Metal oxide/activated carbon composites for the reactive adsorption and

catalytic oxidation of formaldehyde and toluene in air

Won-Ki Kim^a, Kumar Vikrant^a, Sherif A. Younis^{a,b}, Ki-Hyun Kim^{a,*},

Philippe M. Heynderickx^{c,d,**}

 ^aDepartment of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-ro, Seoul 04763, Republic of Korea; ^bAnalysis and Evaluation Department, Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt; ^cCenter for Environmental and Energy Research (CEER)-Engineering of Materials via Catalysis and Characterization, Ghent University Global Campus, 119-5 Songdomunhwa-Ro, Yeonsu-Gu, Incheon 406-840, Republic of Korea; ^dDepartment of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, 653 Coupure Links, Ghent B-9000, Belgium

Abstract

The synergistic effect of 'reactive adsorption and catalytic oxidation (RACO)' has been investigated to develop an efficient method to remove volatile organic compounds (VOCs: formaldehyde (FA) + toluene) using an amorphous-manganese dioxide-activated carbon (Am-MnO₂-AC) composite. The RACO of FA and toluene was examined individually and as a mixture using Am-MnO₂-AC at multiple-isothermal conditions from room temperature (RT) to 300°C. The values for 10% adsorption breakthrough volume (BTV10%) of FA and toluene, when measured as single compounds by Am-MnO₂-AC at RT, were 45.9 and 152 L·g⁻¹, respectively, while those for their mixture were 34.9 and 122 L·g⁻¹, respectively. The BTV10% values for FA measured in single and mixture were 270-280 times higher than their counterparts for the pristine AC. The conversion of FA and toluene (as individual components) into carbon dioxide was completed at 100 and 275°C, respectively. Then, the performance of Am-MnO₂-AC was examined more thoroughly against a dual component system using its crystalline form (e.g., δ -MnO₂) and two other metal-doped forms (i.e., cobalt and silver). The thermal catalytic oxidation of FA and toluene on Am-MnO₂-AC was suggested to follow the Langmuir-Hinshelwood mechanism. The enhanced RACO performance of Am-MnO₂-AC was ascribed to its higher surface porosity and higher concentration of oxygen vacancies (e.g., Mn³⁺/Mn⁴⁺ of 0.707 and adsorbed oxygen (O_A)/lattice oxygen (O_L) of 1.79). The present study is expected to provide insights into the practical application of metal oxide/AC composites for cleaner indoor air quality.

Keywords: Manganese dioxide; Activated carbon; Reactive adsorption; Thermal catalysis; Volatile organic compounds

*Corresponding Author: <u>kkim61@hanyang.ac.kr</u>; <u>Philippe.Heynderickx@Ghent.ac.kr</u>

Abbreviation/acronym/symbol full form

volatile organic compounds	VOCs
Formaldehyde	FA
Activated carbon	AC
Room-temperature	RT
Amorphous-MnO ₂	Am-MnO ₂
Gas hourly space velocity	GHSV
metal-metal oxide interaction	MMOI
Reactive adsorption and catalytic oxidation	RACO
Gaseous working standard	G-WS
Primary standard	PS
Polyester aluminum	PEA
High-performance liquid chromatography	HPLC
Large volume injection	LVI
Gas chromatography	GC
Flame ionization detector	FID
Direct injection	DI
Mass spectrometry	MS
Thermal desorption	TD
Quality assurance	QA
Fixed standard volume	FSV
Response factor	RF
Coefficient of determination	\mathbb{R}^2
Relative standard error	RSE
Method detection limit	MDL
Breakthrough	BT
CO ₂ yield	Y
Weisz-Prater	WP
Knudsen diffusivity	D_{iK}
Average pore radius	r _{p,av}
Brunauer-Emmet-Teller	BET
Langmuir-Hinshelwood	LH
The used catalyst mass	m _{cat}
Powder X-ray diffraction	PXRD
Fourier-transform infrared	FTIR
Thermogravimetric analysis	TGA
Field-emission scanning electron microscope	FE-SEM
BET surface area	$\mathbf{S}_{\mathrm{BET}}$
Pore volume	V _{pore}
Pore diameter	$\mathbf{D}_{\mathbf{p}}^{\mathbf{r}}$
Inductively coupled plasma optical emission spectrometry	ICP-OES
X-ray photoelectron spectroscopy	XPS
binding energy	BE
Lattice oxygen	O_L
Adsorbed oxygen	OA
Breakthrough volume	BTV
Catalytic conversion efficiency	X
Gaseous oxygen	O_G
Apparent pre-exponential factor	$k_{app,\infty}$

Apparent activation energy

Eapp

1. Introduction

Due to rapid industrialization and urbanization, the deterioration of air quality has become a ubiquitous phenomenon worldwide (Zhu et al., 2019). If volatile organic compounds (VOCs, e.g., formaldehyde (FA) and toluene) are present in indoor air above the regulation guideline levels, they can pose a severe threat to human health (Plaisance et al., 2020). FA is a common carcinogenic aldehyde with a strong odor that is released from diverse sources and or activities (e.g., plywood, wood resin, adhesives, and carpets) (Vellingiri et al., 2020). Likewise, toluene is an aromatic VOC often liberated from various consumer products (e.g., paints, thinners, wallpaper adhesives, inks, and flooring) as well as industrial activities (e.g., during petroleum refining and petrochemical manufacturing) (Cheng et al., 2019). In a recent study, considerably high concentration levels of FA (up to 295.5 μ q/m³) and toluene (up to 532.8 μ q/m³) were measured in the living rooms of 11 newly renovated buildings in Taiwan (Lin et al., 2022). Note that these observed values exceed their guideline values of 98.2 μ g/m³ (Taiwan Environmental Protection Authority) and 300 μ g/m³ (in terms of total VOC (TVOC): World Health Organization), respectively (Lin et al., 2022). In light of the environmental and health impacts of these VOCs, it is essential to develop effective technologies to remove them.

The adsorption technique is one of the most preferable and/or economical options for removing VOCs from indoor air. For such applications, activated carbon (AC) has been a typical commercial adsorbent due to its low cost, extensive availability, and high efficiency against various VOCs (Ha et al., 2020). However, the pristine form of AC generally suffers from poor performance against polar VOC targets with low boiling points (e.g., FA). In addition, the liberation of adsorbed VOCs from spent AC restricts its sustainable application over prolonged periods (Twumasi et al., 2012). The development of the AC composites with advanced catalytic potential (such as reactive adsorption in

combination with thermal catalysis) has been proposed as one of the practical strategies to overcome such disadvantages (Huang et al., 2020).

Such composites can be synthesized by binding the porous AC with metal oxides (as reactive species for thermal catalysis) (Topka et al., 2019). The porous structure and large surface area of AC can provide a wide and uniform dispersion of metal oxides, thereby providing abundant oxygen species and oxygen vacancies for catalytic activities (Zhang et al., 2020). In addition, the higher surface affinity of AC adsorbent to most VOCs allows the metal oxide sites to efficiently induce the catalytic oxidation of the VOC molecules (Wu et al., 2000). Note that thermal catalytic oxidation is a viable option for oxidizing VOCs into carbon dioxide (CO₂) and water (H₂O) as the end-products and/or other less harmful compounds. Accordingly, the combination of porous AC with metal oxides can show better performance than the typical adsorbents (Jiang et al., 2020).

Recently, the potential of thermal catalysts with noble/precious metals (e.g., platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh), and gold (Au))-based has been explored for the removal of VOCs in light of their good thermochemical stability even at high temperatures with enhanced resistance to corrosion and chemical attack (Zeng et al., 2020). However, the use of precious metal catalysts in environmental applications is generally constrained due to their high cost, sintering at elevated temperatures, deactivation/poisoning by contaminants (e.g., chloride and sulfurous compounds), and depletion of limited resources (Fang and Guo, 2018). In this respect, the use of non-precious metal oxides (e.g., copper (Cu), manganese (Mn), cobalt (Co), cerium (Ce), iron (Fe), and chromium (Cr)) is recommended as an alternative due to their easy and inexpensive availability, high electron mobility, and variable valences (Liu et al., 2016; Wang and Astruc, 2017).

Manganese dioxide (MnO₂) is an environmentally-friendly and inexpensive metal oxide catalyst with high activity and thermochemical stability (Li et al., 2019). MnO₂ has a variety of crystallinephase structures such as amorphous-MnO₂ (Am-MnO₂), hollandite-type α -MnO₂, rutile-type β -MnO₂, ramsdellite-type R-MnO₂, birnessite-type δ -MnO₂, and γ -MnO₂ (intergrowth of β and R- phases). The selection of crystalline phases can significantly influence the thermal catalytic activity of MnO₂ in various applications (Yang et al., 2013). For instance, am-MnO_x showed a high catalytic ability to oxidize 90% of benzene, toluene, and xylene (1,000, 1,020, and 230 ppm, respectively) in air (space velocity (SV) = 60,000 mL g⁻¹)) into CO₂ at 235°C due to its large microporosity (0.15 cm³·g⁻¹), surface area (85.9 m²·g⁻¹), and a large number of lattice oxygen vacancies (Tang et al., 2014).

Similarly, α -MnO₂ was demonstrated to have a high catalytic activity towards 100 ppm (i.e., 0.53 mg·m⁻³) of FA with the rapid promotion of surface reactive oxygen species. As such, it was capable of achieving 100 and 96% of conversion efficiencies (at 60°C and RT, respectively) at gas hourly SV (GHSV) values of 90 and 600 L·g_{cat}⁻¹·h⁻¹, respectively (Rong et al., 2018). It was also reported that Am-MnO₂ showed enhanced basic properties (e.g., in terms of oxygen mobility, surface oxygen vacancies, and specific surface area) relative to other crystalline phases of MnO₂ (Ali et al., 2013; Yu et al., 2019). Hence, many efforts were made to promote catalytic activities based on the metalmetal oxide interaction (MMOI) through the binding of various metals (e.g., Ag, Co, and Cu) to crystalline MnO₂ (He et al., 2021). MMOI can exert electronic, geometric, and dual functional effects so that oxygen transport and electron replenishment can be facilitated at the interface between doped metals and metal oxide catalysts (Narayanasamy et al., 2021).

To learn more about the potential of the reactive adsorption and catalytic oxidation (RACO) of metal oxide AC composites (Am-MnO₂-AC), reactive adsorbents were prepared and tested for the removal of FA and toluene by running two different experiments (i.e., strategies). In experiment 1 (E1), the RACO performance of Am-MnO₂-AC was first explored for both targets (as single and dual components—see Section 2.2 for details). In experiment 2 (E2), the RACO performance of Am-MnO₂-AC was assessed using both targets (as dual components) in reference to three AC composites (i.e., one crystalline MnO₂ (δ-MnO₂) and two others doped with Co or Ag (i.e., Co-MnO₂-AC and Ag-MnO₂-AC)). E2 was conducted against the mixture to simplify the performance assessment

needed to cover multiple composite samples. The removal of each target was discussed in terms of the RACO mechanism with respect to the quantities of CO₂ produced via oxidation. The results of this research are expected to offer valuable insights into the application of the RACO system for the removal of hazardous VOCs from the air. Therefore, the overall results of the present study are expected to help establish an economical production strategy and commercialization of the metal oxide/AC composite for the RACO-based treatment of VOCs in line with the sustainable development goals (SDGs (2030 Agenda)).

2. Materials and methods

2.1. Materials, composite catalysts, and gas phases

For the preparation of the AC composite catalysts, AC was purchased from Duksan Pure Chemicals Co., Ltd (Ansan, Republic of Korea). The as-purchased AC product (coded as AC-0) was then sorted out in the size range of $< 0.6 \ \mu m$ for the preparation of composites. The detailed procedures for synthesizing AC-based MnO₂ composite catalysts, i.e., Am-MnO₂-AC, Co-MnO₂-AC, δ -MnO₂-AC, and Ag-MnO₂-AC along with the utilized characterization tools are described in the supplementary information (S.1 and S.2). Gaseous working standards (G-WS) of the VOCs used for the removal experiments were prepared in two different modes: (i) a single component for each target in the gas phase (i.e., FA (100 ppm) and toluene (100 ppm) in ultraclean air (21% oxygen (O₂) in nitrogen (N₂) balance)) and (ii) a mixture of both target VOCs in ultraclean air (100 ppm each).

For the preparation of 100 ppm (10 Pa) G-WS of FA, its primary standard (PS) was first prepared by the sublimation of 150 mg paraformaldehyde (Sigma-Aldrich, St. Louis, Missouri, USA) at 100°C using a temperature controller (TC200P, Misung Scientific. Co. Ltd, Seoul, Korea) under N₂ flowing at 100 mL·min⁻¹. The gaseous FA concentration collected into the polyester aluminum (PEA (Top Trading ENG, Seoul, Korea)) bag was quantified using the 2,4-dinitrophenylhydrazine (DNPH)- based high-performance liquid chromatography (HPLC) protocol after storing the PS at room temperature for 2 h (Vellingiri et al., 2020). The toluene PS of 1,000 ppm was purchased in a cylinder (Green Gas, Pocheon, Korea). The G-WS of the two VOC targets (FA and toluene) was finally prepared at 100 ppm in a 150 L PEA bag by diluting the gaseous PS of FA and/or toluene with ultraclean air.

