

Synthesis, characterization and photocatalytic activity of porous manganese oxide doped titania for toluene decomposition

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Abstract

The present study describes the photocatalytic degradation of toluene in gas phase on different porous manganese oxide doped titanium dioxide. As synthesized birnessite and cryptomelane type porous manganese oxide were doped with titania and tested for photocatalytic decomposition of toluene in gas phase. The effects of the inlet concentration of toluene, flow rate (retention time) were examined and the relative humidity was maintained constantly. Thermal and textural characterization of manganese oxide doped titania materials were characterized by X-ray diffraction (XRD), thermogravimetry (TG), BET and TEM-EDAX studies. The aim of the present study is to synthesize the porous manganese oxide doped titania and to study its photocatalytic activity for toluene degradation in gas phase. Cryptomelane doped titania catalyst prepared in water medium [K-OMS-2 (W)] is shown the good toluene degradation with lower catalysts loading compared to commercial bulk titania in annular type photo reactor. The higher photocatalytic activity due to various factors such as catalyst preparation method, experimental conditions, catalyst loading, surface area, etc. In the present study manganese oxide OMS doped titania materials prepared by both aqueous and non-aqueous medium, aqueous medium prepared catalyst shows the good efficiency due to the presence of OH bonded groups on the surface of catalyst. The linear forms of different kinetic equations were applied to the adsorption data and their goodness of fit was evaluated based on the R^2 and standard error. The goodness to the linear fit was observed for Elovich model with high R^2 (≥ 0.9477) value.

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Keywords: Birnessite; Cryptomelane; Manganese oxide; OMS; Titanium dioxide; Toluene

1. Introduction

Volatile organic compounds (VOCs) are widely used in (and produced by) both industrial and domestic activities [1]. This extensive use results in their occurrence in aquatic, soil and atmosphere environments [2]. Many VOCs are toxic and some are considered to be carcinogenic, mutagenic, or teratogenic [3]. The pollution of indoor volatile organic compounds (VOCs) has been increasingly concerned in recent years. Heterogeneous photocatalysis is regarded as a promising technique for purifying indoor VOCs. A large quantity of work has been devoted in this field in the past decade [4–6]. The TiO_2 -sensitized photo degradation of organic compounds has been proposed as an alternative advanced oxidation process (AOP) for the decontam-

ination of water and air. The AOP is initiated from the generation of hole–electron pairs on the semiconductor, absorbing the ultraviolet (UV) light with energy equal to or higher than the band gap energy (E_g) of semiconductor. Electrons and holes are photogenerated in the bulk of the semiconductor, and move to the particle surface, electrons reduce an electron acceptor such as molecular oxygen and holes can oxidize electron donors including adsorbed water or hydroxide anion to yield hydroxyl radicals.

The common VOCs such as halogenated hydrocarbons, ketones, alcohols and aromatic compounds have been widely used in many industries and are often found in the emission flow [7]. The sol–gel method synthesized anatase–rutile phase transformation of TiO_2 containing various amount of Mn^{2+} ions have been recently reported and they studied the effects of manganese(II) dopants on acceleration of rutile phase formation [8]. Manganese oxides have been reported to be among the most efficient transition-metal oxide catalysts for catalytic disposal of pollutants [9,10]. It has been widely used in selective catalytic

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reduction of NO_x with NH_3 [11,12], CO and VOC oxidation [13,14]. Heterogeneous photocatalysis in the presence of semiconductor oxides is a fast growing field of basic and applied research, especially for the case of the oxidation of organic pollutants in water or in air [15–17]. In particular, photocatalytic oxidation offers various advantages compared with traditional treatment methods because the photoreactions occur at 25 °C and atmospheric pressure, under radiation of the near-UV region and at measurable rates [18] until to very low concentration levels. Toluene is a widespread reagent used for the preparation of many compounds, such as benzaldehyde, benzyl alcohol, benzoic acid, chloro derivatives, etc. Consequently, it can be found in many industrial waste effluents. Toluene is a very noxious organic compound and many strategies have been identified to reduce its presence in the environment. Heterogeneous photocatalytic method has been tested for toluene abatement and previous papers report the partial or complete oxidation of toluene both in gas–solid [19–23] and in liquid–solid systems [24–28]. As to concern the gas–solid regime, Ibusuki and Takeuchi [19] carried out the complete photo-oxidation of toluene on TiO_2 at 303 K. They found that the presence of water vapour was beneficial in order to achieve the almost complete mineralisation of toluene and benzaldehyde having been detected only in very small amounts. However, the product distribution and the catalyst stability strongly depend on the nature of the catalyst and the experimental conditions. Furthermore, Obee and Brown [20] studied the influence of the competitive adsorption of water and toluene vapours on the photo-oxidation rate.

