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Physicochemical properties of manganese dioxide synthesized using C₂–C₅ alcohols as reducing agents and their catalytic activities for CO oxidation

Young-Ho Lee^a, Jung-Hyun Park^b, Chae-Ho Shin^{a,*}

^a Department of Chemical Engineering, Chungbuk National University, Chungbuk 28644, Republic of Korea

^b Division of Physical Science and Engineering, KAUST catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), 4700 KAUST, Thuwal 23955-6900, Saudi Arabia

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ABSTRACT

MnO₂ catalysts were synthesized in an aqueous solution of KMnO₄ and C₂–C₅ alcohols using a simple redox method at room temperature. The crystalline structure of all samples was δ-MnO₂ after being calcined at 300 °C. However, other physicochemical properties of the samples varied depending on the symmetry of the alcohols used. For the catalytic oxidation of CO, MnO₂ catalysts prepared with 1° alcohols performed better than the samples prepared in 2° alcohols. Catalytic activities were correlated to the quantity of labile oxygen species of the catalysts. In CO-TPD analysis, the relative area of desorbed *CO₂, which is the product of the reaction between adsorbed CO and lattice oxygen species, becomes larger for MnO₂ prepared with 1° alcohols than with 2° alcohols. These results were primarily resulted from the innate hydrogen dissociation behavior of alcohol in solution. The pK_a was found to be an important factor in determining the physicochemical properties and catalytic activity toward CO oxidation of MnO₂.

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1. Introduction

Manganese dioxide (MnO₂) is a useful material in various industrial fields where it is used as a cathode material for metal-air batteries and fuel cells and as a catalyst for oxidation reactions, because of its high electron storage capacity and oxygen storage ability [1–5]. MnO₂ has also been used as ionic- and molecular-sieves and as a catalyst, because it displays great cation-exchange and molecular adsorption properties [6,7]. Furthermore, it is seen as a promising candidate material because of its low cost, environmental compatibility, and natural abundance [2,3,8].

The physicochemical properties of MnO₂ can be controlled by using different Mn precursors and synthesis conditions, e.g., sol-gel, gas condensation, microemulsion, solid state, hydrothermal, melting salt reflux, redox precipitation, and sonochemical processes [6,9–13]. In particular, the crystalline structure of MnO₂ has an effect on its performance as a catalyst for CO oxidation. The catalytic activity improves in the order α-MnO₂ ≈ δ-MnO₂ > γ-MnO₂ > β-MnO₂ [10,14,15].

Alcohols exist in a variety of structural isomers with their own intrinsic physicochemical properties such as hydrogen ion dissociation behavior (pK_a). Several studies have examined the preparation of MnO₂ using alcohols. Subramanian et al. synthesized MnO₂ from methanol, ethanol, isopropanol, glycerol, and ethylene glycol respectively in potassium permanganate (KMnO₄) solution, and Wu et al. also prepared MnO₂ from KMnO₄ and ethanol [8,9]. However, to the best of our knowledge, systematic studies on the effects of the alcohol's physicochemical properties, e.g., hydrogen dissociation behaviors and steric hindrance effects in solution, have not been performed.

In order to perform a systematic study on the role of the alcohol used for synthesis, we synthesized MnO₂ catalysts using KMnO₄ with primary (1°), secondary (2°), and tertiary (3°) C₂–C₅ alcohols as reducing agents at room temperature and characterized using various analytical tools such as X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of CO (CO-TPD), and temperature-programmed reduction of H₂ (H₂-TPR) to elucidate their physicochemical properties. In addition, catalytic CO oxidation was performed to determine the relationship between oxygen species and catalytic activity in CO oxidation.

* Corresponding author.

E-mail address: chshin@chungbuk.ac.kr (C.-H. Shin).

2. Experimental

2.1. Materials

In this study, KMnO_4 (99.3 mol%), ethanol (99.9 mol%), 1-propanol (99.0 mol%), 2-propanol (99.5 mol%), 1-butanol (99.0 mol%), isobutanol (99.0 mol%), 2-butanol (99.5 mol%), *tert*-butanol (99.0 mol%), and 1-pentanol (99.0 mol%) were purchased from Samchun Chemicals and used without further purification. The alcohols used in this study were denoted as $\text{C}_{\text{X}=2-5}$ in accordance with their number of carbons.

2.2. Catalyst preparation

MnO_2 was prepared by mixing 0.2 M KMnO_4 and 0.81 mol $\text{C}_2\text{--C}_5$ alcohols at room temperature for 1 h under vigorous stirring. Black powder was obtained in 1° alcohols, while brown powder was observed for 2° alcohols from the purple-colored solution. No precipitate formed with *tert*- C_4 (3° alcohol). The powder was filtered by 4 L distilled water, and dried at 80 °C for 12 h. Finally, the sample was calcined at 300–500 °C for 2 h with a heating rate of 2 °C min^{−1} under flowing air.

