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Article

Au/ γ -MnO₂ catalyst for solvent-free toluene oxidation with oxygen

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ARTICLE INFO

Article history:

Received 12 April 2013

Accepted 3 June 2013

Published 20 September 2013

Keywords:

Manganese dioxide

Nano-gold catalyst

Toluene oxidation

Solvent-free

ABSTRACT

α -, δ -, and γ -MnO₂ were synthesized by a redox method and Au/ γ -MnO₂ catalysts with different Au loadings (0.5%–3.0%) were synthesized by an in situ reduction method. The supports and catalysts were characterized by X-ray diffraction, scanning electron microscope, transmission electron microscopy (TEM), and N₂ adsorption. TEM images showed that the Au particles were about 10 nm. The catalysts were used in solvent-free toluene oxidation with oxygen. The results showed that toluene conversion increased with increasing Au loading, which was ascribed to the increasing amount of Au particles and also the smaller Au particles. The Au loading gave a uniquely high selectivity to benzaldehyde. The Au/ γ -MnO₂ catalysts exhibited good reusability in liquid phase toluene oxidation.

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1. Introduction

Selective oxidation of hydrocarbons has been studied for its industrial, scientific and commercial values [1]. Toluene oxidation has received a lot of attention. All the toluene derivatives, such as benzyl alcohol, benzaldehyde, benzoic acid, and benzyl benzoate, are commercially significant versatile intermediates in the manufacture of pharmaceuticals, dyes, solvents, perfumes, plasticizers, and preservatives. Although the toluene oxidation technology seems mature, there still remains a challenge [2]. Industrially, toluene oxidation is catalyzed by a homogeneous metal salt catalyst using a halogenic or acidic solvent because of the advantage of high conversion, but the use of such solvents and a homogeneous catalyst cause pollution and waste [3,4]. Thus, a solvent-free method for toluene oxidation catalyzed by a heterogeneous catalyst has attracted attention. There are already some studies on the solvent-free oxidation of toluene. Li et al. [5] used different manganese oxides as catalyst to directly oxidize toluene to benzoic acid with molecular oxygen and obtained a conversion of 39% using Mn₃O₄ as catalyst.

With MnO₂ catalyst, a conversion of 6.5% was reached but the main product was changed to benzaldehyde. The Hutchings group [6] used a Au-Pd/C catalyst and reached higher conversion of 50% after reaction for 48 h at 160 °C with benzyl benzoate as the main product. These findings suggested that noble metals and manganese oxides are good candidates for solvent-free toluene oxidation.

Manganese oxides have been studied for decades. It is well known as a material for clean energy storage due to its low material cost, acceptable environmental characteristics, and chemical stability [7,8]. Recently, the modification of their crystal forms, particle size, and morphology have received a lot of attention. The MnO₂ crystal structure of both natural manganese ores and synthetic crystals exist in five main different crystal forms and more than thirty kinds of secondary crystals. Three of the five different forms, α (2×2 tunnel structure), γ (1×1 and 1×2 tunnel structure), and δ (layer structure), are also called manganese oxide octahedral molecular sieves (OMS) [9]. The basic unit of OMS uses a manganese atom and six oxygen atoms to form hexagonal close packing structure and cubic

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This work was supported by the National Natural Science Foundation of China (21276050).

DOI: 10.1016/S1872-2067(12)60633-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 9, September 2013

closest packing structure. The MnO_6 octahedra can share their edges and vertices to generate a wide range of periodic structure. The structure obtained depends on the preparation conditions and the presence of specific cations in the solution [10]. Therefore, different ion exchange and adsorption capacities are obtained.

Au was believed to be an inert metal in catalysis until Haruta et al. [11] used small (< 5 nm) Au particles as a catalyst for CO oxidation at low temperature. This led to a boom in research in the field of Au catalysis. The size and nature of Au particles, and also their practical applicability in catalytic reactions have received a great deal of attention [12]. Most Au catalysts were used in three kinds of reactions: CO oxidation, alkene epoxidation, and selective oxidation of alkanes. Many factors are known to affect Au activity, such as particle size and geometric structure, type of support, methods of preparation, calcination, and washing, and the presence of trace compounds (water, hydroxyls, Na, Cl). Jana et al. [13] obtained a variety of Au particles of different size (from 5 to 40 nm) by changing the capping agents, reducing agent, and some other conditions. However, their report did not mention any excellent catalytic effect and did not include a practical way to load Au particles on supports. Chen et al. [14,15] reported that in CO oxidation, Au particles loaded on metallic oxide have high efficiency when they are of the size between 2.5 and 3.5 nm. However, their study did not provide a convenient method to get this catalyst. Other metallic oxides used as support include zirconia [16], cerium oxide [17], iron oxide [18], magnesium oxide [19], and titanium oxide [20]. All of these showed excellent catalytic effects. Therefore, it would be a good choice to synthesize a catalyst using nanosized Au particles as active centers and manganese (IV) oxide as support.

