-free oxidation of benzyl alcohol using molecular oxygen as oxidant under controlled microwave irradiation has been developed for the production of chlorine-free benzaldehyde. Influence of different catalyst parameters (different manganese oxides and other kinds of transition metal oxides) and reaction conditions (reaction period and temperature) on the process performance has been studied. Under optimized reaction conditions, the MnO_2 catalyst showed a superior catalytic performance in the highly selective oxidation of benzyl alcohol as compared to other manganese oxide materials such as MnO , Mn_2O_3 and Mn_3O_4 . Moreover, a very stable catalytic activity as a function of cycling test was observed for the MnO_2 catalyst.

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Keywords: Benzaldehyde; Manganese oxides; Aerobic oxidation; Microwave irradiation; Solvent-free

1. Introduction

Liquid phase oxidation of benzyl alcohol to benzaldehyde is a widely investigated reaction as it provides chlorine-free benzaldehyde required in perfumery and pharmaceutical industries [1,2]. Stoichiometric oxidants, such as manganese and chromium salts are frequently used for this purpose, but these reagents are expensive and have serious toxicity issues associated with them [3–5]. Recently, a number of studies on the benzyl alcohol to benzaldehyde oxidation by molecular oxygen (O_2) or H_2O_2 in the presence of a solvent, using various transition metal oxide-based catalysts have been reported [6–11]. There is also usage of noble metal-based catalysts as highly active system for the solvent-free oxidation of benzyl alcohol, which however generally suffers from further oxidation of the aldehyde to carboxylic acid [12–15]. From the viewpoint of atomic economy and environmental demand, it is highly

attractive to develop new facile and cost-effective procedures that can allow more efficient aerobic oxidation of benzyl alcohol under solvent-free conditions.

On the other hand, microwave-assisted organic synthesis has attracted increasing attention by providing a much faster, simpler, and more energy efficient technique toward rapid and solvent-free synthesis as compared to the conventional methods. However, most of the processes reported on this area are mainly based on homogeneous catalysis [16–18]. We report here a novel microwave-accelerated process for the liquid phase aerobic oxidation of benzyl alcohol to benzaldehyde in presence of easily separable and reusable manganese oxides under solvent-free conditions.

2. Experimental

2.1. Catalyst preparation

Four kinds of different manganese oxides nominal composition MnO , MnO_2 , Mn_2O_3 and Mn_3O_4 were prepared using the solution-based or solid-state reaction procedures

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described in Refs. [19,20] as follows: (a) MnO was prepared by reduction of MnCO_3 sample by H_2 at 500 °C for 4 h and then cooled to ambient temperature in flowing N_2 stream. (b) A 100 mL solution containing equal amount of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (both ca. 0.08 M) was hydrothermally processed at 120 °C for 12 h followed by filtration and washing to obtain MnO_2 . (c) Mn_2O_3 was prepared by calcination of MnCO_3 sample (AR) at 500 °C in flowing air for 4 h. (d) Mn_3O_4 was obtained by an initial calcination of a MnCO_3 sample at 400 °C in flowing N_2 for 4 h followed by an air exposure for 2 h.

For comparison, other transition metal oxides (all subjected to a final calcination at 350 °C for 2 h) such as V_2O_5 ($35.9 \text{ m}^2 \text{ g}^{-1}$), CuO ($43.1 \text{ m}^2 \text{ g}^{-1}$), Fe_2O_3 ($66.3 \text{ m}^2 \text{ g}^{-1}$), Co_2O_3 ($80.1 \text{ m}^2 \text{ g}^{-1}$) and NiO ($72.8 \text{ m}^2 \text{ g}^{-1}$) synthesized according to literature sol–gel or precipitation procedures [21] were also tested under the same conditions.

2.2. Catalyst characterization

The BET specific surface areas of the samples were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. The X-ray powder diffraction (XRD) of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered $\text{Cu K}\alpha$ radiation at 40 kV and 20 mA.

2.3. Activity test

The slurry containing the catalyst (0.5 g) and benzyl alcohol (20 mL) was stirred in a 50 mL glass reactor at temperature range from 80 to 140 °C for 1–5 h, in the presence of oxygen at 0.1 MPa. Reactions were carried out using a microwave enhanced organic synthesizer (type MAS-I, SINEO, Shanghai). The microwave power was set to 600 W and the temperature was measured throughout the reaction and evaluated by an infrared detector, which indicated the surface temperature. Products were analyzed by GC (Trace GC ultra) fitted with an HP-5 capillary column and the determination of different products in the reaction mixture was performed by means of GC–MS. There are two products from the reaction: benzaldehyde and benzyl ether.