Luo and Ollis [21] and Einaga et al. [22], studying the toluene degradation in humidified air, report that the influence of water is complex in the sense that an optimum water concentration was found when the maximum reactivity was observed. In any case no significant amounts of intermediate species were detected. Recently the selective photo-oxidation of gaseous toluene to benzaldehyde on TiO_2 powders has been reported as an effective method to transform this compound to a valuable chemical compound [23]. Moreover, Cao et al. [24] reported the photocatalytic oxidation of toluene by using nanostructured TiO_2 catalysts. They found a severe deactivation of TiO_2 due to the accumulation of partially oxidized intermediates. The complete recovery of catalytic activity required a thermal treatment of the photocatalysts at a temperature above 693 K. They reported the formation of cresols, benzaldehyde and benzyl alcohol depending on the pH of the solution and on the used semiconductor. The formation of benzaldehyde was also confirmed by Navio et al. [25], in their experiment acetonitrile was used as solvent and investigated the influences in the presence of water in product distribution. Recently the use of surfactant to enhance the photocatalytic reaction rate for toluene degradation has also been reported [26,27]. The presence of surfactant or humic acids was found beneficial for degrading various substrates and a sequestration effect has been hypothesized for explaining this effect [27]. The main aims of the present study were to synthesize the porous manganese oxide doped titania and to find out the more active manganese oxide OMS doped titanium dioxide for photocatalytic activity for toluene degradation in gas phase at lower catalyst loading.

2. Materials and methods

The commercially available poly crystalline titanium dioxide (Nacalai Tesque, Japan) was used in the present work. To identify the crystalline phases of the samples, Rigaku Geigerflex X-ray diffractometer was used. The $\text{Cu K}\alpha$ radiation was generated at 40 kV and 30 mA. Samples were scanned from 5° to 85° (2θ) at a rate of 5 s per step for all porous manganese oxide doped titania samples. Brunauer–Emmett–Teller (BET) surface area of all samples at 77 K were obtained using Quantachrome (Model 1987) instrument. All the samples were degassed at 573 K for 12 h. The instrument used for nitrogen adsorption analysis is NOVA 2000 from Quantachrome Corporation. The morphology and elemental analysis of the catalyst (average of five data points at different locations of the solid) were measured by energy dispersive X-ray spectroscopy. Transmission electron micrographs (TEM) were examined using Philips CM12/STEM, Scientific and Analytical Equipment.

2.1. Synthesis of potassium birnessite and cryptomelane (porous manganese oxides)

Potassium birnessite (K-OL-1 type manganese oxide) was synthesized by the oxidation of 0.50 M solution of manganese(II)acetate in strong alkaline medium. Hydrous $\text{Mn}(\text{OH})_2$ suspension was obtained by the drop wise addition of 70 mL of 5.0 M KOH solution to 40 mL of 0.50 M manganese(II) acetate. As synthesized manganese oxide suspension was then oxidized by 50 mL of 0.1 M potassium permanganate solution ($\text{MnO}_4^-/\text{Mn}^{2+}=0.25$) followed by ageing the precipitated suspension for 4–5 days aging. In general molar ratio between $\text{MnO}_4^-/\text{Mn}^{2+}=0.2\text{--}0.4$ is the favour for the formation of layered structured birnessite. After 4–5 days aging, the suspension was filtered, washed 4–5 times with double distilled water (DDW) and dried at 298 K. Cryptomelane type manganese oxide K-OMS-2 material was synthesized by oxidation of manganese(II) sulfate by potassium permanganate in strong acidic medium under suitable reflux conditions. Hundred millilitres of 0.4 M solution of potassium permanganate was mixed with 31.0 mL of 1.7 M solution of manganese(II) sulfate hydrate solution. The molar ratio between potassium permanganate and manganese(II) sulfate was fixed at 0.76 ($\text{MnO}_4^-/\text{Mn}^{2+}=0.76$) for preparing cryptomelane K-OMS-2 material in acidic medium. After the addition of an aqueous manganese(II) sulfate solution to the potassium permanganate solution, 15–20 mL of concentrated nitric acid (6.0 M) was added dropwise to maintain acidic medium and the mixed solution was then stirred at 363 K for 24 h. The synthesized material was washed with DDW and then the solid brown–black K-OMS-2 material was dried at 383 K for 8 h [28].