In our previous study [21], we synthesized ultra fine supported Pd nanoparticles as the catalyst, studied their performance for solvent-free selective toluene oxidation with air, and obtained a toluene conversion of 10% at 200 °C. Another finding was that the toluene conversion increased with the concentration of oxygen in the air without significant change in the product composition. To continue this study, in this paper, we prepared three kinds of MnO_2 nanostructure (α -, γ -, δ - MnO_2) by a redox method and from these, we chose γ - MnO_2 as the support. Au/ γ - MnO_2 catalysts with different Au loadings were prepared by a technique of in situ reduction. The samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N_2 adsorption. Finally, we studied the efficiency of this Au/ γ - MnO_2 catalyst in catalytic toluene oxidation with oxygen, which has not been reported yet.

2. Experimental

2.1. Preparation of MnO_2 nanoparticles and Au/ MnO_2 catalyst

All three kinds of manganese oxide, α -, γ -, and δ - MnO_2 , were prepared by the redox reaction of Mn^{2+} and Mn^{7+} but with varying reaction conditions. In the synthesis of α - MnO_2 , 0.338 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was dissolved in 20 ml deionized water. The solu-

tion was fully mixed at 90 °C, and then 6 ml concentrated nitric acid was added. Under vigorous stirring, 60 ml of aqueous KMnO_4 (0.5 mol/L) was dropped into the mixture. After refluxing for 10 h, a deep brown product was finally obtained. It was then centrifuged and washed several times with deionized water to remove residual reactants. The product was dried at 65 °C for 16 h. γ - MnO_2 was synthesized by mainly following the procedure of Yu et al. [22]. A known amount of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was dissolved in 100 ml deionized water. Under vigorous stirring at 80 °C in a water bath, 1 ml of concentrated sulfuric acid was added, and 60 ml of aqueous KMnO_4 (0.1 mol/L) was then added by dripping. After additional stirring at 80 °C for 24 h, a black product was obtained. Finally, the product was centrifuged, washed and dried in a similar way to that of α - MnO_2 . To prepare the δ - MnO_2 nanostructure, 0.338 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was first dissolved in 20 ml deionized water. Then 6 ml concentrated nitric acid was added and the mixture was heated to 60 °C. KMnO_4 (0.33 mol/L) was dropped into the solution under stirring, and after refluxing of 24 h, a black product was obtained. Finally, the mixture was centrifuged, washed and dried as with α - MnO_2 .

Au/ γ - MnO_2 catalyst was prepared by an in situ reduction method. Chloroauric acid and ascorbic acid were used as precursor and reductant, respectively. PVP of 0.204 g was dissolved in 300 ml H_2O and heated in a water bath with stirring. At 80 °C, the required amount of aqueous chloroauric acid was added into the solution by dripping. After stirring, 0.9 g of MnO_2 powder, which was dispersed in 150 ml of deionized water by ultrasonic treatment, was added into the solution. Six hours later, 30 ml aqueous ascorbic acid (0.01 mol/L) was dropped into the mixture and stirred for another 1 h. Finally, the product was obtained by filtration and washed several times with deionized water until the filtrate did not react with AgNO_3 solution. Then absolute alcohol was used to remove any residual reactants. Finally, the product was dried at 60 °C for 16 h. Au/ γ - MnO_2 samples with different Au loadings were obtained by changing the amount of chloroauric acid and were labeled as n Au/ γ - MnO_2 , where n referred to the mole percentage of loaded particles on γ - MnO_2 ($n = 0.5\%, 1.0\%, 1.5\%, 2.0\%, 3.0\%$).

