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RESEARCH NOTE

Oxidative Destruction of Chlorobenzene and *o*-Dichlorobenzene on a Highly Active Catalyst: $MnO_x/TiO_2–Al_2O_3$

Yan Liu, Zhaobin Wei, Zhaochi Feng, Mengfei Luo, Pinliang Ying, and Can Li[1]

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, P. R. China

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A highly active catalyst, $MnO_x/TiO_2–Al_2O_3$, was prepared by impregnating MnO_x species on TiO_2-modified Al_2O_3. The TiO_2 species in $TiO_2–Al_2O_3$ support is in a monolayer dispersion, and the MnO_x species is again highly dispersed on $TiO_2–Al_2O_3$ support. The total oxidation of chlorobenzene and *o*-dichlorobenzene on $MnO_x/TiO_2–Al_2O_3$ catalyst can be achieved at 300°C and 250°C respectively, at the space velocity of 8000 h^{-1}. The activity of $MnO_x/TiO_2–Al_2O_3$ catalyst (Mn loading 11.2 wt%) is gradually increased in the first 10–20 h and then keeps stable at least for the measured 52 h at 16,000 h^{-1}. Furthermore, no chlorinated organic byproducts are detected in the effluent during the oxidative destruction of chlorobenzene and *o*-dichlorobenzene. It is proposed that the partially chlorinated and highly dispersed manganese oxide on a monolayer TiO_2-modified Al_2O_3 is responsible for the high and stable activity for the total oxidation of chlorinated aromatics. © 2001 Academic Press

Key Words: **PCDD/PCDF; chlorobenzene; *o*-dichlorobenzene; oxidation; supported manganese oxide catalyst; TiO_2-modified Al_2O_3 supports; TPR.**

INTRODUCTION

Polychlorinated dibenzo-dioxins and dibenzo-furans (PCDDs and PCDFs) are deadly, persistent organic pollutants. They can be formed in the bleaching of wood pulp with chlorine-based oxidants, the incineration of chlorine-containing compounds and organic matter, and the recycling of metals. The United Nations Environmental Program (UNEP) International Agreement on persistent organic pollutants lists 12 “priority” pollutant compounds and classes of compounds for global phaseout. All are organochlorines. Thus, many methods have been tried to destroy the chlorinated organics including PCDDs and PCDFs. Among these methods are incineration (1, 2), hydrodechlorination (3, 4), biological process (5), steam reforming (6), and photocatalytic degradation (7, 8). Catalytic oxidation of chlorinated aromatics to HCl, H_2O, and carbon oxides is the most viable and economic approaches due to its low destruction temperature and its excellent selectivity toward the formation of harmless products (9–11).

Although supported noble metal catalysts have been claimed to be very effective for the total oxidation of many volatile organic compounds (VOCs) (12, 13), problems associated with high cost and poor stability in the presence of HCl and Cl_2 have hindered their further development in the total oxidation of chlorinated organics (14, 15). Based on the work done to date, some transition metal oxides (9–11, 16–20), especially manganese oxides (21, 22), appear to have much promise. Our previous work on the total oxidation of chlorobenzene (CB) over MnO_x/Al_2O_3 and MnO_x/TiO_2 catalysts has indicated that the catalytic activity of CB oxidation for MnO_x/TiO_2 is much higher than that for MnO_x/Al_2O_3 (22). To take advantage of the high surface area of Al_2O_3 and the unique properties of TiO_2, in this work, we investigated the total oxidation of CB and *o*-dichlorobenzene (*o*-DCB) on $MnO_x/TiO_2–Al_2O_3$ catalyst, in which manganese oxide is highly dispersed on TiO_2-modified Al_2O_3. It is found that this catalyst shows very high and stable activity for the total oxidation of both CB and *o*-DCB.

EXPERIMENTAL

Catalyst Preparation

TiO_2-modified Al_2O_3 support, denoted as $TiO_2–Al_2O_3$, was prepared by the following methods: γ-Al_2O_3 (Degussa, 108 m^2/g, Belgium, 208–210 m^2/g) was dispersed into tetrabutyl titanate solution in ethanol, then successively stirred and dried in a rotary evaporator at 90°C/0.04 MPa and in an oven for 6 h at 130°C, and finally calcined at 500°C for 4 h. In this work, Al_2O_3 was modified by a monolayer amount of TiO_2. After the modification, the BET surface area of

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[1] To whom correspondence should be addressed. Fax: 86-411-4694447. E-mail: canli@ms.dicp.ac.cn.