2.3. Catalyst characterization

Elemental analysis, which was especially needed to quantify residual potassium ion (K^+) in samples, was performed using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7300DV, Perkin Elmer).

Crystalline structure was characterized by X-ray diffraction (XRD, D8 Discover with GADDS, Bruker AXS) with $\text{Cu K}\alpha_1$ radiation operating at 40 mA and 40 kV in the range of $2\theta = 10\text{--}80^\circ$. Particle size (D_{hkl}) was measured in nm using the Scherrer–Warren equation,

$$D_{\text{hkl}} = \frac{K\lambda}{\beta \cos \theta}$$

where K is a dimensionless shape factor (0.89), λ is the wavelength of the X-rays ($\lambda = 0.15406$ nm), β is the line broadening at full width at half maximum (FWHM) in radians, and θ is the diffraction angle in degree. XRD patterns of manganese oxides were compared with the JCPDS standard files of 80-1098 ($\delta\text{-MnO}_2$), 44-0141 ($\alpha\text{-MnO}_2$), 80-0382 (Mn_3O_4), and 78-0424 (MnO).

Specific surface area (S_{BET}) and total pore volume (V_p) were determined by N_2 -physisorption (ASAP2020, Micromeritics) at -196°C . Prior to measurement, each sample was degassed at 200 °C until reaching a pressure of at least 10^{-3} Torr. S_{BET} was calculated in the range of $P/P_0 = 0.05\text{--}0.20$, while V_p was measured at $P/P_0 = 0.995$.

The oxidation states of the Mn and O species on the catalyst surface were identified by XPS (ESCALAB 210 Electron Spectrometer) with $\text{Al K}\alpha$ radiation ($h\nu = 1486.6$ eV). All binding energies were referenced to the C 1s peak at 284.6 eV from adventitious carbon.

The morphology of the MnO_2 catalysts synthesized with $\text{C}_2\text{--C}_5$ alcohols and calcined at 300–500 °C for 2 h was examined with scanning electron microscopy (SEM, LEO-1530, Carl Zeiss) at 3 kV.

Thermal behavior was observed using differential thermal analysis (DTA, SDT 2960, TA Instruments). An as-prepared MnO_2 sample (as- MnO_2 , 0.01 g) was loaded into an alumina pan, and the DTA instrument's weight sensor was allowed to stabilize for 20 min at room temperature. The temperature was then increased from room temperature to 800 °C at a rate of 10 °C min^{−1} under flowing air (110 cm³ min^{−1}).

H_2 -TPR of MnO_2 (0.03 g) was carried out in a U-shaped quartz reactor (I.D. 12 mm). Prior to analysis, samples were pretreated at 300 °C for 1 h at a heating rate of 2 °C min^{−1} under flowing Ar

(30 cm³ min^{−1}) and being cooled to room temperature. The reactant gas (10% $\text{H}_2\text{-Ar}$) was flowed through the reactor at a rate of 30 cm³ min^{−1} while the sample was heated to 400 °C at a rate of 10 °C min^{−1}. H_2 consumption was detected using a quadrupole mass spectrometer (QMS, ThermoStar GSD 301T, Pfeiffer Vacuum) and calculated from the $\bullet\text{H}_2$ ($m/z = 2$) signal.

CO-TPD was performed in the same apparatus used for H_2 -TPR. After pretreatment of the sample at 300 °C for 1 h under flowing Ar, CO was preadsorbed in the catalyst bed under flowing 5% CO-Ar (30 cm³ min^{−1}) for 1 h. Then the reactor was purged with an Ar stream (30 cm³ min^{−1}) for 30 min to remove weakly adsorbed CO from the catalyst surface. Finally, the sample was heated from room temperature to 800 °C at a rate of 10 °C min^{−1}. Desorbed CO was detected as $\bullet\text{CO}_2$ ($m/z = 44$), which is the reaction product between adsorbed CO and lattice oxygen species in MnO_2 by the QMS.

2.4. Catalytic activities

The catalytic CO oxidation reaction was performed in a fixed bed configuration with the U-shaped quartz reactor. Prior to initiating the catalytic reaction, the catalyst (0.05 g) was pretreated at 300 °C for 1 h at a heating rate of 2 °C min^{−1} under flowing N_2 (200 cm³ min^{−1}). The reactant stream of 1% CO , 4% O_2 , 19% Ar, and 76% N_2 was flowed at a rate of 200 cm³ min^{−1}. CO concentration in the product stream was detected each second by an infrared gas analyzer (Model 7500, Teledyne Analytical Instruments). CO conversion was calculated by the consumed molar percentage.