2.2. Catalyst characterization

XRD characterization of MnO_2 and Au/ MnO_2 samples was carried out on a Bruker D8 Focus X-ray diffractometer using $\text{Cu K}\alpha$ radiation and a nickel filter ($\lambda = 0.15406$ nm) with a voltage and current of 40 kV and 40 mA, respectively. SEM images were obtained from a Hitachi S-4300 field emission scanning electron microscope operated at 10 kV. TEM studies were performed with a FEI Tecnai G2 transmission electron microscope. The sample was prepared by grinding and ultrasonic dispersal in ethanol solution, placed on a copper TEM grid, and the solvent evaporated. N_2 adsorption isotherms were determined at -196 °C with an automatic Beishide 3H-2000 instrument after a pretreatment under vacuum at 300 °C for 3 h. The specific surface area was determined by the BET method, and the total pore volume was the volume adsorbed at $p/p_0 = 0.99$. The average pore size was calculated from the analysis of the desorp-

tion branch of the N_2 isotherm using the BJH method.

2.3. Solvent-free toluene oxidation

Selective oxidation of toluene was performed in an autoclave (50 ml) with mechanical stirring. After the vessel was charged with 30 ml of toluene and 300 mg of catalyst, it was filled with pure oxygen to a desired initial pressure of 1.0 MPa. The reaction time was measured as soon as the temperature reached 160 °C. After reaction for 8 h, the reaction mixture was cooled and collected. The products were analyzed by an Ouhua GC 6890 gas chromatograph equipped with an FID and a capillary column (SE-54). Nitrogen was the carrier gas with a flow rate of 6.6 ml/min. The injector and detector temperatures were 300 and 310 °C, respectively. The oven temperature program was: start at 100 °C, ramp at 30 °C/min to 260 °C, keep for 1 min. The results were compared with those of known commercial pure standard samples. Conversion and product selectivity were calculated based on the carbon balance with calibration curves.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD results

The XRD patterns of the three different manganese oxides are shown in Fig. 1. The crystal form of α - MnO_2 matches cryptomelane-M, a kind of α - MnO_2 with a space group of $I2/m$ (12) (JCPDS Card No. 44-1386), which shows peaks at 2θ of 12.8° (101), 17.8° (200), 28.6° (301), 37.4° (211), 41.6° (310), 49.5° (411), 59.9° (512), 65° (020), and 69.7° (514). The weak diffraction peaks of δ - MnO_2 indicated low crystallinity. The peaks at 2θ of 37° (111) and 66.2° (020) matched those of the single inclined phase δ - MnO_2 with a space group of $C2m/12$ (JCPDS Card No. 80-1089, $a = 0.5149$ nm, $b = 0.2843$ nm, $c = 0.7176$ nm). In the XRD patterns of γ - MnO_2 and 1.5% Au/ γ - MnO_2 catalyst, some broad peaks and some sharp peaks were observed, as well as shifting in the positions of the peaks. Broadening of

Fig. 1. XRD patterns of three MnO_2 samples and Au/ γ - MnO_2 catalyst. (1) α - MnO_2 ; (2) δ - MnO_2 ; (3) γ - MnO_2 ; (4) 1.5% Au/ γ - MnO_2 .

diffraction peaks occurs when certain types of random intergrowth of pyrolusite (1×2 tunnel structure) and ramsdellite (1×2 tunnel structure) manganese dioxide exist, based on the “de Wolff model” published in 1959 [23]. After comparison with the reference data for the IBA-11 XRD patterns [24], the sample of Fig. 1(3) was confirmed to be a crystal form of γ - MnO_2 . On the other hand, Fig. 1(4) shows a similar XRD pattern to Fig. 1(3) except that it has the peaks at 2θ of 38.5° (111), 44.8° (200) due to the Au particles (JCPDS Card No. 1-1172). This indicates that the loading of Au particles did not change the crystal parameters of MnO_2 . The size of the Au particles on the MnO_2 support was larger than 4 nm. The XRD patterns of α -, δ -, and γ - MnO_2 showed that an increasing synthesis temperature led to better crystallinity of the MnO_2 nanostructure.