2.2. Experimental procedure

In this work, the packed bed tubes were prepared for all types of AC-composites (i.e., three types of reactive adsorbents (Co-MnO₂-AC, δ -MnO₂-AC, or Ag-MnO₂-AC) and the raw AC (AC-0) as reference) for conducting the removal experiments against FA and toluene. To this end, each type of material was physically mixed with quartz sand (50-70 mesh particle size (Sigma-Aldrich, St. Louis, Missouri, USA)) in an equal mass ratio (50 mg catalyst : 50 mg quartz sand). The above mixture was then poured into a quartz tube (90 mm length x 4 mm internal diameter) and packed between two quartz wool plugs to make a packed bed system. Then, the packed bed was thermally conditioned CT2000 Tube Cleaner; Chemtronics, Inc., Kennesaw, GA, USA) at 250°C for 3 h under N₂ (99.999%) purging (200 mL·min⁻¹) to remove the surface impurities and pre-adsorbed moisture from the packed bed.

Figure 1 shows the schematic of the experimental setups for removing two VOC targets. Briefly, the packed bed was inserted into the temperature controller. All the experiments were conducted in the dark. The packed bed inlet was connected to the VOC (FA, toluene, or their mixture) G-WS bag. In contrast, the outlet was connected to a T-junction linked to a mini pump (MP-∑30NII from Sibata Scientific Technology, Ltd., Saitama, Japan) and a large volume injection (LVI) system (PRG-2010; Shimadzu Corp., Kyoto, Japan). The mini pump pulled the VOC G-WS through the packed bed at a flow rate of 200 mL·min⁻¹. The bed temperature was checked in real-time by inserting a thermocouple (Center-306 by Center Technology, New Taipei City, Taiwan) through the T-junction. The VOC concentration in the reactor effluent was analyzed using LVI-gas chromatography (GC)

(GC-2030 by Shimadzu Corp., Kyoto, Japan) interfaced with a flame ionization detector (FID). For the GC-FID analysis, the GC oven and FID temperatures were fixed at 100 and 250°C, respectively. A DB-1 capillary column (30 m length, 0.32 mm ID, and 5 μ m film thickness) was used to separate FA and toluene using N₂ (99.999%) as the carrier gas (24 mL·min⁻¹). Hydrogen (H₂ (99.999%) (30 mL·min⁻¹))) and air (200 mL·min⁻¹) were used as the fuel for the FID.

The CO₂ concentration generated by the thermal catalytic oxidation of VOCs was measured using GC-FID fitted with a methanizer system (iGC7200A GC; DS science INC, Gwangju, Korea) under the direct injection (DI) mode. Then, 200 μ L samples of the reactor effluent were collected using a 500 μ L gastight syringe (Trajan Scientific Australia Pty Ltd, Victoria, Australia) every 10 min for analysis by the GC-FID/methanizer system to monitor CO₂ production during thermal catalysis. Also, the GC-mass spectrometry (MS) analysis was performed to analyze the volatile organic by-products formed during the toluene oxidation reaction. The packed bed effluent was analyzed using a CarbopackTM tube (CarbopackTM C (50 mg) + B (50 mg) + X (50 mg))-based sampling protocol and analyzed using the thermal desorption (TD) (Unity II by Markes International, Ltd., Rhondda Cynon Taff, UK)-GC-MS (QP2010; Ultra Shimadzu Corp., Kyoto, Japan) method (Vikrant and Kim, 2020).

In this research, the RACO potential of Am-MnO₂-AC was assessed using two different target VOCs (i.e., FA and toluene) in two types of experiments (i.e., E1 and E2) as described above (Table S1). In all experiments, the performance was examined at multiple-isothermal conditions in a twostep process. In the first step, removal experiments were carried out at room temperature for 200 min (up to 40 L of VOC). In the next step, the materials were subjected to thermal oxidation by ramping up to 300°C at 25°C (a ramping rate of 25°C per 30 min corresponding to the supply of 6 L WS)) until reaching a total volume of 106 L. In this E1, the performance of AC-0 was also tested as the reference material. In E2, the testing approach applied for Am-MnO₂-AC was extended to cover all other metal-AC composites (δ-MnO₂-AC, Co-MnO₂-AC, and Ag-MnO₂-AC). In the case of E2, the performance assessment was made using the two targets as dual components to simplify the comparative analysis.

2.3. Data analysis

2.3.1. Quality assurance and quality control

During the course of the experiment, the reliability of the analytical system was assessed using routine quality assurance (QA) tests. The GC-FID-based calibrations of FA and toluene were conducted using the fixed standard volume (FSV) approach at five standard concentrations of FA (25, 50, 100, 200, and 250 ppm) and toluene (5, 10, 30, 50, and 100 ppm) (Kim, 2006). The response factors (RF) for FA and toluene were 34.1 and 2,558 ng⁻¹, respectively. The coefficient of determination (R^2) was > 0.99 for both the calibration curves. The reproducibility values of each target, if expressed in terms of relative standard error (RSE), were 1.31 and 1.04% for FA and toluene, respectively. The method detection limit (MDL) values for FA and toluene were 3.43 and 0.20 ng, respectively. For the quantitative analysis of CO₂, the GC-FID/methanizer system was calibrated using five concentration levels of CO₂ (100, 250, 500, 1,000, and 2,000 ppm) using the FSV method ($R^2 > 0.99$). The CO₂ RF, RSE, and MDL were 3,049 ng⁻¹, 3.92%, and 3.02 ng, respectively.

2.3.2. Breakthrough value

The breakthrough (BT) level was computed as the outlet/inlet VOC concentration $(\frac{c_{out}}{c_{in}})$ versus the loaded G-WS volume (L) at different interval points (n) using Eq. (1) (Kim et al., 2020).

$$\frac{C_{out}}{C_{in}} = \frac{0.5 \times [(C_{out})_n + (C_{out})_{n-1}]}{C_{in}}$$
(1)

2.3.3. Light-off curves

The steady-state continuity equation for compound i in a plug flow reactor is given by Eq. (2), where X_i , m_{cat} , $F_{i,0}$, and $r(X_i)$ represent the conversion of compound i (mol_i·mol_{i,0}⁻¹), the used catalyst

mass (kg_{cat}), the inlet molar flow rate of compound i (mol_i·s⁻¹), and the reaction rate (mol_i·kg_{cat}⁻¹·s⁻¹), respectively.

$$\frac{dX_i}{d\frac{m_{cat}}{F_{i,0}}} = r(X_i) \tag{2}$$

The ratio $\frac{m_{cat}}{F_{i,0}}$ is the space-time (kg_{cat}·s·mol_{i,0}⁻¹) (Heynderickx et al., 2009; Thybaut et al., 2010).

The apparent first-order reaction rate is calculated using Eq. (3). The inlet O_2 concentration was ~ 2,000 times higher than the inlet substrate concentration in the present work. Hence, the O_2 concentration was assumed to be constant to maintain a first order reaction with respect to the substrate concentration.

The outlet concentration of the target VOC, i (i = FA or toluene) can be computed by the inlet concentration and the corresponding conversion efficiency, as described in Eq. (4). The relationship between the conversion and space-time is also given by Eq. (5).

$$r = k_{app} C_i \tag{3}$$

$$C_{i} = C_{i,0}(1 - X_{i})$$
(4)

$$X_{i} = 1 - \exp\left(-k_{app} \cdot C_{i,0} \cdot \frac{m_{cat}}{F_{i,0}}\right)$$
(5)

A light-off curve can be constructed for different isotherm conditions, i.e., the conversion versus temperature can be estimated using the Arrhenius relation presented in Eq. (6).

$$\boldsymbol{k_{app}} = \boldsymbol{k_{app,\infty}} \cdot \exp\left(-\frac{\boldsymbol{E_{app}}}{\boldsymbol{RT}}\right) \tag{6}$$

Suppose that the compound i is expressed in $mol_i \cdot m^{-3}$, while the unit of k_{app} (and $k_{app,\infty}$) unit is $m^3 \cdot kg_{cat}^{-1} \cdot s^{-1}$. The molar ratio of the target compound (ppm_i) is converted into $mol_i \cdot m^{-3}$ at 25°C using Eq. (7). The initial concentration of 100 ppm corresponds to $4.09 \cdot 10^{-3}$ mol $\cdot m^{-3}$ using Eq. (7).

$$(C_i) = (ppm_i) \cdot \frac{1}{24.464} \cdot 10^{-3}$$
(7)

2.3.4. Carbon dioxide yield

For the inflow of a mixture made of FA and toluene, the total outflow of CO_2 can be expressed by Eq. (8).

$$F_{CO_2} = F_{FA,0} \cdot X_{FA} + 7 \cdot F_{T,0} \cdot X_T \tag{8}$$

Eq. (8) is valid under the condition that no selective oxidation products are formed. That is, only total oxidation occurs through complete mineralization into CO_2 . The CO_2 yield (Y) is the flow rate ratio during and after the completion of oxidation into CO_2 , as expressed below in Eq. (9).

$$Y = \frac{F_{FA,0} \cdot X_{FA} + 7 \cdot F_{T,0} \cdot X_T}{F_{FA,0} + 7 \cdot F_{T,0}}$$
(9)

From Eq. (9), it is clear that for single compound data, the Y equals the conversion of the compound. The produced CO_2 accounts only for 12.5% of the total signal in the case mixtures, while only FA is involved in the reaction to reach the full-scale conversion. The above reasoning is crucial for assessing the estimated total oxidation kinetic parameters (see Section 3.3). The Y for only FA conversion is readily obtained from Eq. (10) at equal experimental inlet molar flow rates (same inlet concentration and total volumetric flow rate).

$$(Y)_{only FA converted} = \left(\frac{F_{FA,0} \cdot X_{FA} + 7 \cdot F_{T,0} \cdot 0}{F_{FA,0} + 7 \cdot F_{T,0}}\right)_{F_{FA,0} = F_{T,0}, X_{FA} = 1} = \frac{1}{8}$$
(10)

2.3.5. Intrinsic oxidation kinetics for FA and toluene

The internal/external mass and heat transfer criteria are important for assessing the role of intrinsic kinetics for catalytic processes (i.e., without diffusion). The criterion for the absence of internal mass transfer is known to be the most difficult to satisfy (Heynderickx et al., 2009). Hence, if this criterion is satisfied, the other criteria for external mass transfer and heat transfer are apt to be satisfied as well. Therefore, the internal mass transfer criterion has been evaluated for the tested porous materials (Heynderickx et al., 2009; Thybaut et al., 2010).

The effects of the internal mass transfer on the catalytic conversion of VOCs can be assessed by Eq. (11). Here, $R_{V,A}^{obs}$, $D_{A,eff}$, $C_{A,s}$, d_p , and n imply the observed volumetric reaction rate (mol_i m_{pellet}⁻³ s⁻¹), the effective diffusivity (m² s⁻¹), the surface concentration of the rate-limiting compound (FA or toluene), the catalyst particle diameter (m), and the reaction order (-), respectively.

$$\frac{\mathbf{R}_{\nu,A}^{obs}}{D_{A,eff} C_{A,s}} \left(\frac{d_p}{6}\right)^2 < \frac{1}{12n} \tag{11}$$

Note that the specific value for the volumetric oxidation reaction rate is required for FA or toluene to evaluate the so-called Weisz-Prater (WP) criterion given in Eq. (11) (Weisz and Prater, 1954). The estimated parameters in Table 5 can be used to quantify the reaction rate, as expressed in Eq. (3). The temperature at which the CO₂ yield is inflected is adopted to evaluate the reaction rate coefficient, because this point corresponds to the highest oxidation rate. As calculated using Eq. (3), the oxidation reaction rate for FA or toluene can be expressed in mol_i kg_{cat}⁻¹ s⁻¹. To obtain the volumetric oxidation rate for compound i (FA or toluene) (in mol_i m_{cat}⁻³ s⁻¹) as required in Eq. (11), the total oxidation reaction rate (mol_i kg_{cat}⁻¹ s⁻¹) is multiplied by a factor (ρ_{cat} ·(1- ε_p)) (unit: kg_{cat} m_{cat}⁻³ · m_{cat}³ m_{pellet}⁻³ = kg_{cat} · m_{pellet}⁻³) based on the volume of catalyst pellet in the reactor. Typical values for the catalyst solid density (assumed as pure AC) and the catalyst particle porosity are 2,000 kg_{cat}·m_{cat}⁻³ and 0.75 m_f³·m_{pellet}⁻³.

The effective diffusivity of the compound i in a catalyst pellet, $D_{i,eff}$, depends on its porosity and pore structure. Effective diffusivity can be approximated by Eq. (12), with ε_p and τ_p as the catalyst particle porosity and tortuosity, respectively (Froment and Bischoff, 1990).

$$\mathbf{D}_{i,eff} = \frac{\varepsilon_P}{\tau_P} \left(\frac{1}{D_{i,m\,k}} + \frac{1}{D_{i,K}} \right)^{-1} \tag{12}$$

The calculation of the bulk diffusivity of component i in a gas mixture, $D_{i,mix}$, has been explained previously (Froment et al., 2011). The tortuosity inside the catalyst particle reduces the diffusivity of the substrate (FA or toluene) due to the effect of the so-called zig-zag factor in the pores and the restriction factor associated with the widening and narrowing of these pores. A typical value for the tortuosity is between 2 and 5 m·m⁻¹ (Chorkendorff and Niemantsverdriet, 2017). As the actual tortuosity values are difficult to quantify experimentally, the highest tortuosity value of 5 m·m⁻¹ was adopted. As a result, the WP criterion can be considered the most severe among all possible tortuosity conditions.