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$TiO_2–Al_2O_3$ support is 118 m^2/g and 212 m^2/g for the former and the latter, respectively.

MnO_x/TiO_2, MnO_x/Al_2O_3, and $MnO_x/TiO_2–Al_2O_3$ catalysts were prepared by respectively impregnating the supports, TiO_2 (Degussa, 47 m^2/g), γ-Al_2O_3 (Degussa, 108 m^2/g), and TiO_2-modified Al_2O_3, with appropriate amounts of manganese acetate aqueous solution. The samples were stirred continuously at 100°C until the total evaporation of H_2O. Finally, all samples were dried at 130°C for 3 h, and subsequently calcined at 300°C for 0.5 h and 500°C for 2 h.

Catalyst Activity and Characterization

The reaction was carried out at atmospheric pressure in a tubular quartz glass, fixed-bed reactor. The feed gas contained 1300 ppm CB or *o*-DCB and 15% oxygen (balanced with N_2). Under standard reaction conditions, 133.3 ml/min of this mixture was fed over 1.0 ml catalyst, which gives a space velocity of 8000 h^{-1}. The reactants and reaction products were analyzed using an online gas chromatograph equipped with flame ionization and thermal conductivity detectors. The analysis of CB, *o*-DCB, and CO/CO_2 were conducted through SE-54 and Carbosieve S-II columns, respectively.

The products trapped in chlorobenzene for 12 h at ~7°C are analyzed by gas chromatograph using an SE-54 column and flame ionization detector with vaporization temperature at 280°C, detector temperature at 280°C, and an injection volume of 1 μl. The programmed temperature is realized for the SE-54 column. The temperature is kept at 80°C for 5 min, then increased at 10°C/min to 250°C, and kept at 250°C for 60 min.

Temperature-programmed reduction (TPR) experiments were carried out using 25 mg catalysts under a gas flow (30 ml/min) of hydrogen (10%) and argon (90%). The temperature of the catalysts was linearly increased at 20°C/min. A thermal conductivity detector was used to monitor the hydrogen consumed during TPR course.

XPS spectra were recorded on a LHS-12 280 W X-ray photoelectron spectrometer using Al-Kα (1486.6 eV) as the exciting source. An analyzer pass energy of 50 eV was used. $Al_{2p} = 74.1$ eV (for γ-Al_2O_3) was used as an internal reference to correct the charge shifts. The samples were pressed into self-supported wafers and mounted on the stainless-steel manipulator. The base pressure of the system was 2×10^{-7} Pa.

RESULTS AND DISCUSSION

The catalytic performances of CB oxidative destruction on manganese oxide catalysts, supported on different supports, are shown as the function of temperature in Fig. 1. MnO_x supported on TiO_2 and $TiO_2–Al_2O_3$ exhibits higher activities for CB oxidation than that supported on Al_2O_3. For $MnO_x/TiO_2–Al_2O_3$ catalyst, the conversion of CB is only about 5% at 200°C and 250°C, which is even lower than that of MnO_x/Al_2O_3 catalyst. However, its activity is significantly increased when the temperature is increased from 250°C to 350°C. At 350°C, the conversion of CB reaches 97% for $MnO_x/TiO_2–Al_2O_3$ catalyst, while it is only 62% for MnO_x/TiO_2 catalyst, indicating that MnO_x supported on a monolayer TiO_2-modified Al_2O_3 is more active for the total oxidation of CB than that supported on bulk TiO_2. A blank reactor experiment indicates no significant oxidation of CB at temperatures up to 500°C.

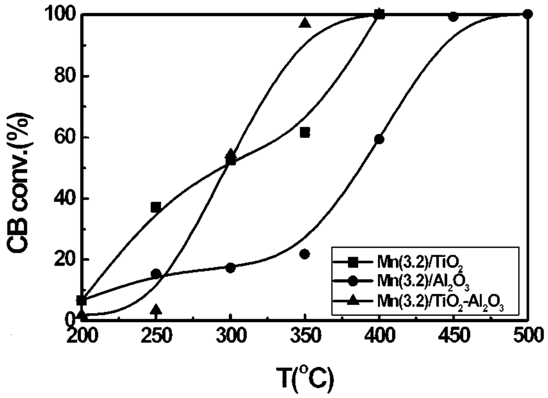

FIG. 1. Comparison of chlorobenzene conversion for manganese oxide supported on different supports (catalyst: 1 ml; GHSV: 8000 h^{-1}; *P*: 0.1 MPa; 1300 ppm chlorobenzene, 15% O_2 and nitrogen balance; S_{BET} (TiO_2): 47 m^2/g; S_{BET} (Al_2O_3): 108 m^2/g; S_{BET} ($TiO_2–Al_2O_3$): 118 m^2/g).

