available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Removal of high concentrations of formaldehyde in industrial exhaust by catalytic oxidation

Richu Wei ^{a,b}, Honglin Chen ^b, Xiaoming Zhang ^{b,*}, Jishuan Suo ^b^a University of Chinese Academy of Sciences, Beijing 100049, China^b Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, Sichuan, China

ARTICLE INFO

Article history:

Received 24 May 2013

Accepted 16 August 2013

Published 20 October 2013

Keywords:

Platinum-ceria/activated carbon catalyst

Formaldehyde waste gas

Glyphosphate production

Formaldehyde removal

ABSTRACT

A Pt-CeO₂/AC catalyst was developed for the removal of high concentrations of formaldehyde (HCHO) in industrial exhaust under mild conditions. The HCHO removal was integrated into a *N*-(phosphonomethyl)glycine production process to remove in situ the high concentrations of HCHO in its exhaust stream. The HCHO produced and emitted (100–300 mg/m³) in *N*-(phosphonomethyl)glycine synthesis was completely removed by passage through the catalyst bed. The effects of temperature, space velocity, and HCHO content on removal efficiency were systematically studied. Almost all the HCHO was oxidized at gas hourly space velocities (GHSV) below 20000 h⁻¹, and the HCHO content was decreased to below 0.1 mg/m³, that is, the HCHO conversion rate was 99.10%–100%. When the GHSV was in the range of 30000–50000 h⁻¹ and the catalyst bed temperature was 12 °C, the HCHO content in the treated gas was still less than 1.5 mg/m³, and the HCHO conversion rate was 97.56%–99.99%. The 1%Pt-4%CeO₂/AC catalyst is now in the pilot phase of its use in treating glyphosphate production exhaust gas containing high concentrations of HCHO, and good initial progress has been made. The concentrations of HCHO in the treated industrial exhaust were less than 10 mg/m³, which effectively has no HCHO health hazard, and there are good prospects for industrialization.

© 2013, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Formaldehyde is an important chemical widely used in many industries to manufacture building materials and household products. It is also a byproduct of combustion and chemical processes. The emission of formaldehyde can cause serious damage to the environment and humans. It is a known carcinogen. Many studies have been carried out on the abatement and removal of formaldehyde from the atmosphere, and a number of effective methods have been developed. These include catalytic oxidation [1–20], adsorption purification [21–25], plasma purification [26], and HCHO capture [27–30]. Most of these studies focused on the removal of formaldehyde from indoor environments, in which the concentration of HCHO

is several mg/kg. In addition to emissions from building projects and decorative materials, waste exhaust gases from industrial processes, such as those used to produce chemicals, electronics, medical products, and pesticides are sources of high concentrations of formaldehyde. In these cases, several hundred or even several thousand mg/kg of formaldehyde are present in the exhaust gas stream. The recovery cost is very high, and its direct emission into the atmosphere can cause serious health problems. The methods described above, which were developed for indoor formaldehyde removal, are not suitable for the treatment of industrial waste gases because the concentrations of formaldehyde are too high and the corresponding treatment costs are unacceptable.

Pt catalysts have been widely researched for the removal of

* Corresponding author. Tel: +86-28-85226215; Fax: +86-28-85223978; E-mail: xm.zhang@cioc.ac.cn

formaldehyde at room temperature [31–36]. A 1 wt% Pt/TiO₂ catalyst was shown to be effective for HCHO oxidation at room temperature, and 100% conversion of HCHO (100 mg/kg) was achieved at a gas hourly space velocity (GHSV) of 50000 h⁻¹ [37,38]. Pt/CeO₂ catalyst with 3 wt% Pt can catalyze the oxidation of HCHO (500 mg/kg) to CO₂ and H₂O at a GHSV of 60000 h⁻¹ at 100 °C [39]. A Na-Pt/TiO₂ catalyst was effective for the conversion of HCHO (600 mg/kg) to CO₂ and H₂O at a GHSV of 120000 h⁻¹ [40]. All these catalysts were Pt catalysts supported on a metal oxide, and the catalyst prices were high due to the high content of Pt. Recently, an efficient Pt-CeO₂/AC (AC: activated carbon) catalyst was developed for in situ removal of formaldehyde for the treatment of glyphosphate waste solution using a combined vacuum-distillation and catalytic oxidation process. The addition of Ce into the Pt catalyst increased the catalytic activity and decreased the catalyst price [41]. The high concentration of formaldehyde vapor formed during the distillation was directly oxidized to CO₂ and H₂O under mild conditions in the presence of air and the catalyst. In the present study, the Pt-CeO₂/AC catalyst was used for the catalytic oxidation of waste gases containing high concentrations of formaldehyde produced during glyphosphate production. In this process, formaldehyde was produced during the air oxidation of *N*-(phosphonomethyl)iminodiacetic acid to *N*-(phosphonomethyl)glycine (i.e. glyphosphate), an important herbicide. By installing a Pt-CeO₂/AC catalyst column in the outlet stream of the glyphosphate synthesis, the high concentration of formaldehyde in the exhaust gas stream was directly oxidized to CO₂ and H₂O, and the concentration of formaldehyde was decreased from several hundred mg/m³ to below 1 mg/m³.