2.2. Synthesis of porous manganese oxides doped titania catalysts

Different weight percentage loading of manganese oxide OMS-titania catalysts was prepared by suitable condition. In

the present study, 5 and 10 wt% potassium birnessite (K-OL-1) doped titania (2.0 g commercial titanium dioxide) was prepared in non-aqueous medium, 5, 10 and 15 wt% cryptomelane (K-OMS-2) doped titania and 5 wt% MnSO₄ doped titania (5 wt% manganese sulfate stirred with titania in acetone) has also been synthesized, which is designated as 5 wt% MnSO₄. The appropriate amount (2.0 g) of titanium dioxide mixed with suitable amount of K-OL-1 and K-OMS-2 material in 20 mL acetone and only one sample prepared in water medium such as 2.0 g of titanium dioxide stirred with 20 mL of water and stirred with K-OMS-2 (10 wt%), which is designated as 10 wt% K-OMS-2 (W). After stirred the mixed titanium dioxide and manganese oxide OMS material were subjected to calcined at 723 K for 4 h. As synthesized manganese oxide doped titania materials are used for photocatalytic experiments.

2.3. Preparation of manganese oxide OMS-titania coated plastic nylon sheet

Appropriate amount of porous manganese oxide doped titania (1.0–2.0 g range) mixed with poly acetonitrile (PAN) in alcoholic medium, were poly acetonitrile is act as binder to stick the materials strongly on the nylon sheet (i.e., cheese paper type) under this experimental conditions. The synthesized viscous solution finely coated on plastic nylon sheet and dried in 303 K. The synthesized sheet kept inside the photocatalytic reactor in the rolled form.

2.4. Experimental setup and analyses procedure

The saturated toluene gas was prepared by passing air through a saturator containing liquid toluene. The humidified air stream was generated by bubbling air through a thermostated glass bottle containing deionized water. Then the saturated toluene gas was mixed and diluted with humidified air stream at the gas mixer (mixing chamber). The obtained toluene gas stream entered into the photoreactor with constant flow rates 5.0 L/min, inlet toluene concentration range between 70 and 80 ppmv and relative humidity (RH) in the range of 20–60%. Feed toluene concentrations and relative humidity were set by varying the ratio of gas flow rates and/or varying the saturator temperature.

The outside of the photoreactor was a cooling water sleeve to maintain stable reaction temperature (293–295 K). The 85 W UV lamp was used to illumination with maximum light intensity output of 254 nm. The lamp was fixed at the center of the photoreactor without any quartz tube protection. The manganese oxide doped titania material coated on nylon sheet (length 8 cm, height 10 cm and thickness 0.18 mm) and rolled like tube shape and then it is inserted in the interior surface of the photoreactor. Gas phase oxidation of toluene was tested on photo annular reactor, which is shown in Fig. 1.

The concentration of toluene was analyzed by gas chromatograph with a flame ionization detector. The gas samples were collected periodically using plastic syringe with suitable interval of time (500 μ L). The gas chromatograph oven temperature was held at 378 K and the detector temperature maintained constant at 523 K.

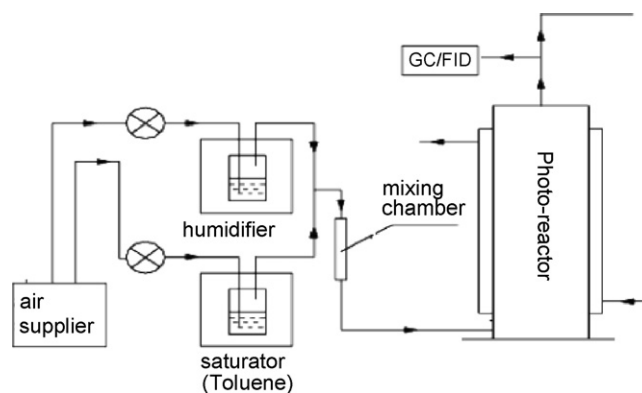


Fig. 1. Schematic representation of photocatalytic reactor.