3.1.2. Surface morphology and crystalline structure of MnO_2 nanostructure

Figure 2 shows SEM and TEM images of the three MnO_2

Fig. 2. SEM (a, c, e) and TEM (b, d, f, g, h) images of the three MnO_2 samples. (a, b) α - MnO_2 ; (c, d) δ - MnO_2 ; (e, f) γ - MnO_2 ; (g, h) HRTEM images of γ - MnO_2 .

nanostructure. The α - MnO_2 sample synthesized at 90 °C looked like thick sticks on a scale of 500 nm and all the units were disordered. This was also confirmed by Fig. 2(b), in which the diameter of nanorods ranged from 20 to 40 nm. This α - MnO_2 sample has been verified by the XRD pattern with the clear lattice structure shown in Fig. 1(1). A different surface morphology for δ - MnO_2 was observed from Fig. 2(c), which was synthesized at 60 °C. Both the SEM and TEM images (Fig. 2(c) and (d)) demonstrated that the nanorods were much slimmer than those of α - MnO_2 . Although they grew equally and orderly, the crystalline structure was not obvious in the XRD pattern (Fig. 1(2)), and this gave rise to some doubt about its capacity for loading metal. Figure 2(e) shows more homogeneous nanostructure than Fig. 2(a) and stouter nanorods than Fig. 2(c), which showed that this kind of MnO_2 should be chosen as a better catalyst support than the first two. From Fig. 2(f), we observed broken lattice fringes and stick structure, which is one of the structural features of γ - MnO_2 [25]. The high resolution transmission electron microscopy (HRTEM) image of these nanorods (Fig. 2(g)) synthesized at 80 °C showed an accurate lattice distance. As presented in the image, 0.37 nm is approximately the surface dimension of the nanorods. Based on this data, the image of Fourier transform (Fig. 2(h)) showed the (201) plane. All these features matched the 1×2 tunnel structure of γ - MnO_2 . This conclusion also matched the XRD pattern.

Figure 3 shows the images of the Au/ γ - MnO_2 catalyst samples with different Au loadings. Compared with the 0.5%

Au/ γ - MnO_2 sample (Fig. 3(a)), an increase in Au particle amount per unit area was seen in the picture of the sample with 1.5% Au loading. At the same time, the size of the Au particles also decreased from 25.7 to 10.4 nm as shown in Fig. 3(b) and (d). The size of the Au particles in the 1.5% Au/ γ - MnO_2 catalyst was larger than 4 nm, which was also indicated by the XRD results. However, on the other hand, the size of the Au particles was inhomogeneous in Fig. 3(d). In Fig. 3(e), the density of Au particles increased to almost twice of that in Fig. 3(a). With the Au loading percentage of 2%, the Au/ γ - MnO_2 catalyst showed the largest density of Au nanoparticles. At the same time, according to Fig. 3(f), the size of the Au particles did not changed much compared with the 1.5% Au/ γ - MnO_2 catalyst. In other words, a higher Au loading amount can give high particle dispersion but had negligible effect on decreasing the size of the Au particles after the loading was larger than 1.5%.

3.1.3. N_2 adsorption

The surface area, pore size, and total pore volume of the three MnO_2 samples were calculated. The BET surface areas of α - MnO_2 , δ - MnO_2 , and γ - MnO_2 were 63, 16, and 65 m^2/g , respectively. γ - MnO_2 has the largest BET surface area, which is much larger than that of the γ - MnO_2 sample (18 m^2/g) synthesized by Jin et al. [25]. The average pore size of the three samples was obtained by the BJH method, which was 21.7, 6.0, and 20.0 nm, respectively. The pore size distribution confirmed the mesoporous structure of the samples. The total pore volume of the three different MnO_2 materials was 0.30, 0.07, and 0.17 ml/g, respectively. The pore volume of our synthesized γ - MnO_2 was much higher than that of the sample (0.0197 ml/g) prepared by Jin et al. [25]. These results also confirmed that γ - MnO_2 is a suitable support for loading Au particles.

3.2. Toluene oxidation with oxygen

The catalytic properties of both unsupported and supported manganese dioxide are listed in Table 1 together with the results of blank tests. The oxidation of toluene was negligible without a catalyst. Supported catalysts gave better catalytic activity. As compared with our previous study [21], higher toluene conversion was observed even on unloaded manganese dioxide. On the other hand, loaded manganese dioxide provided the best benzaldehyde selectivity while the conversion was improved as well. These observations showed that loading Au nanoparticles increased catalytic activity and also gave a uniquely high selectivity to benzaldehyde. Therefore, our further study was mainly focused on the Au/ γ - MnO_2 catalyst.

Table 1

Liquid phase oxidation of toluene with oxygen catalyzed by MnO_2 and Au/ γ - MnO_2 catalysts.