2. Experimental

2.1. Catalyst preparation

First, 2.0 g of Ce(NO₃)₃·6H₂O was dissolved in 200.0 ml of deionized water with stirring. Then 20.0 g of AC (20–60 mesh) was added. After stirring for 18 h, the sample was filtered, washed with deionized water, dried in vacuum at 125 °C for 5 h, and calcined at 350 °C in nitrogen atmosphere for 2 h. The sample produced was designated CeO₂/AC.

For depositing Pt on the catalyst, 20.0 g of CeO₂/AC sample was dispersed in 200.0 ml of deionized water, and 26.6 ml of H₂PtCl₆ solution (3.75 mg/ml) was added dropwise under stirring. Then the pH of the solution was adjusted to 10.5 with aqueous NaOH solution. After stirring continuously overnight, the sample was filtered, washed with deionized water, and dried in vacuum at 125 °C for 8 h. The Pt-CeO₂/AC catalyst was obtained by reducing the sample at 400 °C with H₂ (20% in N₂) for 5 h.

2.2. Catalyst characterization

The metal content of the catalysts was determined using an X Series II device (Perkin Elmer Company, USA). N₂ adsorption isotherms were obtained with an SSA-4200 specific surface area and pore size analyzer (Builder Company, China). The

fresh catalysts were further characterized using X-ray photoelectron spectroscopy (XPS, XSAM 800 photoelectron spectroscope, Kratos Company, Britain). The average particle size was obtained using a high resolution transmission electron microscope (HRTEM) and a Tecnai G² F20 S-Twin device (FEI Company, Germany) with 200 kV accelerating voltage. The phase structure of the catalysts was characterized with an X'pert Pro MPD XRD (PANalytical Company, Holland) using Cu K_α (λ = 0.15406 nm) radiation.

2.3. Activity test

The exhaust tail gas containing high concentrations of HCHO was produced during the air oxidation of *N*-(phosphonomethyl)iminodiacetic acid to *N*-(phosphonomethyl)glycine in an autoclave. This gas was treated with the Pt-CeO₂/AC catalyst. HCHO in untreated gas and treated gas that had passed through a packed bed of the Pt-CeO₂/AC catalyst was adsorbed using a bubble absorption tube with distilled water. Then the absorbance of the adsorbed water was measured using an ultraviolet visible spectrophotometer (UV-2000, USA), and the concentration of HCHO was calculated [42].

3. Results and discussion

3.1. Catalytic performance of 0.5%Pt-4%CeO₂/AC catalyst

The reaction of the AC-catalyzed air oxidation of *N*-(phosphonomethyl)iminodiacetic acid (PMIDA) to *N*-(phosphonomethyl)glycine (PMG) is as follow:

Formaldehyde was gradually produced in the reaction. Most of the HCHO was dissolved in the liquid phase, and the final concentration of HCHO in the reaction stream was about 2%–3% when the initial concentration of *N*-(phosphonomethyl)iminodiacetic acid was 25%. Due to its high volatility, HCHO was inevitably emitted into the exhaust stream of the oxidation autoclave. In order to simulate the experimental conditions of PMG production and evaluate the catalytic performance of the 0.5%Pt-4%CeO₂/AC catalyst, 300 g of 2.5% HCHO solution was placed in the autoclave, air was fed into the autoclave at 0.6 MPa and 65 °C, and the exhaust stream was passed through the 0.5%Pt-4%CeO₂/AC catalyst bed. The concentrations of HCHO before and after passage through the catalyst bed were analyzed quantitatively. The results are listed in Table 1. The concentration of HCHO in the exhaust of the autoclave increased almost linearly as the air flow rate increased. Almost all the HCHO was oxidized when the GHSV was below 20000 h⁻¹, and the HCHO content in the treated exhaust stream was below 0.1 mg/m³, which was far lower than the emission standard for an industrial exhaust. Further increases in the rate of air flow led to an increase in the HCHO concentration in the treated exhaust stream. The catalyst activity was about 325 nmol/(g·h) for the complete removal of HCHO.

3.2. Catalytic performance of 1%Pt-4%CeO₂/AC catalyst

Table 1

Treatment of air contaminated with HCHO at 25 °C.

Air flow rate (ml/min)	HCHO content (mg/m ³)		GHSV (h ⁻¹)	Conversion (%)	Catalytic activity (nmol/(g·h))
	Before treatment	After treatment			
400	15.6	—	4 000	100.00	4.5
600	58.3	—	6 000	100.00	25.0
800	75.0	—	8 000	100.00	42.9
1000	100.0	0.02	10 000	99.98	71.4
1500	140.0	0.03	15 000	99.98	150.0
2000	227.5	0.10	20 000	99.96	324.9
3000	300.6	10.5	30 000	96.51	621.6

Experimental conditions: 0.5%Pt-4%CeO₂/AC (20–60 mesh) catalyst 6 ml (2.8 g). By changing the air flow rate, the GHSV was 4000–30000 h⁻¹.

Based on these experimental results, the catalytic oxidation of HCHO was integrated into the process of *N*-(phosphonomethyl)glycine synthesis. In a typical procedure, 80.0 g of PMIDA, 12.7 g of activated carbon, and 240 g of distilled water were added to a 500 ml autoclave. The autoclave was sealed, the temperature was increased to 65 °C, and the rotational speed was increased to 800 r/min. Then 400 ml/min of air at 0.6 MPa pressure was fed into the autoclave and the reaction was initiated. The vent gases of the autoclave were introduced directly into a packed bed of 1%Pt-4%CeO₂/AC catalyst. The HCHO contents at the inlet and outlet of the catalyst bed were analyzed and the HCHO conversion was calculated.

The oxidation of PMIDA to PMG was carried out in a batch manner. The reaction was terminated when the conversion of PMIDA reached about 98% because prolonging the reaction further can decrease the PMG yield. Under these reaction conditions, the oxidation reaction was complete within 170 min. The HCHO content versus time in the exit stream of the autoclave is shown in Table 2. The HCHO concentration increased gradually and reached a maximum at the end of the reaction. The exit stream of the oxidation autoclave was introduced directly into the 1%Pt-4%CeO₂/AC catalyst bed. The HCHO conversion versus time in the outlet stream of the catalyst bed during the reaction period at different temperatures is shown in Fig. 1. The HCHO in the gas stream from the oxidation of PMIDA was completely oxidized as it passed through the catalyst bed, and the HCHO concentrations in the treated waste gases were below 0.1 mg/m³ throughout the reaction period. A lower temperature in the catalyst bed gave a higher performance with respect to removing HCHO, but the difference was small.

The amount of catalyst was changed in order to assess the dependence of HCHO removal efficiency on the gas hourly space velocity. Figure 2 shows the HCHO conversions at different GHSVs throughout the PMIDA oxidation period. During the initial stage of the oxidation reaction, the HCHO concentrations in the treated stream were very low when the GHSV was varied

from 20000 to 50000 h⁻¹. Differences appeared gradually as the reaction continued. At the end of the oxidation reaction, the HCHO content in the treated waste gas was about 1.5 mg/m³ with 98% of conversion when the GHSV was 50000 h⁻¹, which was about 20 times higher than that observed for 20000 h⁻¹ GHSV. This indicates that 30000 h⁻¹ of GHSV was the optimum GHSV value for the present PMIDA oxidation conditions, and the HCHO content in the treated waste gas was reduced to below 0.2 mg/m³. In this case, the catalyst activity was 517 nmol/(g·h), which was consistent with the results in Table 1.