The Knudsen diffusivity, $D_{i,K}$, was calculated using Eq. (13), where the value of $r_{p,av}$ for the average pore radius was taken as 4.5 nm. Note that 45 Å was taken as the average (i.e., $\sqrt{20 \cdot 100} \approx$ 45) based on the two distinct peaks (around 20 and 100 Å) derived by the Brunauer-Emmet-Teller (BET) analysis.

$$\mathbf{D}_{i,K} = \frac{2}{3} \cdot \mathbf{r}_{P,av} \cdot \sqrt{\frac{8RT}{\pi M_i}}$$
(13)

The concentration of compound i (FA or toluene) at the catalyst particle surface can be assumed as equal to the bulk gas phase concentration, i.e., $C_{A,s} = C_{A,b} = 4.09 \times 10^{-3} \text{ mol} \cdot \text{m}^{-3}$. Knowing that the particle size of all studied catalysts is below 212 µm, the average particle size distribution is assumed to be 106 µm. The reaction order, n, is taken as 1. Table 5 shows the results for evaluating the WP criterion for internal mass transfer (Eq. (11)). Accordingly, we concluded that the WP criterion is fulfilled.

2.3.6. Information on catalyst porosity

The inner pore surface area of the catalyst can be generally expressed as the side area of a cylinder with an average pore size of $r_{p,av}$ and a total (hypothetical) length L (Weitkamp et al., 1999). The

BET surface area, S (expressed as $m^2 \cdot kg_{cat}^{-1}$), when multiplied by the used catalyst mass (m_{cat}, expressed as kg_{cat}), is equal to the inner area (Eq. (14)). The total inner void volume of a catalyst particle can be taken as the volume of a cylinder (V_f) with length L and radius r_{p,av} (Eq. (15)).

$$\boldsymbol{m}_{\boldsymbol{\alpha}\boldsymbol{a}\boldsymbol{t}} \cdot \boldsymbol{S} = 2\boldsymbol{\pi} \cdot \boldsymbol{r}_{\boldsymbol{p},\boldsymbol{a}\boldsymbol{v}} \cdot \boldsymbol{L} \tag{14}$$

$$V_f = \pi \cdot r_{p,av}^2 \cdot L \tag{15}$$

Taking into account of the definition of ε_p (the void fraction inside a catalyst particle), Eqs. (14) and (15) can be employed to assess the relationship between different variables of the catalyst such as particle porosity, BET surface area, average pore size, and density (Eq. (17)):

$$\varepsilon_{p} = \frac{V_{f}}{V_{aat}} = \frac{\pi \cdot r_{p,av}^{2}}{\frac{m_{aat}}{\rho_{aat} \cdot (1 - \varepsilon_{p})}} \cdot \frac{m_{aat} \cdot S}{2\pi \cdot r_{p,av}} = r_{p,av} \cdot \frac{S}{2} \cdot \rho_{aat} \cdot (1 - \varepsilon_{p})$$
(16)
$$\varepsilon_{p} = \frac{1}{1 + \frac{2}{r_{p,av} \cdot S \cdot \rho_{aat}}}$$
(17)

Using Eq. (17) and the obtained BET results for the catalysts (see Section 3.1), the values for the catalyst void fraction for Am-MnO₂-AC, Co-MnO₂-AC, δ -Co-MnO₂-AC, and Ag-MnO₂-AC can be obtained as 0.750, 0.123, 0.713, and 0.622 m_f³·m_{pellet}⁻³, respectively. Since all catalysts are prepared from the same AC material, the same density (~ 2,000 kg·m⁻³) was assumed for all Mn phases.

2.3.7. Apparent kinetics

The total processes governing the oxidation of substrates over catalysts can be interpreted by a Langmuir-Hinshelwood scheme. For instance, in the first (adsorption) stage, oxygen and the substrate are adsorbed on the catalyst surface. Then, in the subsequent stage, the substrate is oxidized into total oxidation products through the reaction of surface adsorbates. For such a Langmuir-Hinshelwood (LH) mechanism with the surface reaction as the rate-determining step, the apparent activation energy for total oxidation can be expressed as the true activation energy minus the adsorption enthalpy of both reactants and additional cross terms involving surface coverages (i = T

or FA, j = i, O₂ and products), see Eq. (18) (Thybaut et al., 2010). Detailed information about this derivation procedure is provided in section S.5 of the Supplementary Information.

$$E_{app} = E_{true} - (-\Delta H_i) - (-\Delta H_{0_2}) + 2\sum_{j=1}^n \theta_j (-\Delta H_j)$$
(18)

In the case of the pre-exponential factor, the unit of k_{app} (m³·kg_{cat}⁻¹·s⁻¹) can be converted into s⁻¹ through Eq. (19).

$$\boldsymbol{k}_{app,\infty}' = \boldsymbol{k}_{app,\infty} \cdot \frac{\rho_{aat}(1-\varepsilon_p)}{\varepsilon_p} = \boldsymbol{k}_{app,\infty} \cdot \frac{2}{r_{p,av} \cdot \boldsymbol{S}}$$
(19)

The units for the conversion in Eq. (19) are $(kg_{cat} \cdot m_{pellet}^{-3})/(m_f^3 \cdot m_{pellet}^{-3}) = m_f^3 \cdot kg_{cat}^{-1}$. For an irreversible reaction, the relation between the pre-exponential factor and ΔS^{\neq} (i.e., the difference between the entropy of the activated complex and reactants) can be expressed by Eq. (20).

$$k'_{app,\infty} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right)$$
(20)

The importance of ΔS^{\neq} is that it contributes to the shift in equilibrium between the reactants and activated complexes through the common thermodynamic relationship $\Delta G^{\neq} = \Delta H^{\neq} - T \cdot \Delta S^{\neq}$. The value for ΔH^{\neq} can be taken as the activation energy (with a maximal deviation of 10%). For activated complexes (relative to the reactants) in bimolecular reactions, the value for ΔS^{\neq} typically becomes negative with decreases in the degrees of freedom (Vyazovkin, 2021).

3. Results and discussion

3.1. Physicochemical characterization of manganese dioxide-AC composites

According to the powder X-ray diffraction (PXRD) analysis, the AC-0 with a broad diffraction peak at 20 of 18° – 33° (002) may be attributed to the existence of a graphitic plane in its structure (Figure 2 (a)). As the graphitic plane (002) is observed in all the composites, it is possible to infer that MnO₂ impregnation should not induce any significant alteration in the lattice structure of AC-0. For the Am-MnO₂-AC composite, the amorphous nature of doped MnO₂ is recognized by the presence of only broad peaks at 37.6° and 66.3° (Yang et al., 2010). In contrast, Co-MnO₂-AC exhibited broad diffraction peaks along with the characteristic peaks for doped Co at the 20 values 37.3°(111), 42.9°(200), 65.3°(220), and 72.4° (311) (ICDD 15-0806) (Khe et al., 2012). In comparison, other δ -MnO₂-AC composites recorded several diffraction peaks at 20 values of 12.5°, 24.7°, 37.3°, and 65.8°, which can be assigned to the (001), (002), (110), and (020) crystal planes of δ -MnO₂ tetragonal phase, respectively (JCPDS No. 80-1098) (Tao et al., 2020). In the case of Ag-MnO₂-AC, it was possible to recognize both the characteristic diffraction peaks of the α -MnO₂ tetragonal phase (JCPDS No. 44-0141) and Ag crystalline planes for metallic Ag (JCPDS No. 89-3722). The characteristic diffraction peaks of the α -MnO₂ phase are shown at 20 values 12.8°(110), 20.8°(200), 28.7°(310), 37.4°(211), 42.4°(301), 50.1°(411), 56.8°(600), 60.0°(521), and 64.6°(002) (JCPDS No. 44-0141). Additionally, the characteristic Ag peaks were found at 20 values of 36.1° (113), 44.4°(200), and 64.6° (220) (Narayanasamy et al., 2021).

The Fourier-transform infrared (FTIR) profiles of the as-prepared materials are shown in Figure 2 (b). Accordingly, the characteristic bands of the carbonaceous matrix (2024-2161 cm⁻¹ for C \equiv C vibration stretch and 880-1160 cm⁻¹ for C-O groups) were observed in all the composite materials. The oscillations of the Mn-O bond (vibration of the O-Mn-O bond) in the MnO₂ containing composites were also observed as sharp bands between 450-750 cm⁻¹ (Yang et al., 2005). Also, the FTIR bands at ~ 1628 cm⁻¹ may reflect the stretching and bending oscillations of surface hydroxyls (OH) on the MnO₂ surface (Mn-OH) (Ghosh et al., 2016). FTIR bands for the Co and Ag species were not clearly observed, possibly because of their low content in the composites.

Figure S1 shows the thermogravimetric analysis (TGA) curves and derivative TGA curves of the tested materials. The tested materials show a weight reduction of 12.4% up to 600°C. The materials showed high thermal stability with a weight reduction of 5.1% up to 300°C (i.e., the highest temperature set during the VOC oxidation experiment). All the tested materials showed weight loss after 55°C to reflect the desorption/vaporization of pre-adsorbed moisture. A second weight-loss

region for AC-0, Am-MnO₂-AC, Co-MnO₂-AC, and Ag-MnO₂-AC was observed at 473, 335, 455, and 388°C, respectively. In the case of δ -MnO₂-AC, a pattern of weight reduction was observed constantly after 177°C.

The surface morphology of the prepared materials was evaluated using a field-emission scanning electron microscope (FE-SEM), as shown in Figure 3. Accordingly, both AC-0 and metal-AC composites (Am-MnO₂-AC, δ -MnO₂-AC, Co-MnO₂-AC, and Ag-MnO₂-AC) exhibited a typical porous carbon structure with cracks and crevices (pore diameter: 4.41-13.18 μ m). The AC-0 adsorbent was covered with an aggregate of MnO₂ nanoparticles adhered to its surface, as seen consistently in all composites (Figure 3 (b, c, d, and e)). The Am-MnO₂ exhibited irregular floc clusters and needle-type structures (diameter: 73-87 nm), as expected from amorphous structures (Figure 3 (f)). Co-MnO₂ also exhibited irregular floc clusters, although the particles were smaller (53-58 nm) with fewer needle-type structures than Am-MnO₂ (Figure 3 (g)). δ -MnO₂ had the typical microsphere shape with diameters in the 560-730 nm range (Figure 3 (h)), whereas Ag-MnO₂ displayed a nanowire structure with a thickness of 110 nm (Figure 3 (i)).

Table S2 summarizes the elemental composition of the prepared composites based on inductively coupled plasma optical emission spectrometry (ICP-OES) and elemental analysis (EA). The results indicate that AC-0 is mainly composed of carbon (80.4 wt.%) and oxygen (18.9 wt.%), with a minor content of nitrogen (0.29 wt.%) (Danmaliki et al., 2017). The atomic weight ratio of the Mn atom in the Am-MnO₂ was 67.3 wt.%, which is in line with the theoretical ratio derivable from the chemical formula (63.2 wt.%). In contrast, the atomic weight ratio values of Mn atoms in the prepared Am-MnO₂-AC, δ-MnO₂-AC, Co-MnO₂-AC, and Ag-MnO₂-AC composites were reduced to 36.5, 45.2, 30.1, and 10.2 wt.%, respectively. These elemental data indicate that their MnO₂ loading (in terms of wt.% of the Mn content) should correspond to 50, 62, 41.3, and 14 wt.%, respectively. Also, the Co-MnO₂-AC was loaded with 2.54 wt.% Co, while Ag-MnO₂-AC was found to contain 1.59 wt%

Ag (Table S2). Such variation in the loading amount of MnO₂ could significantly influence the RACO performance toward the VOC targets, as explained below (see Section 3.2).

In Table 1, the textural properties (BET surface area (S_{BET} ; $m^2 \cdot g^{-1}$), pore volume (V_{pore} ; $cm^3 \cdot g^{-1}$), and average pore diameter (D_p ; nm)) of the prepared materials are summarized based on their N_2 adsorption-desorption isotherms. As shown in Figure S2 (a), all materials exhibited a typical Type-1 N_2 adsorption-desorption isotherm (characteristic of microporous materials) with H3 hysteresis loops as per the International Union of Pure and Applied Chemistry (IUPAC) (Thommes et al., 2015). The H3-type hysteresis loop suggests that the condensation of N_2 into mesopores should have taken place at elevated P/P0 levels. The H3-type hysteresis loop also indicates narrow slit-like pores with irregularly shaped internal pores.

In Table 1, the S_{BET} of AC-0 significantly decreased upon impregnation with MnO₂ species such as: AC-0 (781 m²·g⁻¹) > Am-MnO₂-AC (666 m²·g⁻¹) > δ -MnO₂-AC (553 m²·g⁻¹) > Ag-MnO₂-AC (366 m²·g⁻¹) > Co-MnO₂-AC (31.2 m²·g⁻¹). The decrease in the S_{BET} value is explained by the partial pore blockage upon impregnation with metal oxides, as seen in Figure S2 (b). A decrease in incremental pore volume was observed in the region below 15 Å in the order of AC-0 > Am-MnO₂-AC > δ -MnO₂-AC > Ag-MnO₂-AC > Co-MnO₂-AC. In contrast, all the composites have larger pore size distributions with higher D_P values than AC-0. Figure S3 shows a schematic of the RACO mechanism for the metal oxide/AC composites. It is suspected that the volume of micropores has been reduced with the impregnation of metal oxides (small particle size (53-730 nm)) during the high-temperature treatment in the synthesis of composite material. Hence, the D_P values were found to increase. The Am-MnO₂ particles mainly consisted of small sizes (73-87 nm) along with some floc clusters and needle-type structures that could agglomerate to form larger clusters. Therefore, Am-MnO₂-AC can be accumulated less efficiently in the pores than in other composites (δ -MnO₂-AC, Ag-MnO₂-AC, and Co-MnO₂-AC). δ -MnO₂ particles consisted of a relatively large size (560-730 nm). In contrast, as δ -MnO₂-AC has spherical particles of a certain size and high content of δ - MnO₂ (62%), it can clog the pores more easily than Am-MnO₂-AC. Further, Ag-MnO₂ with a small nanowire structure and thickness of 110 nm can be accumulated more easily in the pores of AC. In the case of Co-MnO₂, as explained in the SEM analysis result, the particle size (53-58 nm) is the smallest: they may be easily accumulated in the pores of AC, as most of them take the form of small flocs. Accordingly, Co-MnO₂-AC has the lowest S_{BET} (31.2 m²·g⁻¹) and V_{pore} (0.024 cm³·g⁻¹) values but the highest D_p value (3.09 nm).