It is usually hard to avoid the formation of chlorinated byproducts (10, 19, 23–26) during the oxidative destruction of chlorinated organics, especially for supported noble metal catalysts. But for $MnO_x/TiO_2–Al_2O_3$ catalyst, not only its activity is very high, but also no chlorinated organic byproducts are detected in the effluent. To make sure, the reaction products were trapped in chlorobenzene for 12 h at ~7°C and then the collected products were analyzed by GC (the minimum level of its detection is $\leq 5 \times 10^{-11}$ g/s (nC_{16})). The results indicate that PCDDs and PCDFs like byproducts are far below the detection level if they were formed during the CB catalytic oxidation.

The CB conversions observed on $MnO_x/TiO_2–Al_2O_3$ catalysts with different Mn loadings were also investigated. As shown in Fig. 2, catalytic activities for both Al_2O_3 and $TiO_2–Al_2O_3$ supports are very low and the complete oxidation of CB requires a temperature as high as 600°C. However, only 1.9 wt% Mn loading on $TiO_2–Al_2O_3$ support can improve the activity considerably and the temperature for the total oxidation of CB can be lowered to 450°C, indicating that manganese oxide is the main active component in $MnO_x/TiO_2–Al_2O_3$ catalyst. With the increase of Mn loadings on $TiO_2–Al_2O_3$, the catalytic activity increases further. When Mn loading reaches 9.6 wt%, the total conversion

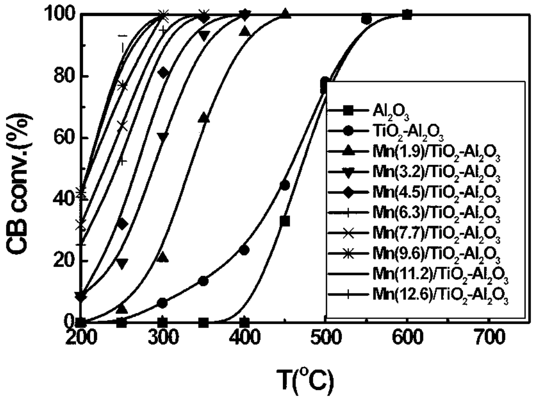

FIG. 2. Comparison of chlorobenzene conversion for Al_2O_3, TiO_2–Al_2O_3, and MnO_x/TiO_2–Al_2O_3 catalysts with different Mn loadings (catalyst: 1 ml; P: 0.1 MPa; 1300 ppm chlorobenzene, 15% O_2 and nitrogen balance; S_{BET} (Al_2O_3): 208–210 m^2/g; S_{BET} (TiO_2–Al_2O_3): 212 m^2/g).

temperature of CB can be lowered to 300°C, which is much lower than temperature values reported in the literature (22, 23).

The catalytic processes for VOCs treatment usually require a gas hourly space velocity (GHSV) as high as 30,000 to 50,000 h^{-1}, so the catalytic activity was tested at GHSV ranging from 8000 to 40,000 h^{-1} on MnO_x/TiO_2–Al_2O_3 (Mn loading 11.2 wt%) catalyst. As shown in Fig. 3, the temperature for the total oxidation of CB can be kept at 300°C when the space velocity is increased from 8000 to 16,000 h^{-1}. However, it goes up with the further increase of the space velocity (i.e., from 16,000 to 40,000 h^{-1}). The temperature for the total oxidation of CB is raised to 400°C when GHSV reaches 40,000 h^{-1}.

