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Direct oxidation of toluene to benzoic acid with molecular oxygen over manganese oxides

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Manganese oxides, which are easily prepared, simple to use and capable of being recycled, have been employed as catalyst in the selective oxidation of toluene to benzoic acid for the first time. Molecular oxygen was used as oxidant under additive- and solvent-free conditions. As a result, 39% conversion of toluene and 93% selectivity of benzoic acid were achieved.

KEY WORDS: toluene; oxidation; manganese oxides; heterogeneous catalysis.

1. Introduction

Selective oxidation of hydrocarbons is an attractive field and still remains a challenge [1], among which the oxidation of toluene is an important process and of greatly scientific importance. Industrially, the oxidation of toluene to benzoic acid with molecular oxygen is a key step for synthesizing ε-caprolactam in Snia–Viscosa process [2,3]. The commercial production of benzoic acid via the oxidation of toluene is often achieved by heating a solution of toluene with cobalt acetate and bromide promoter in acetic acid [2,4]. The use of acidic solvent and bromide promoter results in difficult separation of products and catalyst, large volumes of toxic acidic waste and equipments corrosion. Much effort has been made to improve the efficiency of toluene oxidation [5,6]. However, most investigations still focus on homogeneous systems, and yet need volatile solvent. For example, NHPI/$Co(AcO)_2$ was reported as an efficient catalytic system for toluene oxidation to benzoic acid in acetic acid solvent [7]. In contrast, employing heterogeneous catalysts in liquid-phase oxidation of toluene, especially under solvent-free conditions, the process could overcome those drawbacks, and would be more environmentally friendly. Unfortunately, there is no report on direct oxidation of toluene to benzoic acid by molecular oxygen over heterogeneous catalysts in liquid phase.

A popular stoichiometric oxidation of side chain of aryl compounds to aromatic carboxylic acids is powerful $KMnO_4$ protocol. The oxygen species bounded to high-valent Mn provide source of oxygen for oxidation products, along with the formation of lower-valent Mn species [8]. Manganese is often a component of heterogeneous catalysts for aerobic oxidation of organic compounds, wherein manganese oxides are usual forms [9,10]. It is notable that octahedral molecular sieves constructed by MnO_6 octahedral units were demonstrated to be efficient catalysts for aerobic oxidation of alcohol [11,12]. These showed that lower-valent Mn species formed after donating oxygen could be oxidized to higher valent by molecular oxygen during catalysis. Therefore, it is tempting to suggest that manganese oxides may be directly used as catalysts for aerobic oxidation of hydrocarbons. By preparing various manganese oxides, the present study examined these new heterogeneous catalysts in the oxidation of toluene to benzoic acid.

2. Experimental

2.1. Preparation of manganese oxides

Four kinds of different manganese oxides nominal composition MnO, MnO_2, Mn_2O_3 and Mn_3O_4 were prepared and characterized by X-ray powder diffraction (XRD), which was measured by a Rigaku miniflex diffractometer employing Cu-Kα radiation. The catalysts were prepared by following procedure:

(a) A solution of 60 ml 5 wt% $KMnO_4$ was dropped to 100 ml 5 wt% $MnSO_4$ solution under stirring at 333 K. Then the mixture stirred at 303 K for 10 h. After filtration the solid washed with deionized water for several times and dried at 393 K, then calcined at 673 K for 6 h to produce MnO_2.

(b) Mn_2O_3 was prepared by calcination of $MnCO_3$ sample (AR) at 773 K in flowing air (1 atm) for 4 h and then cooled.

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(c) Mn_3O_4 prepared by following method: $MnCO_3$ sample was calcined at 673 K in flowing N_2 (1 atm) for 4 h, transforming to a green solid. Then, air was introduced. When the colour of sample changed to brown, air was switched to N_2 gas stream and cool down.

(d) MnO was prepared by reduction of $MnCO_3$ sample by H_2 at 773 K for 4 h and then cooled to ambient temperature in flowing N_2 stream to afford green solid. It is believed that the green solid should be MnO since manganese oxides often have the "right" colours: green for MnO, brown for Mn_3O_4, black for Mn_2O_3 and MnO_2 [13]. When exposed to air for few minutes, the green solid changed into light brown colour because fresh MnO phase is not stable in air and can be oxidized easily by dioxygen.