Surface information, including the oxidation states of the surface elements of the MnO₂-AC composites, was obtained from X-ray photoelectron spectroscopy (XPS) analysis. As shown in Figure S4, the peaks of C 1s, Mn 2p, and O 1s can be observed in all the tested MnO₂-AC composites along with the corresponding peaks of Co 2p in Co-MnO₂-AC and Ag 3d in Ag-MnO₂-AC. These observations confirmed the successful synthesis of the composite materials. Figure S5 shows the deconvoluted XPS spectra of Mn 2p, O 1s, Co 2p, and Ag 3d for all the tested MnO₂-AC composites. Based on the XPS data analysis, the oxidation states of surface elements in all the prepared composites are provided in Table 2.

In Figure S5 (b - e), the Mn 2p peak could be deconvoluted into two spin orbitals, Mn $2p_{3/2}$ and Mn $2p_{1/2}$, with the binding energies (BE) of 642.0-642.2 and 653.7-654.0 eV, respectively (Wei et al., 2016). The spin-energy separation between the two peaks of 11.4 to 11.8 eV represent a typical spin-orbit splitting value of MnO₂ (Khan et al., 2018). The Mn $2p_{3/2}$ peaks could also be deconvoluted into two peaks related to the existence of Mn³⁺ and Mn⁴⁺ species in all composites with BE values of 641.3-641.7 and 642.7-643.2 eV, respectively (Huang et al., 2018). Likewise, the Mn $2p_{1/2}$ peaks could also be divided into surface Mn³⁺ and Mn⁴⁺ species with binding energies of 652.9-653.3 and 654.4-654.7 eV, respectively (Mo et al., 2020).

As shown in Figure S5 (g - j), the O 1s for all the tested materials could also be deconvoluted into the two peaks at BE values of 529.5-531.0 and 531.0-532.6 eV to reflect the presence of lattice oxygen (O_L) and adsorbed oxygen (O_A) species, respectively (Luo et al., 2018). Both types of surface

oxygen can affect the oxidation efficiency of VOC as surface adsorbed oxygen tends to be more mobile than lattice oxygen (Liu et al., 2016). According to the principle of electrostatic balance, the coexistence of Mn^{3+} and Mn^{4+} indicates the presence of oxygen vacancies in MnO_2 crystal structures (Ye et al., 2018). The presence of oxygen vacancies is useful in electron movement while being helpful for enhancing the redox properties (catalytic activity) of the prepared composites. Further, a high proportion of O_A implies abundant surface oxygen vacancies (He et al., 2021). Therefore, it is inferred that a high proportion of Mn^{3+} and oxygen vacancies should result in high catalytic activity for VOC oxidation reactions (Zheng et al., 2017).

For Co-MnO₂-AC and Co-MnO₂ samples, the two spin orbitals of Co 2p are centered at BE values of 780 eV ($2p_{3/2}$) and 796 eV ($2p_{1/2}$) (Figure S5 (q and r)) (Yang et al., 2018). The Co $2p_{1/2}$ peaks can also be deconvoluted into two peaks due to the coexistence of Co³⁺ (796-798.5 eV) and Co²⁺ (801.4-802.6 eV) elemental oxidation states (Chen et al., 2017). Likewise, the Ag $3d_{5/2}$ peak in Ag-MnO₂-AC and Ag-MnO₂ samples can be divided into two peaks to reflect the coexistence of Ag⁺ (367.3 - 367.8 eV) and Ag⁰ (368.2 - 368.4 eV) metal species (Figure S5 (s and t)) (He et al., 2021). The addition of metal oxides (e.g., Ag and Co) to MnO₂ is beneficial for catalysis as such additions can facilitate the activation of lattice oxygen (He et al., 2021). The coexistence of Co (Co³⁺ and Co²⁺) and Ag species (Ag⁺ and Ag⁰) indicates the presence of a redox cycle and MMOI (Tang et al., 2006). Based on the XPS data in Table 2, the ratios of Mn³⁺/Mn⁴⁺ and O_A/O_L in all the MnO₂-AC composites were 1.51-1.05 and 2.62-1.21 times higher than that recorded in pristine MnO₂ (Am-MnO₂ and δ -MnO₂) and MMOI materials (Ag-MnO₂ and Co-MnO₂), respectively. These results indicate that the formation of O_A can be promoted by the interactions between MnO₂ and the MMOI (Ag-MnO₂ and Co-MnO₂) at the AC surface.

3.2. Removal performance evaluation of MnO₂-AC composites

3.2.1. RACO performance of amorphous-MnO₂-AC against FA and toluene (E1)

In this study, we investigated the basic aspects of RACO for FA and toluene as both single and dual-components. In E1, the RACO removal of these targets was assessed using Am-MnO₂-AC (plus AC-0 as reference). Table 3 summarizes the breakthrough volume (BTV) set to three BT levels (10, 50, and 100%) and catalytic reaction temperatures for 10, 50, and 90% removal of targets as the key criteria (Bielicka-Daszkiewicz and Voelkel, 2009). The BTV10% and BTV 50% values of single FA are 270 and 8.9 times higher, respectively, for Am-MnO₂-AC than for AC-0. However, in the case of toluene alone, they were 1,57 and 1.4 times higher, respectively, for AC-0 than for Am-MnO₂-AC. Note that the superior performance of AC-0 over Am-MnO₂-AC is apparent in adsorption of toluene as reflected by their differences in the BET results (Table 1). The SBET and Vpore values of AC-0 were 1.17 and 1.15 times greater than those of Am-MnO₂-AC, respectively. These observations imply that the adsorption of toluene should be more affected by surface porosity (Kim et al., 2012). As such, the superiority of Am-MnO₂-AC is confined to FA only, as AC-0 is more effective in removing toluene. It is however striking to find that the superiority of Am-MnO₂-AC for both FA and toluene becomes a dominant trend after 33 L (Figure 4 (a)). For instance, such relative dominance of Am-MnO₂-AC can be confirmed by the BT ratio (C_{out}/C_{in}) of FA and toluene as single components. At 40 L (i.e., the end point of step 1 under RT condition), AC-0 is approaching the adsorption saturation for both targets with BT ratio values of 0.85 and 1.0, respectively. On the other hand, their counterparts for the Am-MnO₂-AC were found to have much lower values of 0.59 and 0.61, respectively. As such, the overall removal potential of Am-MnO₂-AC became far superior for both target VOCs at RT using catalytic activity over time.

Figure 4 (a and b) shows the high fluctuation in the outlet concentration of toluene (for both single components and the mixture) with increasing temperature when tested against AC-0 and Am-MnO₂-AC. Such patterns may be explained by the fact that the thermal oxidation rate of toluene on the

active Mn³⁺/Mn⁴⁺ metal sites is lower at elevated temperatures than the desorption rate of toluene because it takes place on the active surface sites in the porous carbon beds. With further increases in temperature (>150°C), Am-MnO₂-AC induced thermal catalytic oxidation of toluene. As shown in Figure 4 (a and b), AC-0 does not show any enhancement in removal efficiency for FA and toluene at multiple-isothermal conditions. It is thus evident that the pristine AC-0 does not exhibit any thermal catalytic activity, possibly due to the deficiency of the active metallic species in its structure. In contrast, Am-MnO₂-AC realizes the full removal of both FA and toluene introduced individually at 100°C and 275°C, respectively.

As shown in Figure 4 (b), the BT curves for the dual-component (FA/toluene) are plotted for Am-MnO₂-AC (in reference to AC-0). The removal efficiency of Am-MnO₂-AC was reduced noticeably when they were introduced as dual forms relative to individual forms at room temperature. After supplying 40 L of the standard gas at RT, the BT values of FA and toluene (as a dual component mixture) for Am-MnO₂-AC reached 99% (relative to 59 (FA) and 61% (toluene) for the single components). The adsorption performances of Am-MnO₂-AC for FA and toluene as single components were 1.3 to 7.6 times higher than those of the dual-component mixture of FA (34.9 (M) vs. 45.9 (S)) and toluene (122 (M) vs. 357 (S)) when assessed in terms of the BTV10% value ($L \cdot g^{-1}$) at room temperature (Table 3). Here, the symbols S and M are used to denote single and mixture, respectively. On a similar note, Am-MnO₂-AC showed improved catalytic activity to achieve 100% oxidation of the single-FA system at a lower temperature (100% X_F at 100°C) than that for the dualcomponent system (100% X_F at 120°C) (Table 3 and Figure 5). Likewise, the T10%, T50%, T90%, and T100% values for the former decreased by 25-50°C compared to their counterparts for the latter. Note that the percentage after T corresponds to the reaction temperature obtained at each conversion efficiency. In contrast, the reaction temperature values for toluene were reduced by 75-150°C as a single-component compared to the dual-component system. Complete catalytic conversion of dualcomponent FA and toluene to CO₂ (T100%) was achieved at 125 and 300°C, respectively, which is 25°C higher than the results for the single-component system. The observed differences between the single and dual system could be explained based on their competitive inhibitory effects and the formation of their intermediates on the same active adsorption and catalytic sites (Kamal et al., 2016).

3.2.2. Performance comparison of dual VOC system between various types of metal oxide-AC composites (E2)

To learn more about the removal performance of Am-MnO₂-AC investigated in this study, it is desirable to assess its performance in reference to comparable catalytic systems. For this purpose, the performance of Am-MnO₂-AC was assessed for comparison with other metal-AC composites prepared in this work (i.e., δ -MnO₂-AC, Co-MnO₂-AC, Ag-MnO₂-AC, and AC-0 (as the main reference)) (E2). To make this comparison in a simple manner, the experiments were conducted using the dual VOC system under multiple-isothermal conditions. Figure 6 depicts the breakthrough and thermal catalytic profiles of FA/toluene (as a mixture) obtained by all the prepared composites as well as AC-0. Table 4 summarizes the BTV at three BT levels (10, 50, and 100%) as a critical performance metric (Bielicka-Daszkiewicz and Voelkel, 2009).

From the BT profiles in Figure 6 (a), all MnO₂-AC composites showed high adsorbability for FA (relative to AC-0). In contrast, AC-0 displayed the highest adsorption affinity for toluene followed by Am-MnO₂-AC (as the second-best performer). The improved adsorption performance of MnO₂-AC composites for FA should be attributed to their high surface polarity and the synergistic role of MnO₂ in inducing reactive adsorption mechanisms (Figueiredo, 2013). Among all metal- AC composites, Am-MnO₂-AC and δ -MnO₂-AC outperformed all other composites as their BTV100% values for FA were higher than those of AC-0 by 14.2 and 3.4 times, respectively (Table 4). Based on the BTV10% metric, the relative performance for FA removal followed a descending order of: Am-MnO₂-AC (34.9 L·g⁻¹) > δ -MnO₂-AC (7.63 L·g⁻¹) > Ag-MnO₂-AC (5.40 L·g⁻¹) > AC-0 (0.124 L·g⁻¹) > Co-MnO₂-AC (0.101 L·g⁻¹).

In the case of toluene, the BTV10% values decreased in the following order: AC-0 (285 $L\cdot g^{-1}$) > Am-MnO₂-AC (122 L·g⁻¹) > δ -MnO₂-AC (75.3 L·g⁻¹) > Ag-MnO₂-AC (46.8 L·g⁻¹) > Co-MnO₂-AC $(5.52 \text{ L}\cdot\text{g}^{-1})$. Such relative ordering in toluene removal follows a pattern similar to the BET result (Table 1). This observation suggests the crucial role of surface porosity (V_{Pore} and S_{BET}) in toluene capture through diffusion and physisorption mechanisms (Kim et al., 2012). However, it should be noted that the breakthrough adsorption curves of FA and toluene onto all the reactive composites did not obtain a 100% equilibrium BT level as the VOCs are catalytically converted into CO₂ (4 to 9% yield) with the progress of RACO at room temperature (Figure 6 (c)). As adsorption proceeds, doped metal oxides (e.g., pure MnO₂ and Ag- or Co-doped MnO₂) onto AC-0 can act as reactive catalytic sites to alter the prominent pathway of VOC removal from physisorption to reactive catalytic processes at the near-equilibrium stage, i.e., 100% BT, and room temperature (Figure 6 (a-d)). Accordingly, after passing 40 L of the VOC gas mixture through the packed bed at 25°C, thermal catalysis was initiated with an increase in the reaction temperature (e.g., up to 300°C at incremental rate of 25°C). As in the case of Am-MnO₂-AC, the fluctuations of toluene concentration were observed, due possibly to the desorption with an increase in temperature in all packed composite beds (Figure 6 (a and b)). With further increases in temperature (>150°C), thermal catalytic oxidation of toluene was induced in all packed composite beds.