The conversion C (%) of toluene was calculated as follows:

$$C = \frac{(C_i - C_o) \times 100}{C_i} \quad (1)$$

where C_i is the inlet concentration and C_o is the outlet concentration at steady state.

The gas phase oxidation of toluene was tested on both pure titania (bulk) and manganese oxide doped titania materials. All catalysts tested up to 100 min after attain the equilibration and every 10 min, concentration of toluene in the outlet were analyzed by gas chromatography using FID detector at 473 K and high pure nitrogen as used as carrier gas. Toluene samples collected from the tightly connected outlet by using 2 mL plastic syringe.

2.5. Kinetic studies

The kinetic and empirical equations, including the zero, first, Elovich and second order rate equations were applied to the toluene removal efficiency with respect to time. Linear forms of kinetic equations are derived by kinetic model reactions. The linear forms of different kinetic equations were applied to the adsorption data and their goodness of fit was evaluated based on the R^2 and standard error (S.E.).

• Zero order

$$[A] = [A]_o - kt \quad (2)$$

• First order

$$\ln[A] = \ln[A]_o - kt \quad (3)$$

• Second order

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt \quad (4)$$

• Elovich

$$q_t = \left(\frac{1}{\beta}\right) \ln\left(\frac{\alpha}{\beta}\right) + \left(\frac{1}{\beta}\right) \ln t \quad (5)$$

where q_t is amount of sorbate per unit mass of sorbent at time t . α and β are empirical constants. Slope and intercept are $1/\beta$ and $(1/\beta) \ln(\alpha/\beta)$, respectively.

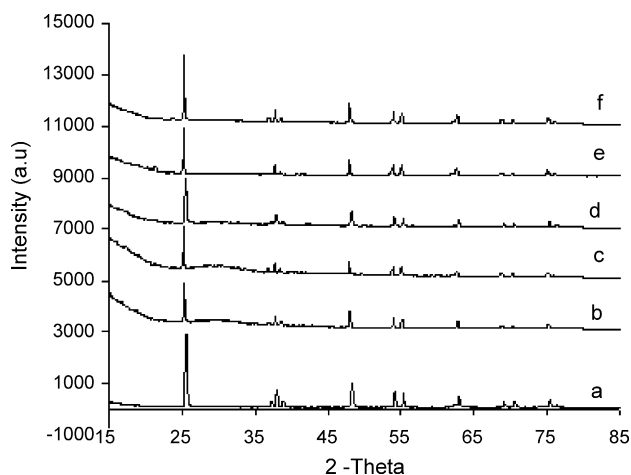


Fig. 2. X-ray diffraction patterns of manganese oxide OMS-titania material (a) TiO_2 , (b) 5 wt% KOL/ TiO_2 , (c) 10 wt% K-OMS-2/ TiO_2 , (d) 15 wt% K-OMS/ TiO_2 , (e) 10 wt% K-OMS/ TiO_2 (W), and (f) 5 wt% MnSO_4 / TiO_2 .

3. Results and discussion

3.1. X-ray diffraction study

X-ray diffraction pattern of different weight percent K-OL-1 and K-OMS-2 type porous manganese oxide doped titania materials are shown in Fig. 2. All samples are showing the major phase of anatase with some amount of rutile phase. The major peak at $25.3^\circ 2\theta$, d -spacing of 3.52 \AA (1 0 0) of anatase is observed. It may be over imposed by presence of higher amount of manganese dopant. Gallardo-Amores et al. [14] reported the photocatalytic oxidation of 2-propanol on lower amount of manganese ion doped titanium dioxide. They observed the mixed phases for manganese doped titanium dioxide patterns in XRD, such as brookite and anatase phase. Manganese oxide was found to be well dispersed on the support surface as Mn^{3+} species, while part of it is stabilized into the TiO_2 bulk as Mn^{4+} species [14]. This cation seems to hinder the support sintering and to favour the anatase to rutile phase transition at higher temperatures more than 973 K. Doping of higher amount of manganese content in titanium dioxide such as up to 15 wt% loading may not cause the major partial phase transformation of anatase phase.