Catalyst	Conversion (%)	Selectivity (%)			
		PhCH ₂ OH	PhCHO	PhCOOH	PhCO ₂ CH ₂ Ph
α - MnO_2	4.2	12.2	49.4	trace	38.4
γ - MnO_2	4.6	trace	55.6	17.4	27.0
δ - MnO_2	4.8	10.6	46.6	trace	42.8
1.5% Au/ γ - MnO_2	13.5	3.5	64.1	16.8	15.6
Blank	0.2	13.3	76.5	10.2	—

Fig. 3. TEM images of the distribution and particle size of Au/ γ - MnO_2 samples. Au loading: (a, b) 0.5%; (c, d) 1.5%; (e, f) 2%.

Fig. 4. Toluene conversion (1) and selectivity for benzyl alcohol (2), benzaldehyde (3), benzoic acid (4), and benzyl benzoate (5) versus Au loading on Au/γ-MnO₂ catalyst.

3.2.1. Influence of Au loading on toluene oxidation

Figure 4 shows the effect of Au loading on toluene oxidation. First, even though benzaldehyde selectivity was decreased when more Au particles were loaded on the support, the supported Au catalysts still gave the highest values. This confirmed the result that the introduction of Au particles helped the transforming of toluene into benzaldehyde. Second, with increasing Au loading, toluene conversion increased from 5.9% to 16.2%, especially between the loadings of 0.5% and 1.5%. Third, the selectivity to benzoic acid decreased nearly 10%, while the other two products increased. There was a distinct rise in benzyl benzoate selectivity between loadings of 0.5% and 2.0%. All these trends showed that even though the adding of more Au particles failed to improve toluene conversion by a lot, it keeps benzaldehyde selectivity high. This result also matched well with the study of Hutchings et al. [6]. According to the TEM images (Fig. 3), the size decrease of Au particles with Au loadings from 0.5% to 1.5% was much sharper than that occurring from 1.5% to 2.0%. Meanwhile, the increase in toluene conversion between 0.5% and 1.5% was much more than that of 1.5% and 2% in Fig. 4. We inferred that the decreasing Au particle size also contributed to increasing toluene conversion in addition to the contribution from the increased loading. Table 2 shows the TOF values based on the total Au loading. We can see that Au has enhanced the catalytic activity a lot. It is also very clear that the size of the Au particle is a crucial factor influencing catalyst activity. The TOF values of the smaller Au particles (9–10 nm) were much bigger than these of

the larger ones (25 nm). The slightly lower TOF value of 2.0% Au/γ-MnO₂ than that of 1.5% Au/γ-MnO₂ was probably due to the decrease of Au particle dispersion with the increase of Au loading [26]. This influence of Au particle size on the catalytic activity is similar to the findings of Valden et al. [27]. As revealed by Kesavan et al. [6], the low coordination number corner and/or edge positions are implicated as active sites for toluene oxidation. Their relatively higher occurrence in the Au/γ-MnO₂ samples with smaller Au particle size can account for the superior performance displayed by these catalysts. However, the active sites of supported Au catalysts are not clearly known even in the well investigated reaction of CO oxidation. Most studies showed that the catalytic activity depended on the particle size and shape, and the reaction mainly takes place at the Au-support interface [28,29]. According to the mechanism of liquid phase toluene oxidation, this reaction is a free radical autoxidation with the recycling of the redox of γ-MnO₂ between Mn(IV) and Mn(III) [25]. Because the specific activities of these Au/γ-MnO₂ catalysts were much higher than that of a Au/C catalyst (TOF = 1.6) [6], it is likely that the interaction of Au and the γ-MnO₂ support is very strong, which would enhance the redox property of γ-MnO₂ a lot. This enhancement successfully converted more toluene into products but did not convert it into a deeper oxidation product. Thus the selectivity to the light oxidation products such as benzyl alcohol and benzaldehyde increased while those of the deep oxidation products such as benzoic acid and benzyl benzoate decreased when Au particles were loaded on γ-MnO₂. However, on the other hand, the selectivity to benzaldehyde showed a small decline while that of deep oxidation products, benzyl benzoate and benzyl alcohol, increased as the Au particle size got smaller. This revealed another aspect of the smaller Au particle, i.e., it led the reaction to deeper stages and transformed benzaldehyde to deeper oxidation products.