The FA concentrations in the outlet stream gradually decreased as the temperature in the composite packed bed increased from 25 to 150°C (Figure 6 (a)). This observation indicates the higher reactivity of the prepared composites, resulting in the rapid thermal oxidation of desorbed FA molecules. Among the tested composites, Am-MnO₂-AC showed the fastest catalytic conversion of FA to CO₂ with a temperature increase from 25 to 300°C. In contrast, Ag-MnO₂-AC exhibited the highest catalytic oxidation efficiency of toluene at low temperatures (25 to 175°C), with 4.6-26.6% toluene conversion to CO₂. Consequently, the influential role of Ag is more prominent at lower temperatures than that of Mn (Zhang et al., 2016). The catalytic oxidation efficiency of Ag-MnO₂-AC against

toluene exceeded 50% with an increase in the bed temperature to 300°C. However, its performance at 300°C was inferior to Am-MnO₂-AC, which achieved a catalytic oxidation of ~100% (Figure 6 (c)). As such, the enhanced catalytic activity of Mn is apparent at elevated temperatures. The Am-MnO₂-AC with a large surface area could also provide more active surface sites for the rapid oxidation of VOCs.

Figure 6 (c) shows the CO₂ yield as a function of the bed temperature. It is possible to confirm the match between the theoretical CO₂ concentration (at 100% VOC conversion) and the experimentally observed yield, as each reactive composite can completely oxidize the VOCs. Figure 7 shows the temperature required to obtain 10, 50, 90, and 100% catalytic conversion efficiencies for the VOCs (FA (X_{FA}) and toluene (X_T)) when passing through the packed beds filled with the reactive composite materials. Notably, a 100% X_{FA} value was achieved upon increasing the temperature of Am-MnO₂-AC and δ -MnO₂-AC packed beds to 125 and 150°C, respectively. In contrast, only the Am-MnO₂-AC composite achieved 100% catalytic conversion efficiency (X_T) of toluene at 300°C, which was superior to all other composites. Overall, Am-MnO₂-AC was considered to be the best-performing catalyst for completely oxidizing the dual VOC component system throughout the tested temperature range.

Based on the XPS data in Table 2, the Mn^{3+}/Mn^{4+} ratio decreased in the following order: Am-MnO₂-AC (0.707) > δ -MnO₂-AC (0.568) > Ag-MnO₂-AC (0.441) > Co-MnO₂-AC (0.373). Similarly, the O_A/O_L ratio of the tested materials decreased in the following order: Am-MnO₂-AC (1.79) > δ -MnO₂-AC (1.16) > Ag-MnO₂-AC (1.15) > Co-MnO₂- AC (0.914) (Table 2). In terms of the relative orderings in the O_A/O_L and Mn³⁺/Mn⁴⁺ ratios, Am-MnO₂-AC achieved maximum values of 1.79 and 0.707, respectively, among all the tested composite materials (Table 2 and Figure S5). Hence, its superior catalytic activity should be accounted for by the compositional properties to a certain degree. In this regard, it has been reported that the abundance of O_A species could also favorably promote VOC oxidation (Wang et al., 2020). Also, many oxygen vacancies can enhance the sequential dissociative adsorption and activation of gaseous oxygen (O_G) with the improved oxygen storage capacity and reduced oxygen transport activation energy (Lyu et al., 2020). These oxygen vacancies can also provide excellent catalytic activity as they promote the transfer of O_L to the surface with the replenishment of oxygen (Du et al., 2018).

3.3. Apparent oxidation kinetics for FA and toluene

In this section, the apparent pre-exponential factor $(k_{app,\infty})$ and apparent activation energy (E_{app}) are determined individually for FA and toluene as single compounds using Eqs. (5) to (7). The apparent kinetic parameters $(k_{app,\infty} \text{ and } E_{app})$ for the oxidation of FA and toluene (as dual component) were then estimated using Eqs. (5) to (9). Note that the apparent pre-exponential factor and activation energy can be different between single and mixture experimental data, as they are a function of surface coverage (Teschner et al., 2012). Using the exponential factor and apparent activation energy, actual reaction rates of FA and toluene can be calculated as a function of their inlet concentration and oxidation temperature. Accordingly, the efficiency of the used catalyst can be evaluated for given inlet conditions.

3.3.1. Apparent oxidation kinetics for FA and toluene as individual target compound

The results for the parameter estimation with single compound data are given in Table 5 (order 1 and 2). The activation energy for the oxidation of FA was $49.0 \pm 5.0 \text{ kJ} \cdot \text{mol}^{-1}$, whereas that for toluene was $28.1 \pm 10.8 \text{ kJ} \cdot \text{mol}^{-1}$. The nature of the substrate can explain the difference in activation energy, i.e., polar FA vs. non-polar toluene. Hence, the latter is more likely to adsorb or at least interact with the catalyst surface to achieve total oxidation. As seen in Figure 8, the calculated yield values (using Eq. (5)) were comparable to the experimental yield data.

3.3.2. Apparent oxidation kinetics for FA and toluene as dual component

For the mixture experiments, it was not possible to simultaneously estimate pre-exponential factors and activation energies for both FA and toluene oxidation. Because the smallest standard deviation was found for the activation energy in FA oxidation, this parameter was kept constant (with respect to the value from the single oxidation experiment) in the regression for all the mixture data. The results for the parameter estimation with the dual system over the different catalysts are summarized in Table 5 (items 3 to 6) with the modelling results depicted in Figure 9.

As shown in Figure 10, the oxidation reaction rates for FA and toluene as a mixture were normalized as a function of the reaction temperature. The kinetics for FA oxidation were not affected significantly by toluene. As shown in Figure 10, the maximum oxidation reaction rate for FA and toluene on the Am-MnO₂-AC catalyst was found to occur at the lowest temperature $(10^{-4} \text{ mol kg}_{cat}^{-1} \cdot \text{s}^{-1})$. In the case of toluene oxidation, the temperature for the maximal reaction rate followed the ascending order: Am-MnO₂-AC < δ -MnO₂-AC < Ag-MnO₂-AC < Co-MnO₂-AC. Thus, a lower oxidation temperature increased the catalyst activity. In contrast, the patterns for FA were notably altered: Am-MnO₂-AC < Co-MnO₂-AC $\approx \delta$ -MnO₂-AC $\approx Ag$ -MnO₂-AC. As shown in Table 5, the pre-exponential factor for FA oxidation in a mixture was 4 to 10 times higher than that for the single composition. On the other hand, the apparent pre-exponential factors obtained for toluene oxidation in mixture experiments were comparable to that of the single compound except for the Ag-MnO₂-AC catalyst. In this case, an exceptionally high apparent activation energy was observed for toluene oxidation with a high apparent pre-exponential factor.

Depending on the compositional differences of the target VOC (either as a single or dual component), changes can take place in surface coverages of any compounds involved in RACO reactions (e.g., FA, toluene, oxygen, or total oxidation products like H₂O and CO₂) along with the possible formation of new surface intermediates. In the specific case of toluene oxidation, such

conditions can be expressed by rephrasing Eq. (18) as a specific difference in the apparent activation energies between single and dual compositions (see Eq. (21)).

$$\Delta E_{app} = (E_{app})_{T,m \text{ ixture }} - (E_{app})_{T,single} = 2\sum_{j=1}^{n} (-\Delta H_j) \cdot \Delta \theta_j$$
(21)

$$\Delta \boldsymbol{\theta}_{j} = \left(\boldsymbol{\theta}_{j}\right)_{T,m \text{ ixture }} - \left(\boldsymbol{\theta}_{j}\right)_{T,singk}$$
(22)

It is interesting that the apparent activation energy values for toluene oxidation were all higher for the dual composition than for a single component (Table 5) to satisfy the condition that $\Delta E_{app} > 0$ (as defined in Eq. (21)). Recall that adsorption enthalpy is always positive (adsorption is an exothermic process: i.e., $-\Delta H_j > 0$). Hence, it can be concluded from Eq. (21) that $\Delta \theta_j > 0$ for some species j. This observation suggests that changes in surface intermediates should be more evident for dual compositions than for single compound conditions. As such, new surface intermediates may form, i.e., $\theta_j = 0$ in single and $\theta_j > 0$ in dual component experiments.

3.4. Regeneration/reusability study for Am-MnO₂-AC

From an economic point of view, it is crucial to synthesize renewable and stable materials for multiple reuse cycles. In this regard, a multi-isothermal condition experiment (Table S1) against dual-component VOCs, i.e., FA and toluene, was repeated three times using Am-MnO₂-AC. Am-MnO₂-AC used for each cycle was thermally conditioned at 250°C for 3 h under N₂ (99.999%) purging (200 mL·min⁻¹) by a tube cleaner. As shown in Figure S6 (a), the BTV 10, 50, and 100% values for the regeneration experiment were similar between the data obtained in each cycle. Also, the T10%, T50%, T90%, and T100% values in multiple-isothermal conditions were the same for all cycles (Figure S6 (b)). These observations suggest that thermal conditioning operations can be used to regenerate Am-MnO₂-AC readily. Additionally, PXRD analysis was performed for Am-MnO₂-AC before and after the regeneration experiment (Figure S7). In the respective PXRD spectra, the diffraction peaks (18°–33°, 37.6°, and 66.3°) for Am-MnO₂-AC, as described in the previous

characterization section (3.1), were observed consistently. Hence, there was no specific phase change in Am-MnO₂-AC even after repetitive VOC removal experiments and thermal conditioning for regeneration.

3.5. Comparison of VOC removal performance and feasibility analysis for Am-MnO₂-AC

In this research, the removal of VOCs can be achieved effectively by RACO using Am-MnO₂-AC. To learn more about the effect of amorphous-manganese dioxide doping on AC, we compared the performance of Am-MnO₂-AC in reference to similar catalysts constructed using different types of metal oxides. In this regard, the removal performance of Am-MnO₂-AC was evaluated using FA and toluene relative to other thermal catalysts reported in the literature (Table S3 and Figure S8). To this end, the reaction kinetic rates (r-values, Eq. (2)) can be used as a key metric for quantitative comparison of VOC oxidation performance (Vikrant et al., 2021). In addition, T90% and T100% were used as the critical performance metric.

In terms of the r value for FA, the best performers can be listed as follows: Am-MnO₂-AC (44.7 mmol·g⁻¹·h⁻¹) > 0.6%-Pt/TiO₂ (40.0 mmol·g⁻¹·h⁻¹) > 0.2%-Pt/MnO₂/TiNT (6.0 mmol·g⁻¹·h⁻¹)). In terms of T100% value, the ranking between catalysts was as follows: Am-MnO₂-AC (100°C) < OMS-2 (120°C) < 3D-MnO₂ mesoporous (130°C) (Figure S8 (a)). In the case of toluene, Am-MnO₂-AC also had the lowest T90% value with the relative order: Am-MnO₂-AC (150°C) < MnO_x-CeO₂ (220°C) < MnO₂ (230°C) (Figure S8 (b)). Hence, the superiority of Am-MnO₂-AC over other comparable materials seems to be apparent for the removal of both FA and toluene, possibly due to the synergistic effect between the non-noble metal oxide and AC. It should also be noted that the MnO₂-AC utilized in the present study did not undergo a high-temperature reduction pre-treatment, unlike the noble metal catalysts. Therefore, Am-MnO₂-AC has the advantage of simplicity in its synthesis and application. It is essential to assess the synthesis cost of novel materials in the economic viewpoint. Table S3 lists the cost (the price of the chemicals (Sigma-Aldrich) used in the synthesis

process divided by the mass of the synthesized material) of the materials reported in the literature. Am-MnO₂-AC used in the present study has the lowest synthesis cost ($0.377 \text{ USD} \cdot \text{g}^{-1}$) due to the utilization of cheap chemicals (AC: $0.026 \text{ USD} \cdot \text{g}^{-1}$) and a simple synthesis method (Kim et al., 2020).

3.6. The mechanisms controlling the oxidation of FA and toluene on Am-MnO₂-AC

Based on the LH reaction mechanism, the abundance of surface oxygen in the catalyst plays a vital role in the catalytic reaction with the adsorbed VOC molecules (e.g., FA and toluene) during the oxidation reaction processes (Mahmood et al., 2021). In general, the enhanced catalytic performance of Am-MnO₂-AC is expected to reflect its higher content of abundant oxygen vacancies with higher Mn^{3+}/Mn^{4+} (0.707) and O_A/O_L (1.79) ratios (Table 2 and Figure S5). The catalytic reactivity of MnO₂ in the decomposition of organic compounds can be regulated by the interactive relationship between the redox cycle of Mn^{3+}/Mn^{4+} and the contribution of O₂ (Giannakoudakis et al., 2019). MnO₂ has a relatively low covalent potential compared to the redox potential of O_2/O_2^{*-} . Hence, the Mn^{3+}/Mn^{4+} redox cycle can significantly affect charge transfer during catalytic conversion (Mo et al., 2019). The Mn^{3+}/Mn^{4+} and O_A/O_L values for Am-MnO₂-AC (0.707 and 1.79) were higher than Am-MnO₂ (0.468 and 0.683). The presence of such oxygen species (O_G, O_A, and O_L) in Am-MnO₂-AC can favorably promote the catalytic oxidation process through the LH reaction mechanism (Santos et al., 2010).