3.2. Thermal and textural characterization of manganese oxide doped TiO_2

The thermal stability of as prepared material were tested by TG analysis (data not shown), all the manganese oxide OMS doped titania samples show the first weight loss or major weight loss observed between 723 and 973 K, which suggest that manganese oxide OMS doped titania material are thermally stable until the temperature reaches 723 K (450°C). The TEM-EDAX pictures of 10 wt% K-OMS-2 (W) is shown in Fig. 3A, manganese oxide particles aggregated strongly and it dispersed on spherical morphology of titania surface. Spherical and thin plate morphology of titania particles clearly visible at higher resolution (Fig. 3A). The titania particle sizes range observed between 100 and 120 nm, the lower magnification picture of manganese oxide doped titania shown in Fig. 3B, it clearly indicates the aggregated particle morphology of titanium dioxide and the corresponding TEM-EDAX spectrum shows the 0.4 at.% Mn and 81 at.% for Ti. About 5 wt% manganese sulfate doped titanium dioxide shows the decrease in surface area ($19.8 \text{ m}^2/\text{g}$) compared bulk TiO_2 Nacalai Tesque ($36 \text{ m}^2/\text{g}$) and its corresponding particle size is $0.443 \mu\text{m}$ (mean value). Impregnation of manganese salt on titania surface some how inhibits the sintering of the titania surface results in decrease in the surface area of as synthesized catalyst (5 wt% MnSO_4 / TiO_2).

In the case of manganese oxide OMS doped TiO_2 show the little higher in surface area value then bulk TiO_2 due to catalyst preparation method and porosity of the dopents. About 5 wt% KOL doped TiO_2 shows the surface area of $37 \text{ m}^2/\text{g}$ and 5 wt% K-OMS-2 doped TiO_2 shows the $41 \text{ m}^2/\text{g}$, 10 wt% K-OMS-2 doped TiO_2 shows the $44 \text{ m}^2/\text{g}$ and 15 wt% K-OMS-2 doped TiO_2 shows the little decreased surface area such as $38 \text{ m}^2/\text{g}$, due to overloading of dopant.

3.3. Catalytic test: gas phase oxidation of toluene on as synthesized materials

Table 1 and Fig. 4 show the inlet concentration of reactant (toluene), catalyst loading amount, and irradiation time and removal efficiency percentage. About 5, 10 and 15 wt% K-OMS-2 coated titania catalysts, which is prepared by acetone medium and it show the total removal efficiency of toluene is

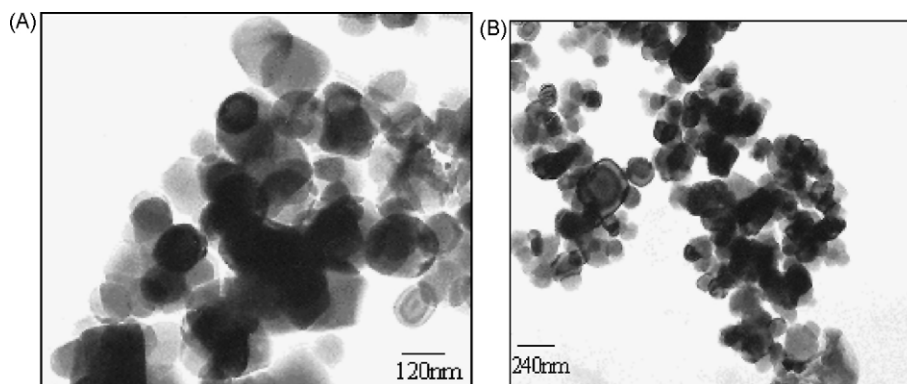


Fig. 3. Transmission electron micrographs of 10 wt% K-OMS-2 (W)-titania catalyst (A) $16,000\times$ and (B) $8000\times$ magnification.