3. Results and discussion

The powder X-ray diffraction patterns of the as-prepared manganese oxides with different nominal composition are shown in Fig. 1. The as-prepared Mn_2O_3 sample was characterized to pure $\alpha\text{-Mn}_2\text{O}_3$ since the peaks in Fig. 1a are exactly matched with a reference file of JCPDS 41-1442. The XRD patterns of sample Mn_3O_4 is shown in Fig. 1b, all the reflections could be indexed to $\gamma\text{-Mn}_3\text{O}_4$ (JCPDS 24-0734). The XRD patterns of the MnO sample (Fig. 1c) showed that it could be indexed to a cubic cell reported for MnO (JCPDS 06-0592). The XRD pattern

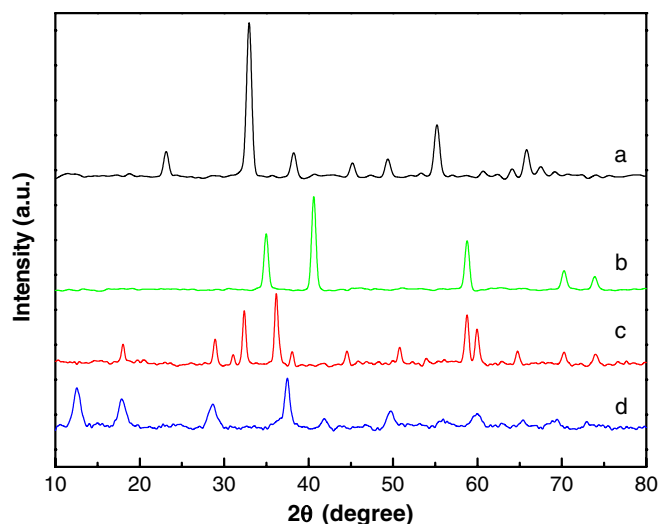


Fig. 1. XRD patterns of manganese oxides: (a) Mn_2O_3 , (b) Mn_3O_4 , (c) MnO and (d) MnO_2 .

of the as-prepared MnO_2 sample is shown in Fig. 1d, which can be attributed to a pure tetragonal phase of $\alpha\text{-MnO}_2$ with lattice constants $a = 9.7847 \text{ \AA}$ and $c = 2.8630 \text{ \AA}$ (JCPDS 44-0141).

The catalytic performances of manganese oxides are shown in Table 1. It could be clearly seen that the prepared manganese oxides can be used to catalyze aerobic oxidation of benzyl alcohol under solvent-free conditions, giving benzaldehyde as the main product. It is known that other transition metal oxides such as V_2O_5 [22], CuO [23], Fe_2O_3 [24], Co_2O_3 [25] and NiO [26] were common catalysts employed in liquid phase selective oxidation. In order to compare the activities with the manganese oxides, these materials were also employed in reactions under same conditions, which however showed much lower conversions or benzaldehyde selectivities. Among the manganese oxides, although the MnO had low activity close to other kinds of catalysts, nominal composition sample Mn_2O_3 , Mn_3O_4 and MnO_2 exhibited much higher activity. In particular, the remarkable catalytic result of sample MnO_2 (37.7% conversion and 98.6% selectivity) clearly showed that manganese oxides are efficient heterogeneous catalysts for the solvent-free oxidation of benzyl alcohol to benzaldehyde in liquid phase under microwave irradiation.

At this situation, it is interesting to note that the most active catalyst MnO_2 has the highest oxidation state of Mn, inferring that the oxidation state of Mn may play an important role in determining the catalytic behavior of the manganese oxide materials. Previous investigations concerning the catalytic oxidation activity of manganese oxide based catalysts have revealed that a higher oxidation state of the Mn species is always associated with a higher activity of the catalyst [27]. This may well account for the lowest activity of the MnO material as compared to other manganese oxides. However, more close inspection of the catalytic activities of the other two manganese oxide

Table 1

Catalytic performance in the solvent-free liquid phase aerobic oxidation of benzyl alcohol over various samples under microwave irradiation

Entry	Catalyst	BET surface area (m ² g ⁻¹)	Conversion (%)	Selectivity (%)	
				Benzaldehyde	Benzyl ether
1	MnO ₂	88.6	37.7	98.6	1.4
2	Mn ₂ O ₃	47.3	15.4	90.7	9.3
3	Mn ₃ O ₄	59.4	17.5	96.1	3.9
4	MnO	41.2	4.0	95.9	4.1
5	V ₂ O ₅	35.9	2.5	94.3	5.7
6	CuO	43.1	3.9	95.7	4.3
7	Fe ₂ O ₃	66.3	6.7	80.8	19.2
8	Co ₂ O ₃	80.1	11.7	87.2	12.8
9	NiO	72.8	13.5	96.5	3.5

Reaction conditions: 20 mL benzyl alcohol, 0.5 g catalyst, $T = 80\text{ }^{\circ}\text{C}$ and pressure = 0.1 MPa; reaction time: 3 h; flow rate of O₂: 30 mL min⁻¹.

samples reveals that sample Mn₃O₄ has a higher activity than that of Mn₂O₃, implying that the oxidation state of Mn species is not necessarily the decisive parameter in determining the catalytic performance of all manganese oxide materials. In this respect, it appears that other factors, such as the specific surface area or the morphological structure of the manganese oxide material may also contribute to some extent to the superior performance of the present MnO₂ or Mn₃O₄ samples.