The lattice oxygen (O_L) is the primary catalytic oxidation active site on the Am-MnO₂-AC surface. O_A with high mobility can replenish O_L from O_G through a series of migration and transformation processes (Sun et al., 2015). The intense interactions between the Am-MnO₂ and the AC support can weaken the O_L while generating O_A as an active participant in the oxidation reaction (Dai et al., 2016). In addition, the porous structure of AC support promotes the diffusion of reactants to facilitate the capture of higher molecular weight compounds (e.g., toluene) for a prolonged period (Zhang et al., 2016). It is thus suggested that the FA oxidation mechanism on metal oxides follows the typical redox reaction mechanism through a two-step process (Wang et al., 2018). The O_G can dissociatively adsorb on the catalyst surface to form active oxygen species. Various intermediate formate species can be formed through the reaction between the adsorbed FA molecules and the surface-active oxygen species, and subsequently oxidize into H_2O and CO_2 (Ding et al., 2020). Although FA can be decomposed into CO_2 and H_2O without complex intermediate oxides, toluene often exhibits complicated oxidation pathways with a ring-opening process (Zhong et al., 2020).

TD-GC/MS analyses of the by-products formed during the thermal catalytic oxidation of toluene were carried out to learn more about the ring-opening process of toluene. Figure S9 shows the obtained TD-GC/MS chromatogram. Figure 11 shows the oxidation pathway of toluene. Initially, O_G and toluene are adsorbed on the catalyst surface, and then O_G is activated as active oxygen atoms migrate through surface oxygen vacancies. Then, the adsorbed toluene molecule is activated to release hydrogen and to form a benzyl group. The benzyl group subsequently reacts with oxygen produced by oxygen vacancies to create benzyl alcohol or benzaldchyde (Brunet et al., 2015). Then, a number of by-products such as benzoic acid, benzene, and phenol are generated through the continuous oxidation process (Zhong et al., 2020). The benzene ring then opens to generate aliphatic intermediate species and by-products (Du et al., 2018). The by-products (3,3-dimethyl-2-oxetanone, tetrahydrofuran, pinacol, 2,4,6-trimethyloctane, and acetic acid) should ultimately be mineralized into end products such as CO_2 and H_2O . Finally, the depleted lattice oxygen can be replenished by the continuous dissociation of O_G through the redox pair Mn³⁺/Mn⁴⁺ and abundant oxygen vacancies (Liu et al., 2019).

4. Conclusions

In this research, Am-MnO₂-AC was prepared and employed to assess the removal performance of two target VOCs (i.e., FA and toluene) based on the sequential adsorption and thermal catalytic process of RACO. The RACO performance of am-AC-MnO₂ was first investigated for the single and dual components under multiple-isothermal conditions. The RACO performance of am-AC-MnO₂

was studied further using dual components in reference to different types of reactive composite materials (Co-MnO₂-AC, δ -MnO₂-AC, and Ag-MnO₂-AC).

Overall, the obtained results revealed that Am-MnO₂-AC is superior in removing both targets as dual components with T100% values of FA and toluene of 125 and 300°C, respectively, with its higher Mn^{3+}/Mn^{4+} (0.707) and $O_A/O_L = 1.79$ ratios. The abundant oxygen vacancies were expected to promote VOC oxidation, to improve oxygen storage capacity, and to lower oxygen transport activation energy. The apparent kinetics for FA and toluene systems (both as the single and dual components) by Am-MnO₂-AC were also explored. The VOC oxidation mechanism followed the LH pathway, as stable surface intermediates were observed quantitatively (evidenced by the TD-GC/MS analysis). FA was entirely mineralized to produce CO₂ and H₂O as the end products without complex intermediate oxides. In contrast, oxygen produced by oxygen vacancies reacted with adsorbed toluene on the Am-MnO₂-AC surface, yielding benzyl alcohol or benzaldehyde. These intermediates were further converted into benzoic acid, benzene, and phenol through a continuous oxidation process through a ring-opening mechanism to generate aliphatic intermediate species and by-products. These should ultimately be mineralized into the final products of CO₂ and H₂O. This study is expected to be useful in designing metal oxide AC composites for the removal of VOCs in indoor environments.

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References

Ali, R., Adil, S., Al-warthan, A., Siddiqui, M.R.H., 2013. Identification of active phase for selective oxidation of benzyl alcohol with molecular oxygen catalyzed by copper-manganese oxide nanoparticles. J. Chem. 2013.

Bielicka-Daszkiewicz, K., Voelkel, A., 2009. Theoretical and experimental methods of determination of the breakthrough volume of SPE sorbents. Talanta 80(2), 614-621.

Brunet, J., Genty, E., Landkocz, Y., Al Zallouha, M., Billet, S., Courcot, D., Siffert, S., Thomas, D., De Weireld, G., Cousin, R., 2015. Identification of by-products issued from the catalytic oxidation of toluene by chemical and biological methods. C.R. Chim. 18(10), 1084-1093.

Chen, H., Wang, M.Q., Yu, Y., Liu, H., Lu, S.-Y., Bao, S.-J., Xu, M., 2017. Assembling hollow cobalt sulfide nanocages array on graphene-like manganese dioxide nanosheets for superior electrochemical capacitors. ACS Appl. Mater. Interfaces 9(40), 35040-35047.

Cheng, Z., Li, C., Chen, D., Chen, J., Zhang, S., Ye, J., Yu, J., Dionysiou, D.D., 2019. A novel array of double dielectric barrier discharge combined with TiCo catalyst to remove high-flow-rate toluene: Performance evaluation and mechanism analysis. Sci. Total Environ. 692, 940-951.

Chorkendorff, I., Niemantsverdriet, J.W., 2017. Concepts of modern catalysis and kinetics. John Wiley & Sons.

Dai, Z., Yu, X., Huang, C., Li, M., Su, J., Guo, Y., Xu, H., Ke, Q., 2016. Nanocrystalline MnO₂ on an activated carbon fiber for catalytic formaldehyde removal. RSC Adv. 6(99), 97022-97029.

Danmaliki, G.I., Saleh, T.A., Shamsuddeen, A.A., 2017. Response surface methodology optimization of adsorptive desulfurization on nickel/activated carbon. Chem. Eng. J. 313, 993-1003.

Ding, J., Yang, Y., Liu, J., Wang, Z., 2020. Catalytic reaction mechanism of formaldehyde oxidation by oxygen species over Pt/TiO2 catalyst. Chemosphere 248, 125980.

Du, J., Qu, Z., Dong, C., Song, L., Qin, Y., Huang, N., 2018. Low-temperature abatement of toluene over Mn-Ce oxides catalysts synthesized by a modified hydrothermal approach. Appl. Surf. Sci. 433, 1025-1035.

Fang, Y., Guo, Y., 2018. Copper-based non-precious metal heterogeneous catalysts for environmental remediation. Chin. J. Catal. 39(4), 566-582.

Figueiredo, J.L., 2013. Functionalization of porous carbons for catalytic applications. J. Mater. Chem. A 1(33), 9351-9364.

Froment, G.F., Bischoff, K.B., 1990. Chemical Reactor Analysis, 2nd ed. Wiley, New York. Froment, G.F., Bischoff, K.B., De Wilde, J., 2011. Chemical Reactor-Analysis and Design. Ghosh, D., Bhandari, S., Khastgir, D., 2016. Synthesis of MnO₂ nanoparticles and their effective utilization as UV protectors for outdoor high voltage polymeric insulators used in power transmission lines. PCCP 18(48), 32876-32890.

Giannakoudakis, D.A., Nair, V., Khan, A., Deliyanni, E.A., Colmenares, J.C., Triantafyllidis, K.S., 2019. Additive-free photo-assisted selective partial oxidation at ambient conditions of 5-hydroxymethylfurfural by manganese (IV) oxide nanorods. Applied Catalysis B: Environmental 256, 117803.

Ha, S.-H., Kim, K.-H., Younis, S.A., Dou, X., 2020. The interactive roles of space velocity and particle size in a microporous carbon bed system in controlling adsorptive removal of gaseous benzene under ambient conditions. Chem. Eng. J. 401, 126010.

He, C., Liao, Y., Chen, C., Xia, D., Wang, Y., Tian, S., Yang, J., Shu, D., 2021. Realizing a redox-robust Ag/MnO₂ catalyst for efficient wet catalytic ozonation of S-VOCs: Promotional role of Ag (0)/Ag (I)-Mn based redox shuttle. Appl. Catal., B, 120881.

Heynderickx, P.M., Thybaut, J.W., Poelman, H., Poelman, D., Marin, G.B., 2009. Kinetic modeling of the total oxidation of propane over anatase and vanadia sputter deposited catalysts. Appl. Catal. B 90, 295-306.

Huang, X., Zhao, G., Chang, Y., Wang, G., Irvine, J.T., 2018. Nanocrystalline $CeO_2 - \delta$ coated β -MnO₂ nanorods with enhanced oxygen transfer property. Appl. Surf. Sci. 440, 20-28.

Huang, Y., Liu, Y., Wang, W., Chen, M., Li, H., Lee, S.-c., Ho, W., Huang, T., Cao, J., 2020. Oxygen vacancy–engineered δ -MnOx/activated carbon for room-temperature catalytic oxidation of formaldehyde. Applied Catalysis B: Environmental 278, 119294.

Jiang, C., Wang, H., Wang, Y., Xue, C., Yang, Z., Yu, C., Ji, H., 2020. Modifying defect States in CeO₂ by Fe doping: A strategy for low-temperature catalytic oxidation of toluene with sunlight. J. Hazard. Mater. 390, 122182.

Kamal, M.S., Razzak, S.A., Hossain, M.M., 2016. Catalytic oxidation of volatile organic compounds (VOCs)–A review. Atmos. Environ. 140, 117-134.

Khan, A., Wang, H., Liu, Y., Jawad, A., Ifthikar, J., Liao, Z., Wang, T., Chen, Z., 2018. Highly efficient α -Mn₂O₃@ α -MnO₂-500 nanocomposite for peroxymonosulfate activation: comprehensive investigation of manganese oxides. J. Mater. Chem. A 6(4), 1590-1600. Khe, C., Aziz, A., Lockman, Z., 2012. Synthesis of cobalt/gold bimetallic particles with porous flake-like nanostructures and their magnetic properties. Nanoscience and Nanotechnology Letters 4(7), 687-692.

Kim, K.-D., Park, E.J., Seo, H.O., Jeong, M.-G., Kim, Y.D., Lim, D.C., 2012. Effect of thin hydrophobic films for toluene adsorption and desorption behavior on activated carbon fiber under dry and humid conditions. Chem. Eng. J. 200, 133-139.

Kim, K.-H.J.A.c.a., 2006. The properties of calibration errors in the analysis of reduced sulfur compounds by the combination of a loop injection system and gas chromatography with pulsed flame photometric detection. 566(1), 75-80.

Kim, W.-K., Younis, S.A., Kim, K.-H., 2020. A strategy for the enhancement of trapping efficiency of gaseous benzene on activated carbon (AC) through modification of their surface functionalities. Environ. Pollut., 116239.

Li, K., Chen, C., Zhang, H., Hu, X., Sun, T., Jia, J., 2019. Effects of phase structure of MnO_2 and morphology of δ -MnO₂ on toluene catalytic oxidation. Appl. Surf. Sci. 496, 143662. Lin, W.-T., Tsai, R.-Y., Chen, H.-L., Tsay, Y.-S., Lee, C.-C., 2022. Probabilistic Prediction Models and Influence Factors of Indoor Formaldehyde and VOC Levels in Newly Renovated Houses. Atmosphere 13(5), 675.

Liu, L., Li, J., Zhang, H., Li, L., Zhou, P., Meng, X., Guo, M., Jia, J., Sun, T., 2019. In situ fabrication of highly active γ -MnO₂/SmMnO₃ catalyst for deep catalytic oxidation of gaseous benzene, ethylbenzene, toluene, and o-xylene. J. Hazard. Mater. 362, 178-186.

Liu, P., He, H., Wei, G., Liang, X., Qi, F., Tan, F., Tan, W., Zhu, J., Zhu, R., 2016. Effect of Mn substitution on the promoted formaldehyde oxidation over spinel ferrite: catalyst characterization, performance and reaction mechanism. Appl. Catal., B 182, 476-484.

Luo, K., Zhao, S.-X., Wang, Y.-F., Zhao, S.-J., Zhang, X.-H., 2018. Synthesis of petal-like δ-MnO₂ and its catalytic ozonation performance. New J. Chem. 42(9), 6770-6777.

Lyu, Y., Li, C., Du, X., Zhu, Y., Zhang, Y., Li, S., 2020. Catalytic oxidation of toluene over MnO₂ catalysts with different Mn (II) precursors and the study of reaction pathway. Fuel 262, 116610.

Mahmood, A., Wang, X., Xie, X., Sun, J., 2021. Degradation behavior of mixed and isolated aromatic ring containing VOCs: Langmuir-Hinshelwood kinetics, photodegradation, in-situ FTIR and DFT studies. Journal of Environmental Chemical Engineering 9(2), 105069. Mo, S., Zhang, Q., Li, J., Sun, Y., Ren, Q., Zou, S., Zhang, Q., Lu, J., Fu, M., Mo, D., 2020. Highly efficient mesoporous MnO₂ catalysts for the total toluene oxidation: Oxygen-Vacancy defect engineering and involved intermediates using in situ DRIFTS. Appl. Catal., B 264, 118464.

Mo, Z., Xu, H., Chen, Z., She, X., Song, Y., Lian, J., Zhu, X., Yan, P., Lei, Y., Yuan, S., 2019. Construction of MnO₂/Monolayer g-C₃N₄ with Mn vacancies for Z-scheme overall water splitting. Appl. Catal., B 241, 452-460.