Table 1
Catalysts loading amount, inlet concentration, removal efficiency of toluene on manganese oxide OMS doped titania catalysts

	Catalyst no.							
	1	2	3	4	5	6	7	8
Cat coated (g)	1.02	1.07	1.24	0.53	0.61	0.51	0.50	2.0
Cat loaded (g/m ²)	27.72	29.07	33.70	14.40	16.57	13.86	13.59	54.35
Inlet (ppmv)	81	84	60	81	92	85	77	76
RT (min)	60	60	30	30	30	30	30	30
Time (min)	Removal efficiency (RE) (%)							
0	–	–	–	–	–	–	–	–
10	5.1	4.8	4.3	3.8	4.8	1.7	7.8	3.8
20	9.6	5.7	7.5	8.9	7.2	4.0	14.8	8.7
30	11.9	7.3	9.2	11.5	10.2	6.3	25.5	14.7
40	12.3	10.8	13.6	16.0	14.2	10.7	30.4	18.1
50	13.3	14.4	15.8	18.6	16.3	12.7	31.5	23.2
60	14.2	15.7	16.8	23.1	19.8	18.2	33.8	26.3
70	15.6	18.3	18.3	27.6	22.9	22.9	35.0	30.0
80	16.8	17.3	20.1	30.4	24.6	24.5	38.3	33.6
90	17.1	18.9	22.5	32.9	26.8	26.1	40.6	38.2
100	17.3	21.4	23.5	34.9	27.7	27.1	41.1	39.1

1, 5 wt% K-OMS-2; 2, 10 wt% K-OMS-2; 3, 15 wt% K-OMS-2; 4, 5 wt% KOL; 5, 10 wt% KOL; 6, 5 wt% MnSO₄; 7, 10 wt% K-OMS-2 (W); 8, TiO₂.

23.5%, where as 10 wt% K-OMS-2 (W)-titania materials prepared in water medium shows the good conversion nearly 41% compared to all other catalysts, in the case of commercial bulk titanium dioxide shows the 39% removal efficiency for toluene with higher catalysts loading (2.0 g) compared to manganese oxide doped titania catalyst loading (0.5 g). In term of catalysts loaded surface area (g/m²), 10 wt% K-OMS-2 W-doped titania, which shows the lower surface area (13.59 g/m²) but it shows the good removal efficiency for toluene in photocatalytic reaction compared to bulk titania (54.59 g/m²). The preparation method on manganese oxide doped titania have also been played the role in the degradation of toluene. Manganese oxide doped titania (prepared in water medium) shows the good conversion for toluene degradation compared to all other catalysts, which is due to adsorbed water molecules on manganese oxide doped titania, and it will cause the subsequent deprotonation in the reaction pathway.

Toluene degradation behavior on birnessite and cryptomelane doped titania (prepared in non-aqueous medium) show the different behavior in the photocatalytic reaction. About 5 and 10 wt% KOL doped titania catalysts show the better conversion 24–35% compared to 5, 10 and 15 wt% K-OMS-2 doped titania catalysts (17–23%) at the end of reaction (after 80 min). Manganese sulfate doped titania a catalyst shows the better conversion for toluene degradation compared to K-OMS-2 doped titania. It is because surface acid and base properties of the as synthesized catalysts may cause the difference in the toluene degradation ability, K-OMS-2 doped titania catalysts are hydrophobic in nature but in the case of birnessite doped titania catalysts have the basic site on its surface and probably it will enhance the toluene degradation. In the case of cryptomelane doped titania prepared in water shows the best formation for toluene degradation compared to all other catalysts including bulk titania. Cryptomelane doped titania prepared in water medium [K-OMS-2 (W)] shows the better removal efficiency from beginning of the reaction itself, i.e. after 20 min of the reaction it shows the 25.5% removal efficiency and it goes on increase up to 100 min, it shows the longer steady state compared to bulk titania catalyst. Bulk titania catalyst show the 26% removal efficiency after 60 min of the photocatalytic degradation of toluene. K-OMS-2 (W) shows the total removal efficiency for toluene degradation around 41%.

D'Hennezela et al. [29], studied the role of hydroxyl radical (\bullet OH) formation on TiO₂/H₂O catalysts for benzene and toluene degradation and they observed the presence of OH radical (from adsorbed water on titania surface) and Cl radical (in the case of HCl treated TiO₂) enhance the intermediate formation and finally facilitate the removal efficiency of the reactant. In the same way, water medium prepared manganese oxide OMS doped titania catalyst shows the good conversion for toluene degradation by OH radical ion formation on the catalyst sur-