3.2.2. Catalyst reusability

Table 3 shows the results of a series of experiments designed to verify the stability and reusability of the 1.0% Au/γ-MnO₂ catalyst. The 300 mg catalyst was first used in an 8 h experiment and then recycled by centrifuging several times. After careful washing and drying, the recycled catalyst was reused for the next cycle. According to the data in Table 3, the 1.0% Au/γ-MnO₂ catalyst kept a good catalytic effect in the first three experiments, which was revealed by the almost constant toluene conversion. However, an obvious drop in toluene conversion appeared in the third recycle. At the same time, benzaldehyde selectivity also decreased with increasing recycle.

The decrease in the conversion may be caused by Au parti-

Table 2

Catalytic performance of Au/γ-MnO₂ catalysts with different loadings.

Catalyst	Au size (nm)	TOF ^a (h ⁻¹)
γ-MnO ₂	—	0.5
0.5% Au/γ-MnO ₂	25.7	27.0
1.5% Au/γ-MnO ₂	10.4	62.7
2.0% Au/γ-MnO ₂	9.1	54.8

^a Turnover frequency calculated based on the total Au loadings by (mole of initial toluene × (conversion of Au/γ-MnO₂ – conversion of γ-MnO₂))/(mole of Au metal × 8 h).

Table 3

Toluene oxidation over recycled 1.0% Au/γ-MnO₂ catalyst.

Recycle time	Conversion (%)	Selectivity (%)			
		PhCH ₂ OH	PhCHO	PhCOOH	PhCO ₂ CH ₂ Ph
0	8.6	1.7	65.5	21.7	11.1
1	8.4	3.1	66.2	20.9	9.8
2	7.9	4.2	62.1	18.3	15.4
3	5.3	6.6	55.2	16.4	21.8
4	5.2	7.8	53.9	15.2	23.1

Graphical Abstract

Chin. J. Catal., 2013, 34: 1683–1689 doi: 10.1016/S1872-2067(12)60633-0

Au/ γ -MnO₂ catalyst for solvent-free toluene oxidation with oxygen

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Well dispersed Au/ γ -MnO₂ catalysts have been prepared by an in situ reduction method. They showed unique selectivity towards benzaldehyde in toluene oxidation.

cle leaching off the support because of the repeated washing. Most Au particles are held by an electrostatic force on the surface of the MnO₂ support, therefore, frequent washing and shaking easily cause the leaching of loaded Au particles. That the toluene conversion and product selectivity of the fourth recycled Au/ γ -MnO₂ was almost the same as that of γ -MnO₂ also indicated the leaching of Au particles. The decreasing benzaldehyde selectivity once again confirmed the unique selectivity contribution of Au particles.

4. Conclusions

γ -MnO₂ was the best support for the highly dispersed Au/ γ -MnO₂ catalyst because of its unique morphology and suitable surface area. The Au loading affected the dispersion and size of Au particles on the surface of the γ -MnO₂ nanorods, and the Au particles were about 10 nm when the Au loading was higher than 1.5%. All three kinds of MnO₂ and the Au/ γ -MnO₂ catalyst were catalytically active for solvent-free toluene oxidation, and the Au/ γ -MnO₂ catalyst showed the best activity. The increasing toluene conversion with the increase of Au loading was not only due to an increasing amount of Au particles, but was also due to having a smaller Au size. Moreover, smaller Au particles tended to promote the reaction into deeper oxidation. The Au/ γ -MnO₂ catalyst showed good reusability in toluene oxidation. However, the supported particles leached out after recycling several times.

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Au/ γ -MnO₂ 催化剂催化无溶剂条件下甲苯氧化反应

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摘要: 采用氧化还原法制备了 α , δ , γ - MnO_2 载体, 采用原位还原法制备了Au负载量为0.5%–3.0%的Au/ γ - MnO_2 催化剂, 并采用X射线衍射、扫描电镜、透射电镜和 N_2 物理吸附等手段对其进行了表征. 透射电镜照片表明Au/ γ - MnO_2 催化剂中Au颗粒的大小约为10 nm. 采用无溶剂存在下的甲苯氧化反应测试所制备样品的催化活性. 结果表明, 甲苯转化率随着Au负载量的增加而增大. 这是由于Au颗粒数量增多, 尺寸减小的缘故. 同时, 负载Au颗粒对苯甲醛具有较高的选择性. Au/ γ - MnO_2 催化剂具有良好的重复使用性.

关键词: 二氧化锰; 纳米金催化剂; 甲苯氧化; 无溶剂

收稿日期: 2013-04-12. 接受日期: 2013-06-03. 出版日期: 2013-09-20.

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基金来源: 国家自然科学基金(21276050).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).