Narayanasamy, K., Sekar, S.S., Roy, D., Dinakaran, K., 2021. Synthesis and characterization of Ag/Au-MnO₂ nanostructure embedded polyvinylidine difluoride high K nanocomposites. Int. J. Polym. Anal. Charact. 26(1), 37-46.

Plaisance, H., Mocho, P., Desauziers, V., 2020. Comparative analysis of formaldehyde and toluene sorption on indoor floorings and consequence on indoor air quality. Indoor Air. Romanos, J., Beckner, M., Rash, T., Firlej, L., Kuchta, B., Yu, P., Suppes, G., Wexler, C., Pfeifer, P., 2011. Nanospace engineering of KOH activated carbon. Nanotechnology 23(1), 015401.

Rong, S., Zhang, P., Liu, F., Yang, Y., 2018. Engineering crystal facet of α -MnO₂ nanowire for highly efficient catalytic oxidation of carcinogenic airborne formaldehyde. ACS Catal. 8(4), 3435-3446.

Santos, V., Pereira, M., Órfão, J., Figueiredo, J., 2010. The role of lattice oxygen on the activity of manganese oxides towards the oxidation of volatile organic compounds. Appl. Catal., B 99(1-2), 353-363.

Sun, H., Liu, Z., Chen, S., Quan, X., 2015. The role of lattice oxygen on the activity and selectivity of the OMS-2 catalyst for the total oxidation of toluene. Chem. Eng. J. 270, 58-65. Tang, W., Wu, X., Li, D., Wang, Z., Liu, G., Liu, H., Chen, Y., 2014. Oxalate route for promoting activity of manganese oxide catalysts in total VOCs' oxidation: effect of calcination temperature and preparation method. J. Mater. Chem. A 2(8), 2544-2554. Tang, X., Chen, J., Li, Y., Li, Y., Xu, Y., Shen, W., 2006. Complete oxidation of formaldehyde over Ag/MnOx–CeO₂ catalysts. Chem. Eng. J. 118(1-2), 119-125. Tao, Y., Li, R., Huang, A.-B., Ma, Y.-N., Ji, S.-D., Jin, P., Luo, H.-J., 2020. High catalytic activity for formaldehyde oxidation of an interconnected network structure composed of δ-MnO₂ nanosheets and γ-MnOOH nanowires. Advances in Manufacturing 8(4), 429-439. Teschner, D., Novell-Leruth, G., Farra, R., Knop-Gericke, A., Schlögl, R., Szentmiklosi, L., Hevia, M.G., Soerijanto, H., Schomäcker, R., Perez-Ramirez, J., 2012. In situ surface coverage analysis of RuO2-catalysed HCl oxidation reveals the entropic origin of compensation in heterogeneous catalysis. Nature chemistry 4(9), 739-745.

Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S., 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and applied chemistry 87(9-10), 1051-1069.

Thybaut, J.W., Poelman, H., Poelman, D., Marin, G.B., 2010. Kinetic modeling of the total oxidation of propane over CuO-CeO2/ γ -Al2O3. Applied Catalysis B: Environmental 95(1-2), 26-38.

Topka, P., Hejtmánek, V., Cruz, G.J., Šolcová, O., Soukup, K., 2019. Activated carbon from renewable material as an efficient support for palladium oxidation catalysts. Chem. Eng. Technol. 42(4), 851-858.

Twumasi, E., Forslund, M., Norberg, P., Sjöström, C., 2012. Carbon–silica composites prepared by the precipitation method. Effect of the synthesis parameters on textural characteristics and toluene dynamic adsorption. J. Porous Mater. 19(3), 333-343. Vellingiri, K., Vikrant, K., Kumar, V., Kim, K.-H., 2020. Advances in thermocatalytic and photocatalytic techniques for the room/low temperature oxidative removal of formaldehyde

in air. Chemical Engineering Journal 399, 125759. Vikrant, K., Kim, K.-H., 2020. Insights into critical sources of bias in quantitation of volatile organic compounds based on headspace extraction approach. Microchemical Journal 157, 105114.

Vikrant, K., Weon, S., Kim, K.-H., Sillanpää, M., 2021. Platinized titanium dioxide (Pt/TiO₂) as a multi-functional catalyst for thermocatalysis, photocatalysis, and photothermal catalysis for removing air pollutants. Appl. Mater. Today 23, 100993.

Vyazovkin, S., 2021. Determining preexponential factor in model-free kinetic methods: How and why? Molecules 26, 3077.

Wang, D., Astruc, D., 2017. The recent development of efficient Earth-abundant transitionmetal nanocatalysts. Chem. Soc. Rev. 46(3), 816-854.

Wang, M., Chen, K., Liu, J., He, Q., Li, G., Li, F., 2018. Efficiently enhancing electrocatalytic activity of α -MnO₂ nanorods/N-doped ketjenblack carbon for oxygen reduction reaction and oxygen evolution reaction using facile regulated hydrothermal treatment. Catalysts 8(4), 138.

Wang, Z., Jia, H., Zheng, T., Dai, Y., Zhang, C., Guo, X., Wang, T., Zhu, L., 2020. Promoted catalytic transformation of polycyclic aromatic hydrocarbons by MnO₂ polymorphs: Synergistic effects of Mn³⁺ and oxygen vacancies. Appl. Catal., B 272, 119030.

Wei, Z., Zhao, T., Zhu, X., Tan, P., 2016. MnO₂-x nanosheets on stainless steel felt as a carbon-and binder-free cathode for non-aqueous lithium-oxygen batteries. J. Power Sources 306, 724-732.

Weisz, P., Prater, C., 1954. Interpretation of measurements in experimental catalysis, Advances in catalysis. Elsevier, pp. 143-196.

Weitkamp, J., Ertl, G., Knözinger, H., 1999. Preparation of solid catalysts. Wiley-VCH. Wu, J.C.-S., Lin, Z.-A., Tsai, F.-M., Pan, J.-W., 2000. Low-temperature complete oxidation of BTX on Pt/activated carbon catalysts. Catal. Today 63(2-4), 419-426.

Yang, Q., Wang, D., Wang, C., Li, X., Li, K., Peng, Y., Li, J., 2018. Facile surface improvement method for LaCoO₃ for toluene oxidation. Catal. Sci. Technol. 8(12), 3166-3173.

Yang, R., Wang, Z., Dai, L., Chen, L., 2005. Synthesis and characterization of singlecrystalline nanorods of α -MnO₂ and γ -MnOOH. Mater. Chem. Phys. 93(1), 149-153. Yang, Y.-j., Liu, E.-h., Li, L.-m., Huang, Z.-z., Shen, H.-j., Xiang, X.-x., 2010.

Nanostructured amorphous MnO_2 prepared by reaction of $KMnO_4$ with triethanolamine. J. Alloys Compd. 505(2), 555-559.

Yang, Y., Huang, J., Wang, S., Deng, S., Wang, B., Yu, G., 2013. Catalytic removal of gaseous unintentional POPs on manganese oxide octahedral molecular sieves. Appl. Catal., B 142, 568-578.

Ye, Z., Giraudon, J.-M., De Geyter, N., Morent, R., Lamonier, J.-F., 2018. The design of MnOx based catalyst in post-plasma catalysis configuration for toluene abatement. Catalysts 8(2), 91.

Yu, Y., Liu, S., Ji, J., Huang, H., 2019. Amorphous MnO₂ surviving calcination: an efficient catalyst for ozone decomposition. Catal. Sci. Technol. 9(18), 5090-5099.

Zeng, Y., Gu, L., Feng, Y., Jiang, W., Ji, W., 2020. Morphologically uniform $Pd/Fe_xMn_{3-x}O_4$ -HP interfaces as the high-performance model catalysts for catalytic combustion of volatile organic compound. Appl. Surf. Sci. 528, 147006.

Zhang, C., Wang, Y., Song, W., Zhang, H., Zhang, X., Li, R., Fan, C., 2020. Synthesis of MnO₂ modified porous carbon spheres by preoxidation-assisted impregnation for catalytic oxidation of indoor formaldehyde. J. Porous Mater., 1-15.

Zhang, Z., Jiang, Z., Shangguan, W., 2016. Low-temperature catalysis for VOCs removal in technology and application: A state-of-the-art review. Catal. Today 264, 270-278.

Zheng, X., Yu, L., Lan, B., Cheng, G., Lin, T., He, B., Ye, W., Sun, M., Ye, F., 2017. Threedimensional radial α -MnO₂ synthesized from different redox potential for bifunctional oxygen electrocatalytic activities. J. Power Sources 362, 332-341.

Zhong, J., Zeng, Y., Zhang, M., Feng, W., Xiao, D., Wu, J., Chen, P., Fu, M., Ye, D., 2020. Toluene oxidation process and proper mechanism over Co₃O₄ nanotubes: Investigation through in-situ DRIFTS combined with PTR-TOF-MS and quasi in-situ XPS. Chem. Eng. J. 397, 125375.

Zhu, J., Zhang, W., Qi, Q., Zhang, H., Zhang, Y., Sun, D., Liang, P., 2019. Catalytic oxidation of toluene, ethyl acetate and chlorobenzene over Ag/MnO₂-cordierite molded catalyst. Sci. Rep. 9(1), 1-10.

Order	Material	BET Surface Area (S _{BET})	Pore Volume (V _{pore})	Average pore diameter (D _p)
		$[m^2.g^{-1}]$	$[cm^3.g^{-1}]$	[nm]
1	AC-0	781	0.518	1.93
2	Am-MnO ₂ -AC	666	0.449	1.96
3	Co-MnO ₂ -AC	31.2	0.024	3.09
4	δ-MnO ₂ -AC	553	0.388	2.08
5	Ag-MnO ₂ -AC	366	0.264	2.13

Table 1. Summary of the BET results for the tested materials.