The stability of MnO_x/TiO_2–Al_2O_3 catalyst (Mn loading 11.2 wt%) was tested for the catalytic oxidation of CB at 250°C. It is found that the activity increases slowly during the first 10–20 h to about 70% of conversion and keeps stable at least during the measured 52 h at 16,000 h^{-1}. There exists an induction period to obtain the stable activity, as that for MnO_x/TiO_2 catalyst (22). After the reaction, the used and the fresh catalysts are characterized by XPS. As shown in Fig. 4, for the used catalyst, a prominent feature has appeared at 646.4 eV, which is assigned to "shake-up" satellites and is characteristic of the Mn^{2+} oxidation state (27). No Cl 2p emission is found in the fresh catalyst, while it is found at 198.4 eV for the used one (see Fig. 4), which is associated with Cl^-species (28), indicating Cl^- enters the MnO_x/TiO_2–Al_2O_3 catalyst. The Mn $2p_{3/2}$ binding energy for $MnCl_2$ is 642.6 eV (29) and it is 641.6 eV for the used catalyst, suggesting that MnO_x is only partially chlorinated. However, no deactivation is observed during the investigation, indicating that this partially chlorinated MnO_x has even higher, more stable activity for the total oxidation of CB.

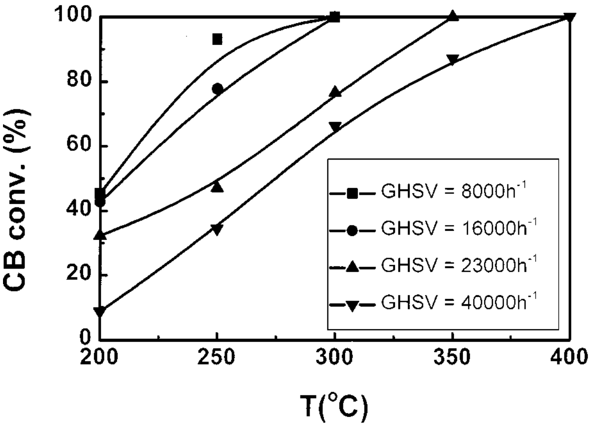

FIG. 3. Effect of GHSV on the activity of MnO_x/TiO_2–Al_2O_3 (Mn loading 11.2 wt%) catalyst for CB oxidation (1300 ppm chlorobenzene, 15% O_2 and nitrogen balance; P: 0.1 Mpa; S_{BET} (TiO_2–Al_2O_3): 212 m^2/g).

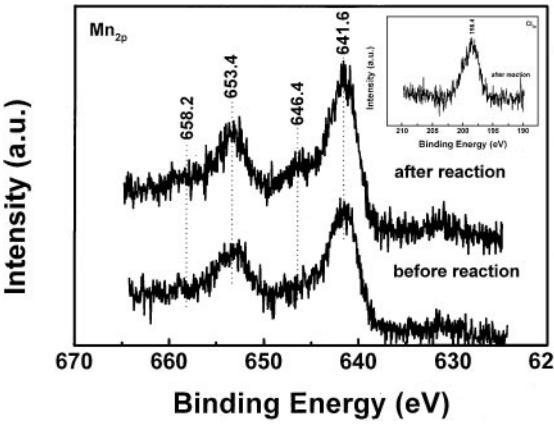

FIG. 4. XPS spectra of the fresh and the used MnO_x/TiO_2–Al_2O_3 (Mn loading 11.2 wt%) catalysts after the stability experiment (1300 ppm chlorobenzene, 15% O_2 and nitrogen balance; P: 0.1 Mpa; GHSV: 16000 h^{-1}; T: 250°C; time: 52 h; S_{BET} (TiO_2–Al_2O_3): 212 m^2/g).

MnO_x/TiO_2–Al_2O_3 catalysts with different Mn loadings were also used in the destruction of *o*-DCB, which was chosen as a model compound because of its structural similarity to the part of dioxins (20). As shown in Fig. 5, with the increase of Mn loadings on TiO_2–Al_2O_3, the catalytic activity in *o*-DCB oxidation is also increased. When Mn loading reaches 15 wt%, the total oxidation temperature is lowered to 250°C. This novel result has never been reported before (16, 20, 25).

During the oxidative destruction of *o*-DCB, no chlorinated organic byproducts are detected, just as the case for the oxidation of CB. Moreover, even at lower temperatures, this catalyst is still quite active: at 150°C, 55% conversion of *o*-DCB can be obtained.