Figure 3 shows the reusability of the catalyst with respect to its ability to remove HCHO from the exhaust stream. The same

Fig. 1. HCHO conversion through the catalyst bed. Reaction conditions: catalyst 1.20 ml (0.41 g), GHSV 20000 h⁻¹. **Fig. 2.** HCHO conversion at different GHSV at the same temperature. Reaction conditions: tail gas speed 400 ml/min, catalyst 1.2 ml, temperature 12 °C. The catalyst volume was decreased over time to increase the gas hourly space velocity.**Table 2**

HCHO content in the tail gas during PMG production.

Reaction time (min)	HCHO content (mg/m ³)
30	7.80
65	25.80
100	53.79
135	109.13
170	174.61

Fig. 3. HCHO conversion at 10 °C during catalyst recycle. Reaction conditions: catalyst 0.80 ml (0.28 g), GHSV 30000 h⁻¹.

catalyst was used repeatedly in different cycles of PMDA oxidation. The HCHO conversion remained higher than 99.9% in all runs, and the HCHO content of the treated gases remained below 0.2 mg/m³, suggesting that the 1%Pt-4%CeO₂/AC catalyst was quite stable and can remove high concentrations of HCHO from the industrial exhaust stream.

Based on the results, 40 kg of 1%Pt-4%CeO₂/AC catalyst was prepared and used to treat the exhaust stream of a PMG production plant. Waste gases containing 100–300 mg/m³ HCHO were fed into the catalyst bed at a flow rate of 3000 m³/h. The HCHO content in the treated stream was below 10 mg/m³, which satisfied the emission standard for an industrial exhaust.

3.3. Characteristics of the catalysts

The metal content and pore structure of the Pt-CeO₂/AC catalysts were characterized. The results are shown in Table 3. The Pt and Ce contents in the catalysts were lower than the amounts of these substances added during catalyst preparation. The physical characteristics of the two catalysts were almost the same.

The XRD patterns of the CeO₂/AC, Pt/AC, and Pt-CeO₂/AC catalysts are shown in Fig. 4. The characteristic peaks of Pt (2θ = 39.8° and 67.5°) were observed in the XRD patterns of Pt/AC

Table 3

Metal contents and pore structure of the Pt-CeO₂/AC (40–80 mesh) catalysts.

Catalyst	Metal contents (wt%)		<i>A</i> _{BET} (m ² /g)	<i>V</i> (cm ³ /g)	<i>D</i> (nm)
	Pt	Ce			
0.5%Pt-4%CeO ₂ /AC	0.35	1.53	810	0.42	1.04
1%Pt-4%CeO ₂ /AC	0.80	2.06	817	0.43	1.04

Fig. 4. XRD patterns of the CeO₂/AC, Pt/AC, and 1%Pt-4%CeO₂/AC catalysts.

and Pt-CeO₂/AC, indicating that Pt was highly dispersed on the catalyst surface.

XPS is a valuable tool for characterizing the electronic properties of a material and its chemical state. Figure 5 shows the XPS spectra of the Pt-CeO₂/AC catalyst for Pt and Ce. The peaks at 71.4 and 74.65 eV were attributed to metallic Pt, and the peaks at 73.1 and 76.4 eV were attributed to the presence of PtO or Pt(OH)₂, and the peaks at 74.71 and 77.9 eV were attributed to the presence of PtO₂ [43,44] (Fig. 5(a)). The peaks at 887.04 and 905.25 eV were typical of Ce³⁺, and the main features of Ce⁴⁺ appeared at 883.07, 890.14, 898.88, 901.65, 908.0, and 917.63 eV [45,46] (Fig. 5(b)). The relative composition of Ce³⁺ was 14.90% and that of Ce⁴⁺ was 85.10%.

4. Conclusions

A Pt-CeO₂/AC catalyst was effective for the removal of high concentrations of HCHO from an industrial exhaust under mild

Fig. 5. XPS spectra of the 1%Pt-4%CeO₂/AC catalyst. (a) Pt 4f; (b) Ce 3d.