The benefit of using microwave irradiation as an energy source for the solvent-free oxidation of benzyl alcohol is obvious when comparing the catalytic activity of MnO₂ with the activities obtained by conventional heating (thermal energy) (Fig. 2). The fact that the coupling of microwave irradiation can allow a significant enhancement in

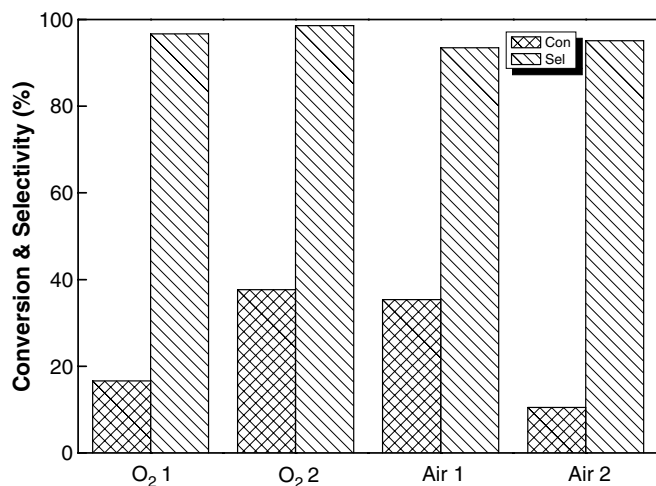


Fig. 2. Influence of heating method, oxygen resources and gas flow rates on benzyl alcohol conversion and selectivity to benzaldehyde over MnO₂ catalyst. Experimental conditions: 20 mL benzyl alcohol; 0.5 g α -MnO₂ catalyst; pressure = 0.1 MPa; $T = 80\text{ }^{\circ}\text{C}$; reaction time = 3 h. O₂ 1: pure oxygen as oxygen resource in a flow rate of 30 mL · min⁻¹ under conventional oil bath; O₂ 2: pure oxygen as oxygen resource in a flow rate of 30 mL · min⁻¹ under MW irradiation; Air 1: air as oxygen resource in a flow rate of 120 mL · min⁻¹ under MW irradiation; Air 2: air as oxygen resource in a flow rate of 30 mL · min⁻¹ under MW irradiation.

the benzyl alcohol conversion as compared to conventional heating is possibly a consequence of the formation of “molecular hot spots” over MnO₂ due to the strong microwave absorbing nature of the material [28], which may greatly facilitate the present solvent-free oxidation process. Subsequent experiments using air in place of O₂ under similar microwave-accelerated reaction conditions have obtained the similar activities. Note that although the selectivity to benzaldehyde in air is slightly lower than in pure oxygen, it can still achieve 97% above. Additionally, the flow rate of air is also identified as a key parameter influencing the microwave-accelerated benzyl alcohol oxidation. This demonstrates that in principle, air can also be used for this green process which is of great potential for commercial applications.

Fig. 3 depicts the influence of reaction time on the conversion of benzyl alcohol and selectivity to benzaldehyde over MnO₂ catalyst. For safety reasons, extended microwave irradiation with reaction time longer than 5 h was not studied. When the reaction period is increased from

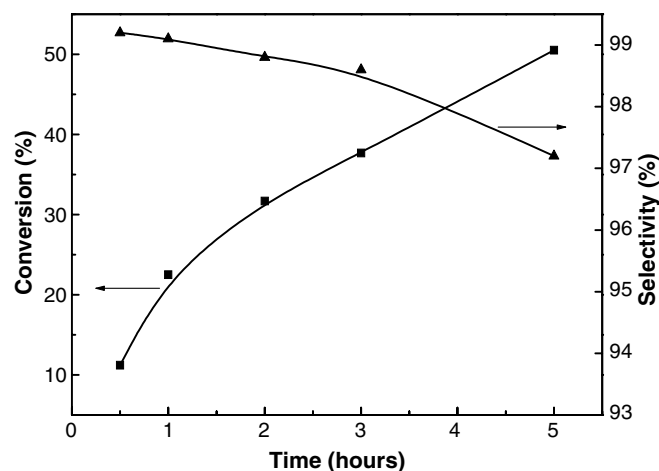


Fig. 3. Influence of reaction time on benzyl alcohol conversion and selectivity to benzaldehyde over MnO₂ catalyst under microwave irradiation. Experimental conditions: 20 mL benzyl alcohol; 0.5 g catalyst; pressure = 0.1 MPa; $T = 80\text{ }^{\circ}\text{C}$; flow rate of O₂: 30 mL · min⁻¹.