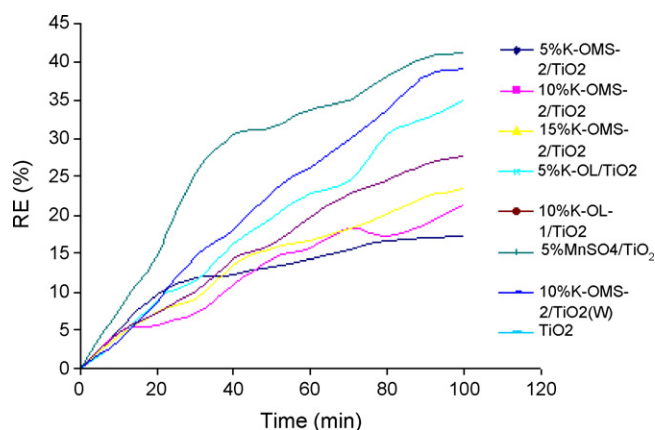


Fig. 4. Gas phase photocatalytic degradation of toluene on different manganese oxide doped titania catalysts.

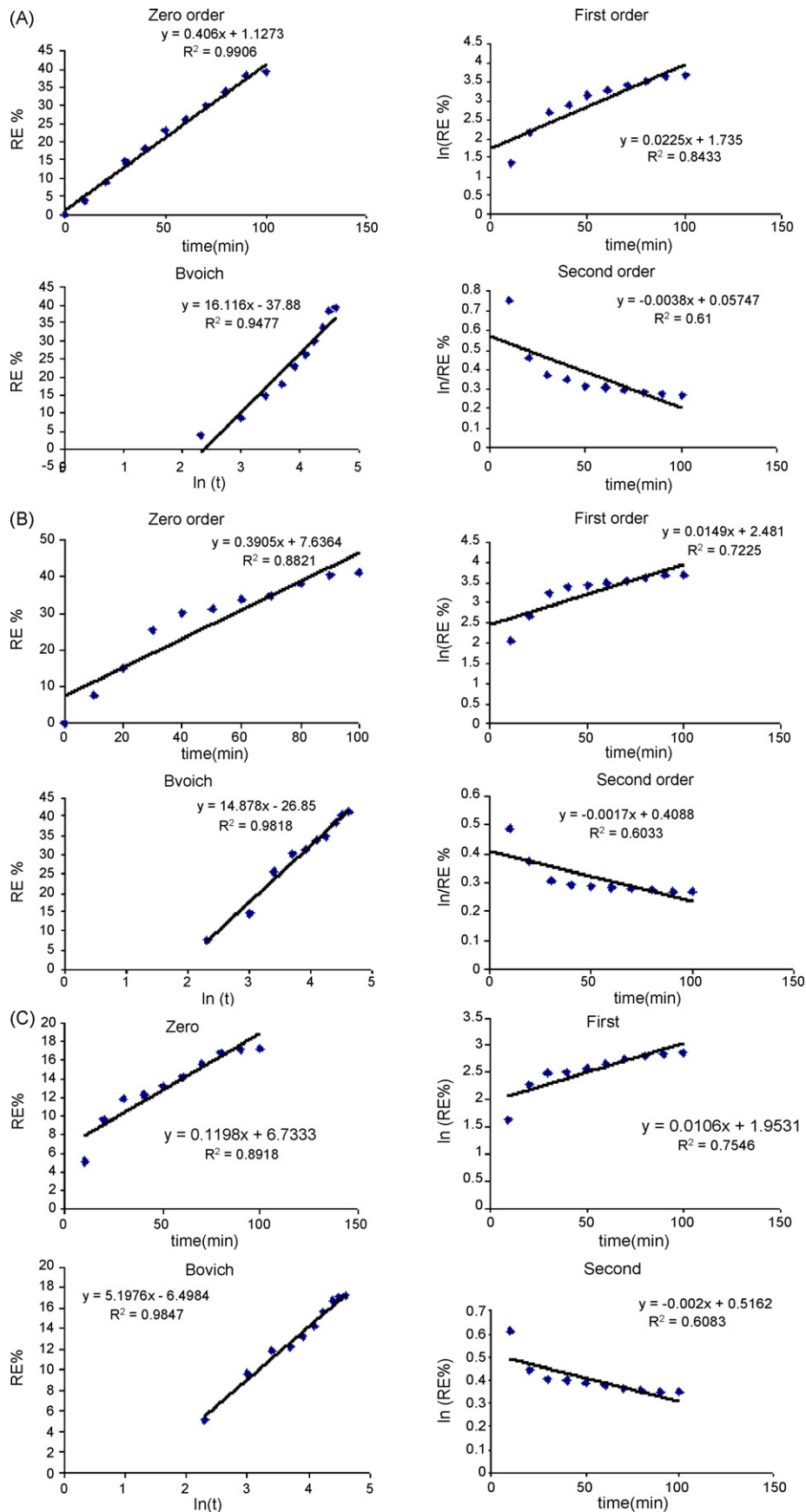


Fig. 5. Kinetic models of different manganese oxide doped titania catalysts of (A) 5 wt% K-OMS-2-titania, (B) 10 wt% K-OMS-2 (W)-titania, and (C) TiO₂.

face. The regeneration of the manganese oxide doped titania has also been studied and the used catalyst shows same performance after treated with water followed by calcinations in air. Therefore, the presence of adsorbed water or water medium prepared manganese oxide doped titania materials can provide the higher removal efficiency for degradation of toluene compared alcoholic route prepared catalysts and bulk titanium dioxide. In the present study, we used higher inlet concentration of toluene [77–92 ppmv] (Table 1) compared to other reports. Pengyi et al. [30], were studied the toluene degradation in the inlet concentration range of 5–20 ppmv and the steady state is same like our research data. This suggest that as prepared catalysts (manganese oxide doped titania) was attained the stable steady state and liner removal efficiency even at higher amount of inlet concentration.

3.4. Kinetic studies

Kinetic models of 5 wt% K-OMS-2 doped titania, 10 wt% K-OMS-2 (W)-titania and TiO_2 was chosen to describe the kinetics of reaction and are shown in Fig. 5A–C. The goodness of fit was evaluated based on R^2 value. Based on our kinetic data, Elovich kinetic and zero order models are showing the highest R^2 value compared to other kinetic reaction models such as first and second order rate equations. Based on R^2 -value the kinetic reaction models follow the following order for toluene removal efficiency

Elovich > Zero order > First order > Second order