Graphical Abstract

Chin. J. Catal., 2013, 34: 1945–1950 doi: 10.1016/S1872-2067(12)60696-2

Removal of high concentrations of formaldehyde in industrial exhaust by catalytic oxidation

Richu Wei, Honglin Chen, Xiaoming Zhang*, Jishuan Suo

University of Chinese Academy of Sciences;

Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences

The Pt-CeO₂/AC catalyst was used to remove the high concentration formaldehyde in industrial exhaust, and the HCHO content in the treated stream dropped below 0.1 mg/m³ at GHSV of 20000 h⁻¹.

conditions. By connecting a packed catalyst bed to the outlet of the oxidation autoclave of a PMG production system, the HCHO in the exhaust stream was completely oxidized as it passed through the catalyst bed. The HCHO content of the treated gas stream was below 1 mg/m³. The catalyst and method can be used in various industrial processes that have high concentrations of formaldehyde.

References

- [1] Spivey J J. *Ind Eng Chem Res*, 1987, 26: 2165
- [2] Scirè S, Minicò S, Crisafulli C, Satriano C, Pistone A. *Appl Catal B*, 2003, 40: 43
- [3] Scirè S, Minicò S, Crisafulli C, Galvagno S. *Catal Commun*, 2001, 2: 229
- [4] Sawyer J E, Abraham M A. *Ind Eng Chem Res*, 1994, 33: 2084
- [5] Papaefthimiou P, Ioannides T, Verykios X E. *Catal Today*, 1999, 54: 81
- [6] Wang W, Zhang H B, Lin G D, Xiong Z T. *Appl Catal B*, 2000, 24: 219
- [7] Cordi E M, Falconer J L. *Appl Catal A*, 1997, 151: 179
- [8] Saleh J M, Hussain S M. *J Chem Soc, Faraday Trans*, 1986, 82: 2221
- [9] Imamura S, Uchihori D, Utani K, Ito T. *Catal Lett*, 1994, 24: 377
- [10] Álvarez-Galván M C, de la Peña O'Shen V A, Fierro J L G, Arias P L. *Catal Commun*, 2003, 4: 223
- [11] Cordi E M, O'Neill P J, Falconer J L. *Appl Catal B*, 1997, 14: 23
- [12] Larsson P O, Andersson A. *Appl Catal B*, 2000, 24: 175
- [13] Mazzocchi C, Kaddouri A. *J Mol Catal A*, 2003, 204-205: 647
- [14] Kim S C. *J Hazard Mater*, 2002, 91: 285
- [15] Sekine Y. *Atmos Environ*, 2002, 36: 5543
- [16] Huang H B, Leung D Y C. *ACS Catal*, 2011, 1: 348
- [17] Shi C, Wang Y, Zhu A M, Chen B B, Au C. *Catal Commun*, 2012, 28: 18
- [18] Liu B C, Liu Y, Li C Y, Hu W T, Jing P, Wang Q, Zhang J. *Appl Catal B*, 2012, 127: 47
- [19] Park S J, Bae I, Nam I-S, Cho B K, Jung S M, Lee J-H. *Chem Eng J*, 2012, 195-196: 392
- [20] Wang Y, Zhu A M, Chen B B, Crocker M, Shi C. *Catal Commun*, 2013, 36: 52
- [21] Wachs I E, Madix R J. *Surf Sci*, 1979, 84: 375
- [22] Wachs I E, Madix R J. *Appl Surf Sci*, 1980, 5: 426
- [23] Lu X, Zhang Q E, Lin M C. *Phys Chem Chem Phys*, 2001, 3: 2156
- [24] Zhou J, Mullins D R. *Surf Sci*, 2006, 600: 1540
- [25] Li C, Domen K, Maruya K-I, Onishi T. *J Catal*, 1990, 125: 445
- [26] Li J, Xue H D, Liang W J, Li J, Jin Y K, Li Y L. *Beijing Univ Technol* (李坚, 薛红弟, 梁文俊, 李洁, 金毓奎, 李依丽. 北京工业大学学报), 2006, 32: 534
- [27] Koizumi M. *JP 2002 273 145*. 2002
- [28] Rozyznov B V, Coyle W J, Wood W E, Beaverson N J. *US 6 541 560*. 2003
- [29] Kakkar R, Kapoor P N, Klabunde K J. *J Phys Chem B*, 2004, 108: 18140
- [30] Cowan J, Abu-Daibes M, Banerjee S. *Environ Sci Technol*, 2005, 39: 5101
- [31] Tang X F, Chen J L, Huang X M, Xu Y D, Shen W J. *Appl Catal B*, 2008, 81: 115
- [32] He Y B, Ji H B. *Chin J Catal* (何运兵, 纪红兵. 催化学报), 2010, 31: 171
- [33] An N H, Yu Q S, Liu G, Li S Y, Jia M J, Zhang W X. *J Hazard Mater*, 2011, 186: 1392
- [34] Liu L L, Tian H, He J H, Wang D H, Yang Q W. *J Environ Sci*, 2012, 24: 1117
- [35] Tian H, He J H, Liu L L, Wang D H. *Ceram Int*, 2013, 39: 315
- [36] An N H, Zhang W L, Yuan X L, Pan B, Liu G, Jia M J, Yan W F, Zhang W X. *Chem Eng J*, 2013, 215-216: 1
- [37] Zhang C B, He H, Tanaka K-I. *Catal Commun*, 2005, 6: 211
- [38] Zhang C B, He H, Tanaka K-I. *Appl Catal B*, 2006, 65: 37
- [39] Shi Y Z, Zhang N, Luo M F, Lu J Q. *J Chin Soc Rare Earth* (石艳芝, 张娜, 罗孟飞, 鲁继青. 中国稀土学报), 2011, 29: 271
- [40] Zhang C B, Liu F D, Zhai Y P, Ariga H, Yi N, Liu Y C, Asakura K, Flytzani-Stephanopoulos M, He H. *Angew Chem Int Ed*, 2012, 51: 9628
- [41] Wei R C, Chen H L, Zhang X M. *Ind Catal* (魏日出, 陈洪林, 张小明. 工业催化), 2012, 20(10): 68
- [42] State Environmental Protection Administration. *Water and Wastewater Monitoring Analysis Method*. 4th Ed. Beijing: China Environmental Science Press (国家环境保护总局水和废水监测分析方法编委会. 水和废水监测分析方法. 第4版. 北京: 中国环境科学出版社), 2002
- [43] Wu F, Liu Y H, Wu C. *J Wuhan Univ Technol Mater Sci Ed*, 2011, 26: 377
- [44] Scibioh M A, Kim S K, Cho E A, Lim T H, Hong S A, Ha H Y. *Appl Catal B*, 2008, 84: 773
- [45] Reddy B M, Thrimurthulu G, Katta L, Yamada Y, Park S E. *J Phys Chem C*, 2009, 113: 15882
- [46] Larachi F, Pierre J, Adnot A, Bernis A. *Appl Surf Sci*, 2002, 195: 236