2.2. Catalytic oxidation tests

The catalytic oxidation reaction was carried out in a 500 ml capacity autoclave. Toluene and 2.3 wt% of prepared manganese oxide catalyst was put into the autoclave, which was heated to 468 K under vigorous stirring. Then the autoclave was charged with 1.0 MPa of O_2 while O_2 was fed continuously to keep a constant pressure (1.0 MPa). After a certain term of reaction, the reaction mixture was cooled and dissolved in 50 ml ethanol, and then catalyst was separated by filtration. The reaction products were analyzed by a gas chromatograph. Authentic standard samples were used to identify the products. The conversion and product distribution were evaluated with calibration curves.

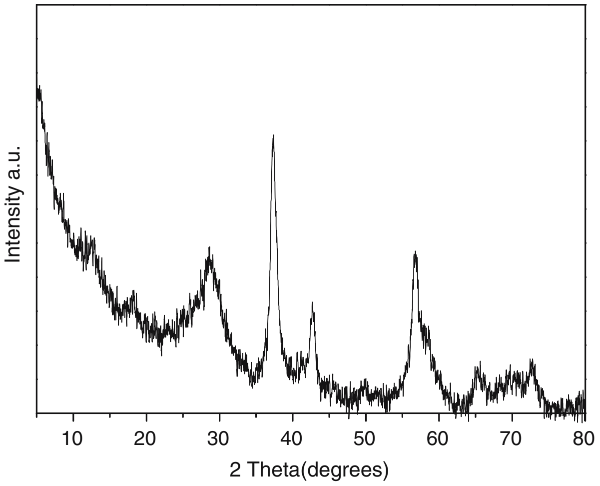

Figure 1. The XRD patterns of MnO_2.

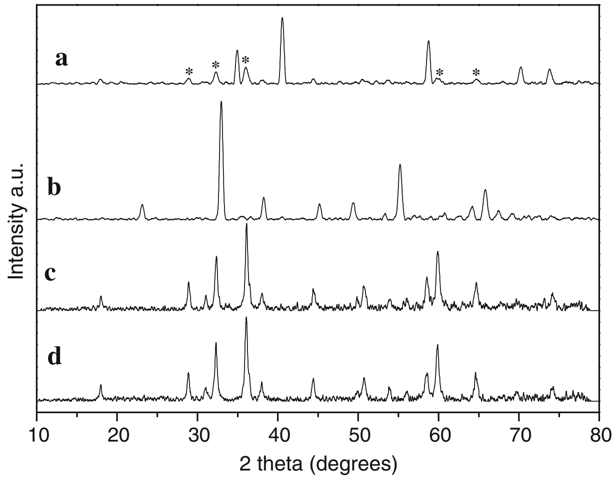

Figure 2. XRD patterns of as-prepared manganese oxides (a) MnO, *marked the peaks of Mn_3O_4, (b) Mn_2O_3, (c) Mn_3O_4, (d) Mn_3O_4 after reaction.

3. Results and discussion

The XRD patterns of as-prepared manganese oxides are shown in figures 1 and 2. The XRD patterns of MnO_2 (figure 1) accorded with the reported result [14]. The as-prepared Mn_2O_3 (black solid) catalyst was characterized to pure α-Mn_2O_3 since the peaks in the XRD patterns (figure 2, line b) are exactly matched with a reference file of JCPDS 41-1442. Line c of figure 2 is the patterns of as-prepared Mn_3O_4, all the strong and sharp diffraction peaks were perfectly indexed to γ-Mn_3O_4 (JCPDS 24-0734). The XRD patterns of the "MnO" sample (figure 2, line a) showed that it consists mainly of MnO (JCPDS 06-0592) with a little amount of Mn_3O_4 (marked with *).

The catalytic performances of manganese oxides are showed in Table 1. It could be clearly seen that the prepared manganese oxides can be used to catalyse aerobic oxidation of toluene, giving benzoic acid as a main product. It is known that cobalt acetate, some manganiferous salts, and other kinds of metal oxides were usual catalysts for oxidation. In order to compare the activities with the manganese oxides, these compounds were also employed in reaction under same conditions. V_2O_5 was commonly used in vapour-phase oxidation of toluene [15–17], but in the liquid phase oxidation it gave very low conversion (3.4%) and selectivity of benzoic acid (27.1%). Co_2O_3, CuO, Fe_2O_3, and manganiferous salts all showed low conversions and benzoic acid selectivities. Cobalt acetate was the catalyst used in the commercial process but also showed a relative low activity under this condition. Among the manganese oxides, although the MnO_2 had low activity close to other kinds of catalysts, nominal composition MnO sample, Mn_2O_3 and Mn_3O_4 exhibited much higher activity. In particular, the remarkable catalytic result of Mn_3O_4 (38.7% conversion and 93.3% selectivity) clearly showed that manganese oxides are efficient heterogeneous catalysts for the oxidation of toluene to benzoic acid in liquid phase even without any solvent and additive.