0.5 to 5 h, the benzyl alcohol conversion is almost exponentially increased from 11.2% to 50.5%, but the selectivity for benzaldehyde is decreased. The decrease in the benzaldehyde selectivity is attributed to the increase in the rate of benzyl ether formation due to the increase in the intermolecular dehydration of benzyl alcohol under prolonged microwave irradiation. The benzaldehyde selectivity decrease is, however, quite small.

The catalytic activities of the MnO_2 sample were also found to be strongly dependent on the reaction temperature. Fig. 4 shows the influence of reaction temperature on benzyl alcohol reaction over catalyst MnO_2 . In all cases, benzaldehyde was obtained as the major product, and only small amounts of the other product, viz., benzyl ether, were observed. It is seen that the benzyl alcohol conversion increases with increase in reaction temperature. At temperatures lower than 110 °C, the selectivity to benzaldehyde was always high above 90%. However, beyond this temperature, a rapid decrease in selectivity to main product of benzaldehyde was observed, which could be attributed to the side reaction mentioned above.

In order to examine the possible reusability under present microwave-assisted reaction conditions, recycle tests of catalyst MnO_2 have been taken. After the reaction, the catalyst was filtered and washed with deionized water and acetone for several times, then dried at 120 °C for 12 h to remove acetone and used for another reaction. It is remarkable that the MnO_2 sample maintained its high catalytic activity affording a high benzyl alcohol conversion above 32% even after four recyclings and reuse of the catalyst (see Table 2). The observed results clearly evidenced the high efficiency of the present microwave-assisted process for the facile and convenient liquid phase aerobic oxidation of benzyl alcohol to benzaldehyde in presence of easily separable and reusable manganese oxides under solvent-less conditions.

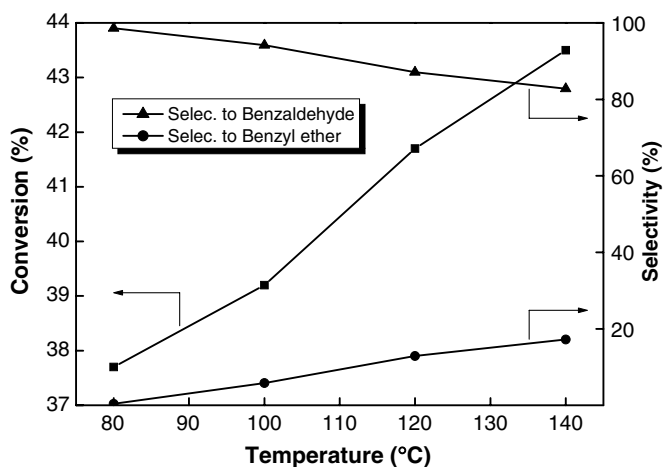


Fig. 4. Influence of reaction temperature on the conversion of benzyl alcohol and product selectivity over MnO_2 catalyst under microwave irradiation. Experimental conditions: 20 mL benzyl alcohol; 0.5 g catalyst; pressure = 0.1 MPa; time: 3 h; flow rate of O_2 : 30 mL \cdot min⁻¹.

Table 2
Reusability of the MnO_2 catalyst

Entry	Conversion (%)	Selectivity (%)	
		Benzaldehyde	Benzyl ether
1	37.7	98.6	1.4
2	35.6	98.7	1.3
3	34.1	97.4	2.6
4	32.8	98.3	1.7

Reaction conditions: 20 mL benzyl alcohol, 0.5 g catalyst, $T = 80$ °C and pressure = 0.1 MPa; reaction time: 3 h; flow rate of O_2 : 30 mL min⁻¹.

4. Conclusion

In summary, benzaldehyde can be effectively produced by a novel liquid phase solvent-free oxidation of benzyl alcohol in the presence of manganese oxides using molecular oxygen as oxidant under controlled microwave irradiation. Notably, α - MnO_2 was shown to be the most effective material that can allow the highly efficient oxidative transformation of benzyl alcohol to benzaldehyde as compared to other materials. Prolonged reaction time or higher reaction temperature is beneficial for further boosting the conversion of benzyl alcohol. Moreover, a very stable catalytic activity as a function of cycling test was observed for the α - MnO_2 catalyst. Work is on going to this new promising and environmental benign protocol for the solvent-free aerobic oxidation of other alcohols to corresponding aldehydes.

Acknowledgements

The financial supports from the National Natural Science Foundation of China (20421303, 20473021, 20633030), the National High Technology Research and Development Program of China (2006AA03Z336), the Research Fund for the Doctoral Program of Higher Education (Grant No. 20050246071) and the National Basic Research Program of China (2003CB615807) are gratefully acknowledged.

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