	-	Mn 2p			Ols			Со 2р			Ag 3d						
Order	Material	Species	Peak Position (eV)	Peak Area	Mn ³⁺ /Mn ⁴⁺	Species	Peak Position (eV)	Peak Area	O _A /O _L	Species	Peak Position (eV)	Peak Area	C0 ²⁺ /C0 ³⁺	Species	Peak Position (eV)	Peak Area	Ag ⁰ /Ag ⁺
		$2p_{3/2} \operatorname{Mn}^{3+}$	641.7	27.2		0	520.7	25.0		$2p_{3/2} \operatorname{Co}^{3+}$	-	-		$3d_{5/2}\operatorname{Ag}^+$	-	-	
		$2p_{3/2} \operatorname{Mn}^{4+}$	643.2	40.6	0.505	OL	529.7	35.9	1 50	$2p_{3/2} \operatorname{Co}^{2+}$	-	-		$3d_{5/2}\operatorname{Ag}^0$	-	-	
1	Am-MnO ₂ -AC	$2p_{1/2} \operatorname{Mn}^{3+}$	653.3	14.2	0.707	0	520 7	(1 1	1.79	$2p_{1/2} \mathrm{Co}^{3+}$	-	-	-	$3d_{3/2}\operatorname{Ag}^+$	-	-	-
		$2p_{1/2} \mathrm{Mn}^{4+}$	654.7	18.0		0 _A	530.7	64.1		$2p_{1/2} \mathrm{Co}^{2+}$	-	-		$3d_{3/2}{ m Ag}^0$	-	-	
		$2p_{3/2} \operatorname{Mn}^{3+}$	641.3	16.9		0	520.4	52.2		$2p_{3/2} \operatorname{Co}^{3+}$	780.7	35.0		$3d_{5/2}\operatorname{Ag}^+$	-	-	
2	C- M-0 AC	$2p_{3/2} \operatorname{Mn}^{4+}$	643.0	53.4	0.272	UL	550.4	52.2	0.014	$2p_{3/2}{ m Co}^{2+}$	784.9	31.4	0.026	$3d_{5/2}{ m Ag}^0$	-	-	
2	Co-MnO ₂ -AC	$2p_{1/2} \operatorname{Mn}^{3+}$	653.1	10.3	0.373	0	522.0	47.0	0.914	$2p_{1/2}{ m Co}^{3+}$	796.0	16.6	0.936	$3d_{3/2}\operatorname{Ag}^+$	-	-	-
		$2p_{1/2} \operatorname{Mn}^{4+}$	654.6	19.5		0 _A	332.8	47.0		$2p_{1/2} \mathrm{Co}^{2+}$	802.6	16.9		$3d_{3/2}\mathrm{Ag}^0$	-	-	
		$2p_{3/2} \operatorname{Mn}^{3+}$	641.6	24.8		0	520.5	16.1		$2p_{3/2} \operatorname{Co}^{3+}$	-	-		$3d_{5/2}\operatorname{Ag}^+$	-	-	
3	δ MpO ₂ AC	$2p_{3/2} \mathrm{Mn}^{4+}$	643.0	37.7	0.568	0L	529.5	40.4	1.16	$2p_{3/2}{ m Co}^{2+}$	-	-		$3d_{5/2}\mathrm{Ag}^0$	-	-	
3	5 0-MINO ₂ -AC	$2p_{1/2} \operatorname{Mn}^{3+}$	653.1	11.4	0.508	OA	521.0	53.6	1.10	$2p_{1/2}{ m Co}^{3+}$	-	-	-	$3d_{3/2}\operatorname{Ag}^+$	-	-	-
		$2p_{1/2} \operatorname{Mn}^{4+}$	654.4	26.1			551.0			$2p_{1/2} \operatorname{Co}^{2+}$	-	-		$3d_{3/2}\mathrm{Ag}^0$	-	-	
		$2p_{3/2} \operatorname{Mn}^{3+}$	641.3	20.4	0.441	0.	531.0	46.5	16.5	$2p_{3/2}{ m Co}^{3+}$	-	-		$3d_{5/2}\operatorname{Ag}^+$	367.3	23.2	
4	$A = A \alpha M_{\rm P} O_{\rm e} A C$	$2p_{3/2} \operatorname{Mn}^{4+}$	642.7	44.0		OL	0L 551.0	10.5	1.15	$2p_{3/2}{ m Co}^{2+}$	-	-	_	$3d_{5/2}\mathrm{Ag}^0$	368.2	37.4	1.76
4 Ag-MIIO ₂ -AC	$2p_{1/2} \operatorname{Mn}^{3+}$	652.9	10.2	01111	0.	532.6	53.5	1.15	$2p_{1/2} \mathrm{Co}^{3+}$	-	-	-	$3d_{3/2}\operatorname{Ag}^+$	373.3	13.0	1.70	
		$2p_{1/2} \operatorname{Mn}^{4+}$	654.4	25.5		0A	5A 55210			$2p_{1/2} \operatorname{Co}^{2+}$	-	-		$3d_{3/2}{ m Ag}^0$	374.2	26.5	
		$2p_{3/2} \operatorname{Mn}^{3+}$	641.8	24.3		Or	529.8	59.4		$2p_{3/2}{ m Co}^{3+}$	-	-	30	$3d_{5/2}\operatorname{Ag}^+$	-	-	
5	Am-MnOa	$2p_{3/2} \operatorname{Mn}^{4+}$	643.2	39.6	0.468	OL	529.0	529.6 59.4	0.683	$2p_{3/2}{ m Co}^{2+}$	-	-	_	$3d_{5/2} \operatorname{Ag}^0$ -	-	-	
5	71111111102	$2p_{1/2} \operatorname{Mn}^{3+}$	653.1	7.60	OA	O ₄ 532.0	532.0	32.0 40.6	40.6	$2p_{1/2} \mathrm{Co}^{3+}$	-	-		$3d_{3/2}{ m Ag}^+$	-	-	-
		$2p_{1/2} \operatorname{Mn}^{4+}$	654.5	28.6		0A	OA 552.0	-52.0 -0.0		$2p_{1/2} \operatorname{Co}^{2+}$	-	-		$3d_{3/2}{ m Ag}^0$	-	-	
		$2p_{3/2} \operatorname{Mn}^{3+}$	641.1	15.1		Or	O _L 529.5 57.0	57.0		$2p_{3/2}{ m Co}^{3+}$	781.8	47.9		$3d_{5/2}{ m Ag}^+$	-	-	
6	Co-MnO2	$2p_{3/2} \operatorname{Mn}^{4+}$	642.7	51.8	0.356	OL			0 754	$2p_{3/2}{ m Co}^{2+}$	784.8	22.1	0.414 3 <i>d</i> _{5/2} A 3 <i>d</i> _{3/2} A	$3d_{5/2}\operatorname{Ag}^0$	-	-	-
0	00 111102	$2p_{1/2} \operatorname{Mn}^{3+}$	652.8	11.10	0.550	0.	530.8	43.0	0.754	$2p_{1/2} \operatorname{Co}^{3+}$	798.5	22.8		$3d_{3/2}{ m Ag}^+$	-	-	
		$2p_{1/2} \operatorname{Mn}^{4+}$	654.3	22.0		0 _A	550.0	15.0		$2p_{1/2} \operatorname{Co}^{2+}$	801.4	7.24		$3d_{3/2} \operatorname{Ag}^0$ -	-		
		$2p_{3/2} \operatorname{Mn}^{3+}$	641.7	19.4		Or	529.7	66.8		$2p_{3/2}{ m Co}^{3+}$	-	-		$3d_{5/2}\operatorname{Ag}^+$	-	-	
7	δ-MnO2	$2p_{3/2} \operatorname{Mn}^{4+}$	642.9	45.8	0 446	OL	525.1	00.0	0 496	$2p_{3/2}{ m Co}^{2+}$	-	-	_	$3d_{5/2} \operatorname{Ag}^0$ -	-	_	
,	0 111102	$2p_{1/2} \operatorname{Mn}^{3+}$	653.4	11.51	0.110	0.	532.2	33.2	0.190	$2p_{1/2} \operatorname{Co}^{3+}$	-	-		$3d_{3/2}\operatorname{Ag}^+$	-	-	-
		$2p_{1/2} \operatorname{Mn}^{4+}$	654.4	23.3		U _A	00212	5512		$2p_{1/2} \operatorname{Co}^{2+}$	-	-		$3d_{3/2}{ m Ag}^0$	-	-	
		$2p_{3/2} \operatorname{Mn}^{3+}$	641.7	17.9		Or	529.9	55.2		$2p_{3/2}{ m Co}^{3+}$	-	-		$3d_{5/2}\operatorname{Ag}^+$	367.8	29.7	
0	A a MaOs	$2p_{3/2} \mathrm{Mn}^{4+}$	643.0	50.5	0.228	OL.	549.9	55.2	0.812	$2p_{3/2} \operatorname{Co}^{2+}$	-	-		$3d_{5/2}\mathrm{Ag}^0$	368.4	29.6	1.27
0	Ag-imitO ₂	$2p_{1/2} \operatorname{Mn}^{3+}$	653.3	7.35	0.338	0	521.0	44.0	0.012	$2p_{1/2} \operatorname{Co}^{3+}$	-	-	-	$3d_{3/2}{ m Ag}^+$	373.8	14.5	1.27
	$2p_{1/2} \mathrm{Mn}^{4+}$	654.6	24.2		UA	331.8	44.8		$2p_{1/2} \operatorname{Co}^{2+}$	-	-		$3d_{3/2}\mathrm{Ag}^0$	374.3	26.2		

Table 2. XPS surface compositional data of the tested materials.

Order	Material	Compound		BTV (L·g ⁻¹)		Catalytic reaction temperature (°C)			
			BTV10%	BTV50%	BTV100%	T10%	T50%	Т90%	T100%
1 AC-0	-	FA (S)	0.170	58.0	-	-	-	-	-
		T (S)	238	522	-	-	-	-	-
	AC-0	FA (M)	0.124	14.8	55.7	-	-	-	-
		T (M)	285	487	670	-	-	-	-
		FA (S)	45.9	515	-	50.0	50.0	100	100
2 Am-MnO ₂ -A		T (S)	152	385	-	50.0	100	150	275
	Am-MnO ₂ -AC	FA (M)	34.9	67.7	791	75.0	100	125	125
		T (M)	122	190	786	125	225	300	300

Table 3. Performance of reactive adsorbents/catalysts of AC-0 and Am-MnO₂-AC against FA and toluene as single (S) and dual-component (M).

S: Single gas, M: Mixture gas of FA and toluene

FA: Formaldehyde, T: Toluene

Order	Material	Compound		BTV (L·g ⁻¹)]	Reaction ter	nperature (°	C)
			BTV10%	BTV50%	BTV100%	T10%	T50%	Т90%	T100%
1 AC		FA (M)	0.124	14.8	55.7	-	-	-	-
	AC-0	T (M)	285	487	670	-	-	-	-
2 Am-MnO ₂ -AC	FA (M)	34.9	67.7	791	75.0	100	125	125	
	AIII-MIIO ₂ -AC	T (M)	122	190	786	125	225	300	300
3 Co-MnO		FA (M)	0.101	10.1	101	250	-	-	-
	CO-MINO ₂ -AC	T (M)	5.52	57.7	772	175	-	-	-
4		FA (M)	7.63	33.0	190	75.0	125	150	150
4	0-MIIO2-AC	T (M)	75.3	176	773	175	225	-	-
5		FA (M)	5.40	25.4	75.9	250	300	-	-
	Ag-MnO ₂ -AC	T (M)	46.8	115	796	100	300	-	-

Table 4. Performance of the utilized reactive adsorbents/catalysts against FA and toluene as dual-component mixture.

M: Mixture gas of FA and toluene

FA: Formaldehyde, T: Toluene

Table 5. Estimated parameters for the removal of FA and toluene as single and dual components using Eqs. (5) and (6). Am-MnO₂-AC = MnO₂-AC; each compound (100 ppm) was fed at 200 mL·min⁻¹ with air as the balance gas, $m_{cat} = 50$ mg. Units for $k_{app,\infty}$, E_{app} , and RSSQ (S.3) are s⁻¹, kJ·mol⁻¹ and mol²·mol⁻², respectively.

Order	Catalyst	Compound	$\mathbf{k}_{app,\infty}$	Eapp	$\mathbf{k}_{app,\infty}$	Eapp	RSSQ
			FA		Т		
1	Am-MnO ₂ -AC	FA	$(2.49\pm0.70)\;10^{+6}$	49.0 ± 5.0	-	-	4.36 10-2
2		Т	-	-	$(8.76 \pm 2.89) \ 10^{+2}$	28.1 ± 10.8	2.07 10-1
3		FA + T	$(3.11 \pm 0.64) \ 10^{+7}$	49.0 ⁽¹⁾	$(1.11 \pm 0.28) \ 10^{+3}$	40.8 ± 12.3	8.52 10-2
4	Co-MnO ₂ -AC	FA + T	$(1.51 \pm 0.19) \ 10^{+7}$	49.0 ⁽¹⁾	$(1.18 \pm 0.75) \ 10^{+3}$	52.4 ± 31.0	3.22 10-2
5	δ-MnO ₂ -AC	FA + T	$(1.33 \pm 0.35) \ 10^{+7}$	49.0 ⁽¹⁾	$(1.01 \pm 0.23) \ 10^{+2}$	32.2 ± 15.0	1.23 10-1
6	Ag-MnO ₂ -AC	FA + T	$(1.00 \pm 0.26) \ 10^{+7}$	49.0 ⁽¹⁾	$(5.28 \pm 3.82) \ 10^{+6}$	85.2 ± 21.5	9.91 10 ⁻²

⁽¹⁾ Kept constant, see Section 3.3

Order	Catalyst	Compound	Left-hand side in Eq. (11)		
			FA	Т	
1	Am-MnO ₂ -AC	FA	0.056 (340, 30.4)		
		Т		0.084 (355, 26.2)	
		FA + T	-	0.072 (505, 27.5)	
2	Co-MnO ₂ -AC	FA + T	-	0.058 (640, 25.4)	
3	δ-MnO ₂ -AC	FA + T	-	0.071 (530, 28.0)	
4	Ag-MnO ₂ -AC	FA + T	-	0.070 (560, 28.5)	

Table 6. Evaluation of the WP criterion for the different catalysts. The values in brackets represent the temperature (K) for the maximal reaction rate (in μ mol kg_{cat}⁻¹·s⁻¹).



Figure 1. Schematic for the RACO experimental setups using FA and toluene.



Figure 2. Physicochemical characterization results of the tested materials: (a) PXRD and (b) FTIR



Figure 3. SEM images of the tested materials: (a) AC-0, (b) Am-MnO₂-AC, (c) Co-MnO₂-AC, (d) δ-MnO₂-AC, (e) Ag-MnO₂-AC, (f) Am-MnO₂, (g) Co-MnO₂, (h) δ-MnO₂, and (i) Ag-MnO₂.



Figure 4. Removal efficiency of Am-MnO₂-AC against FA and toluene as single and dual components: (a) BT profiles of AC-0 and Am-MnO₂-AC against single component VOC system, (b) same as (a) but for dual component VOC system, (c) CO₂ yield from catalytic conversion of single and dual component VOC system, and (d) bed temperature as a function of loaded G-WS volume.



Figure 5. Conversion efficiency (%) of FA and toluene for Am-MnO₂-AC as a function of bed temperature (°C) under multiple-isothermal conditions.



Figure 6. Removal efficiency of the tested materials for FA and toluene as dual components: (a) BT profiles for FA, (b) BT profiles for toluene, (c) CO₂ yield for the dual component VOCs (FA plus toluene) as a function of bed temperature, (d) bed temperature as a function of loaded G-WS volume. (AC-0 (grey), Am-MnO₂-AC (red), Co-MnO₂-AC (blue), δ-MnO₂-AC (yellow), and Ag-MnO₂-AC (green)).



Figure 7. Conversion efficiency (%) of target VOCs (as dual component) as a function of bed temperature (°C) under multiple-isothermal conditions. (a) FA and (b) toluene (Am-MnO₂-AC (red and rhombus), Co-MnO₂-AC (blue and square), δ-MnO₂-AC (yellow and triangle), and Ag-MnO₂-AC (green and circle)).



Figure 8. CO_2 yield data for (a) FA and (b) toluene oxidation over the Am-MnO₂-AC catalyst in single experiments. Circled data are experimentally obtained, while the line is used to represent the calculated CO_2 yield. For the latter, refer to Eqs. (5) and (6) and the parameters reported in Table 5.



Figure 9. CO_2 yield data for FA+T mixture (each 100 ppm) over different composite forms: (a) Am-MnO₂-AC, (b) Co-MnO₂-AC, (c) δ -MnO₂-AC and (d) Ag-MnO₂-AC. Circled data are experimentally obtained, while the lines used to represent the calculated CO₂ yield for the mixture experiments are from Eqs. (5), (6) and (9), and the parameters reported in Table 4. Dashed orange and grey lines represent the single conversion for FA and toluene, respectively.



Figure 10. Normalized oxidation reaction rates for FA (full lines) and toluene (dashed lines) in the dual component experiments for all different catalysts used in this study.



Figure 11. Proposed reaction pathway for toluene oxidation on Am-MnO₂-AC.