It was reported that manganese oxide could be highly dispersed on Al_2O_3 (30). However, the catalytic activity of CB oxidation for MnO_x/Al_2O_3 catalyst is much lower than that for MnO_x/TiO_2 catalyst (see Fig. 1). This is probably

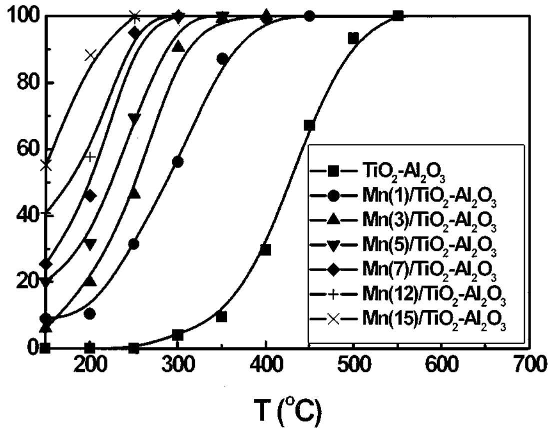

FIG. 5. Comparison of *o*-dichlorobenzene conversion for TiO_2–Al_2O_3 and $MnO_x/TiO_2–Al_2O_3$ catalysts with different Mn loadings (catalyst: 1 ml; GHSV: 8000 h^{-1}; *P*: 0.1 MPa; 1300 ppm *o*-dichlorobenzene, 15% O_2 and nitrogen balance; S_{BET} ($TiO_2–Al_2O_3$): 212 m^2/g).

due to the strong interaction between MnO_x and Al_2O_3, as confirmed by its redox properties: the amount of reducible oxygen is only half that of MnO_x/TiO_2 (22). When MnO_x is dispersed on TiO_2-modified Al_2O_3, as shown in Fig. 6, the amount of reducible oxygen of $MnO_x/TiO_2–Al_2O_3$ increases greatly, indicating that the interaction between MnO_x and Al_2O_3 is dramatically weakened. Moreover, there is only one state of MnO_x (the reduction peak at 390°C, which is attributed to the reduction of the highly dispersed MnO_x (22)) for Mn(3.2)/$TiO_2–Al_2O_3$ catalyst, while there exists another state of MnO_x (the reduction peak at ∼470°C, which is due to the reduction of the bulk MnO_x (22)) for Mn (3.2)/TiO_2 and Mn(3.2)/Al_2O_3 catalysts. Associated with the activity results, it is suggested that the highly dispersed MnO_x is benefit to the highly catalytic activity.

In the visible Raman spectra of $TiO_2–Al_2O_3$, no Raman peaks of TiO_2 crystalline phase were detected for TiO_2-modified Al_2O_3 support with a monolayer amount of TiO_2, indicating that TiO_2 is highly dispersed on Al_2O_3. MnO_x is again highly dispersed on the TiO_2-modified Al_2O_3 support. The property of this well-dispersed TiO_2 must be very different from that of the bulk TiO_2. The active phase must be derived from the interaction and/or reaction between the highly dispersed MnO_x and the monolayer dispersed TiO_2 on Al_2O_3. During the reaction, this active phase can be partially chlorinated to give the high and stable activity for the total oxidation of chlorinated aromatics.

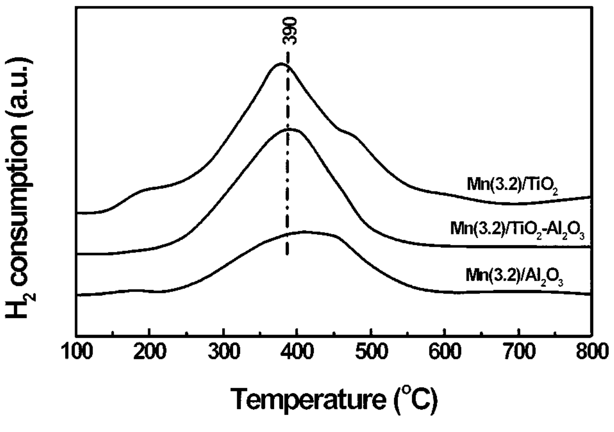

FIG. 6. TPR profiles of manganese oxide catalysts with different supports (see Fig. 1).

In summary, a novel catalyst $MnO_x/TiO_2–Al_2O_3$ is found to be very active for the total oxidation of both chlorobenzene and *o*-dichlorobenzene. The temperature for the total oxidation of chlorobenzene and *o*-dichlorobenzene can be lowered to 300°C and 250°C respectively, at the space velocity of 8000 h^{-1}. No deactivation is observed for at least 52 h at 16,000 h^{-1}. Moreover, no chlorinated organic byproducts are detected in the effluent during the oxidative destruction of chlorobenzene and *o*-dichlorobenzene. It is proposed that the partially chlorinated and highly dispersed manganese oxide on a monolayer TiO_2-modified Al_2O_3 is responsible for the high and stable activity for the total oxidation of chlorinated aromatics.

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