Table 1
The liquid-phase oxidation of toluene[a]

Entry	Catalyst	Conv. (mol %)	Product distribution (mol %)				
			BAC[b]	BAl	BOL	BB	Others
1	MnO_2	6.5	41.8	52.2	1.2	0	4.8
2	Mn_2O_3	26.3	77.6	13.9	0.4	4.1	4.0
3	Mn_3O_4	38.7	93.3	6.0	0.2	0.3	0.2
4	Mn_3O_4[c]	36.4	89.3	4.9	0.9	4.2	0.7
5	MnO	21.1	71.0	2.7	18.3	6.9	1.1
6	V_2O_5	3.4	27.1	50.4	13.0	0	9.5
7	Co_2O_3	4.5	18.5	35.3	43.5	0	2.7
8	CuO	9.5	36.6	29.3	27.0	1.7	5.4
9	Fe_2O_3	8.9	36.9	28.2	28.3	0	6.6
10	$Co(Ac)_2 \cdot 4H_2O$	10.5	43.2	24.6	25.1	0.3	6.8
11	$Mn(Ac)_2 \cdot 4H_2O$	8.3	37.0	3.9	50.1	0	9.0
12	$MnSO_4 \cdot H_2O$	0.2	0	22.0	78.0	0	0
13	$MnCl_2 \cdot 4H_2O$	7.3	30.8	29.5	28.4	0	11.3

[a] Reaction conditions: catalysts = 1.0 g, toluene = 50 ml, pressure = 1.0 MPa, time = 3 h, temperature = 468 K.
[b] BAC = benzoic acid; BAl = benzaldehyde; BOL = benzyl alcohol; BB = benzyl benzoate.
[c] The second run.

Figure 3 showed the effect of reaction time on catalytic performance in the toluene oxidation over Mn_3O_4 catalyst. The conversion increased with the time. The rate of reaction was very slow initially and accelerated at 60 min. The selectivity of benzaldehyde decreased rapidly with the reaction time. The selectivity of benzyl alcohol increased at first and peaked at about 90 min then decreased to a very little amount at the end of reaction. Benzoic acid appeared at 60 min when the reaction became rapidly, furthermore, the selectivity of benzoic acid increased with the time as well as the conversion. In the particular time period of 60–120 min, benzoic acid appearance went with the accelerating of the reaction, at the same time the selectivity of benzaldehyde decreased rapidly. From the graph we draw a conclusion that benzoic acid was the product of further oxidation of benzaldehyde and benzyl alcohol along with the reaction.

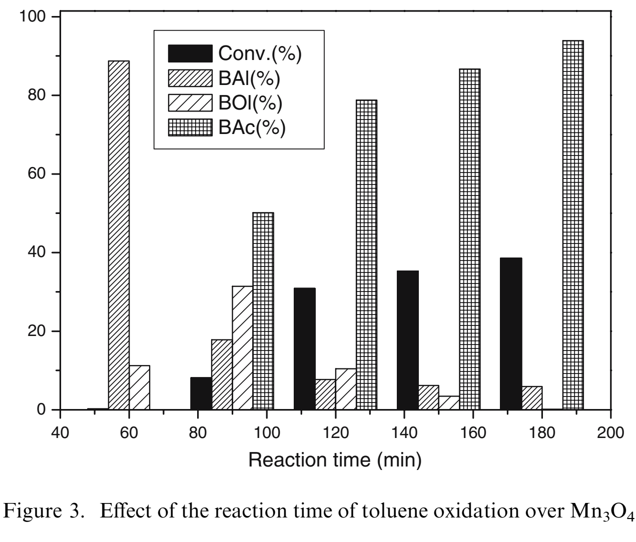

Figure 3. Effect of the reaction time of toluene oxidation over Mn_3O_4.

We conducted recycle tests of catalyst Mn_3O_4 to investigate whether it could be reusable or not. After the reaction, the catalyst was filtered and washed with deionized water and ethanol for several times, then dried at 373 K for 4 h to remove ethanol and used for another reaction. In the second run, the conversion and the selectivity of benzoic acid were 36.4 and 89.3%, both being similar with that of the first run. The XRD patterns (figure 2, line d) of the catalyst before and after reaction are just the same, which can also prove the catalyst structure remains stable after reaction.

4. Conclusions

In summary, we found that manganese oxides could act as efficient heterogeneous catalyst for the liquid phase oxidation of toluene to benzoic acid by molecular oxygen without any additive or solvent. Among the different kinds of manganese oxides, Mn_3O_4 has the highest activity, and the catalyst is easily recovered and recycled.

Acknowledgments

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