催化氧化处理工业废气中高浓度甲醛

魏日出^{a,b}, 陈洪林^b, 张小明^{b,*}, 索继栓^b

^a中国科学院大学, 北京100049

^b中国科学院成都有机化学研究所, 四川成都610041

摘要: 制备了用于温和条件下催化氧化去除工业废气中高浓度甲醛(HCHO)的1%Pt-4%CeO₂/AC催化剂. 将高浓度甲醛的催化氧化过程与双甘膦氧化制备草甘膦的反应过程集成在一起, 使草甘膦合成过程中产生和排放出来的甲醛(100–300 mg/m³)在通过催化剂床层时被完全除去. 系统研究了温度、空速和甲醛含量对甲醛去除率的影响. 在气体空速(GHSV)低于20000 h⁻¹时废气中几乎所有的甲醛都被氧化, 处理后的废气中的甲醛含量低于0.1 mg/m³, 甲醛的转化率为99.1%–100%. 当GHSV为30000–50000 h⁻¹, 催化剂床层温度为12 °C时, 生产废气通过催化剂床层后的甲醛含量小于1.5 mg/m³, 甲醛的转化率为97.56%–99.99%. 1%Pt-4%CeO₂/AC催化剂的中试试验结果表明, 处理后最终尾气中甲醛含量小于10 mg/m³, 有效地防止了甲醛对人们健康的危害, 具有良好的产业化前景.

关键词: 铂-二氧化铈/活性炭催化剂; 甲醛废气; 草甘膦生产; 甲醛去除

收稿日期: 2013-05-24. 接受日期: 2013-08-16. 出版日期: 2013-10-20.

*通讯联系人. 电话: (028)85226215; 传真: (028)85223978; 电子信箱: xm.zhang@cioc.ac.cn

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>).