α and β values from the Elovich equation has also found for catalysts such as 5 wt% K-OMS-2-titania, 10 wt% K-OMS-2 (W)-titania, TiO_2 (Fig. 5A–C). α values of the above catalysts are 0.929, 0.895, 0.863 (ppmv as toluene min^{-1}) and β values are 0.192, 0.672, 0.0621 ((ppmv toluene/1 g) $^{-1}$), respectively. Higher α with lower β values indicates increase in the rate of reaction (based on Elvich reaction). The highest R^2 -value (i.e., $R^2 \geq 0.9477$) observed for Elovich linear fit reaction (Fig. 5C). The high R^2 value (i.e., ≥ 0.8821), and the corresponding standard error (S.E.) was calculated from zero order linear fit such as, S.E. = 2.24 for 5 wt% K-OMS-2-titania, S.E. = 4.99 for 10 wt% K-OMS-2 (W)-titania, S.E. = 1.38 for TiO_2 .

4. Conclusions

The porous manganese oxide doped titania materials were successfully prepared in aqueous and non-aqueous by adopting suitable synthetic procedure. The aggregated particle of manganese oxide (particle size in the range of 100–120 nm) was dispersed on spherical and platy type morphology of titania. The synthesized samples show the good thermal stability and regeneration activity in the catalytic test. Manganese oxide OMS material doped titania show the improved surface area then bulk titanium dioxide. Manganese oxide doped titania prepared in aqueous medium (10 wt% K-OMS-2 (W)) show the good conversion for toluene (41%) with lower catalyst loading (0.5 g) compared to bulk titania, which shows the same conversion at higher catalyst loading amount (2.0 g). Birnessite type man-

ganese oxide such as K-OL-1 manganese oxide doped titania catalyst shows the faster removal efficiency for toluene degradation compared cryptomelane K-OMS-2 doped titania and bulk titania catalysts with lower total removal efficiency at 100 min. Kinetic models are shown the good linear fitness with the highest R^2 value for zero order and Elovich kinetic models. The above observations suggest that the low amount of manganese oxide K-OMS-2 doped titania catalyst coating is sufficient to achieve the better conversion for volatile organic compounds degradation. It can reduce the catalyst synthesis cost compared to commercially available bulk titanium dioxide.

Acknowledgments

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