3. Results and discussion

3.1. Physicochemical properties

Table 1 shows the physicochemical properties of MnO_2 synthesized using $\text{C}_2\text{--C}_5$ alcohols with different chain lengths and shapes. ICP analysis results revealed that all samples contained large a quantity of K^+ (8–13 wt%). Generally, K^+ is difficult to separate from MnO_x , because K^+ resides in the center of the MnO_x tunnel structure [6]. The S_{BET} of MnO_2 had a strong dependence on the kind of alcohol used. The S_{BET} of MnO_2 (C_2) was 187 m² g^{−1}, which was the largest of all the prepared samples. On the other hand, the S_{BET} s of MnO_2 ($2\text{-C}_{\text{X}=3,4}$) were 38 and 44 m² g^{−1}, much smaller than MnO_2 ($1\text{-C}_{\text{X}=2-5}$ and isoC_4). It is believed that the variation of the S_{BET} of MnO_2 may be correlated with the hydrogen dissociation constants (pK_a s) of the alcohols used. The relevant pK_a values are summarized in Table 1 [21–24]. These are intrinsic values determined in reference to H_2O solution. The pK_a s of 1° alcohols ($pK_a = 16.0\text{--}16.6$) are far lower than those of 2° alcohols. The values of pK_a for 2- C_3 and 2- C_4 alcohols are 17.1 and 17.6, respectively. C_2 has the lowest pK_a value of the alcohols used in this study. Because of weak steric hindrance effects, C_2 alcohol itself causes hydrogen ion (H^+) dissociation in H_2O solutions relatively easily. Alcohols with higher pK_a s support very limited H^+ dissociation due to strong steric hindrance effects [22]. At higher H^+ concentrations, Mn^{7+} is reduced to Mn^{4+} more easily during the redox reaction between MnO_4^- and alcohols. When redox reactions proceed rapidly, nucleation and growth rates increase, producing smaller particles [16] with an increased S_{BET} .

Table 1 also shows the exothermal peak temperature of as- MnO_2 analyzed by DTA. Typically, MnO_2 reduces auto-thermally to Mn_2O_3 at ca. 500 °C [4,11]. For samples produced by 1° alcohols the reduction temperature increases in the order of as- MnO_2 (C_2) < 1- C_3 < 1- C_4 < 1- C_5 < isoC_4 . In addition, as- MnO_2 ($1\text{-C}_{\text{X}=2-5}$) has a lower reduction temperature than as- MnO_2 ($2\text{-C}_{\text{X}=2,3}$). These results agree with D_{hkl} growth behavior, because the crystalline structure changed more easily in smaller particles. However, even in these

Table 1 Physicochemical properties of MnO₂ synthesized using C₂–C₅ alcohols^a with different chain lengths and shapes, and pK_a values of the C₂–C₅ alcohols used as reducing agent.

Alcohol	K ⁺ (wt%) ^b	S _{BET} (m ² g ^{−1})	V _p (cm ³ g ^{−1})	D _{hkl} (nm) ^c		T _{Exo} ^d (°C)	pK _a ^e
				300 °C	400 °C		
C ₂	8.3	187	0.55	2.3	37.1	475.6	16.0 [22]
1-C ₃	9.1	175	0.58	2.4	25.5	491.4	16.1 [22]
2-C ₃	10.4	38	0.11	3.0	9.6	510.0	17.1 [22]
1-C ₄	10.4	161	0.50	2.5	19.7	499.1	16.3 [21]
isoC ₄	12.6	85	0.36	2.8	6.3	554.0	–
2-C ₄	10.1	44	0.16	3.7	5.7	547.5	17.6 [23]
1-C ₅	10.0	132	0.59	2.6	18.7	522.6	16.6 [24]

^a Samples calcined at 300 °C except for D_{hkl} of samples calcined at 400 °C.^b Proportion of residual potassium ion in the sample after preparation.^c Particle size calculated by the Scherrer–Warren equation at 2θ = 37.5° (1-C_{X=2–5}), and 12.6° (isoC₄ and 2-C_{X=3,4}).^d Exothermal temperature meaning the reduction of MnO₂ to Mn₂O₃ in DTA.^e Value in H₂O solution. **Fig. 1.** XRD patterns of manganese oxide synthesized by the reaction of KMnO₄ with C₂–C₅ alcohols as reducing agent and calcined at 300–500 °C, and the samples obtained after H₂-TPR up to 400 °C and CO-TPD up to 800 °C. •: α-MnO₂ (JCPDS: 44-0141), ○: δ-MnO₂ (JCPDS: 80-1098), ◆: MnO (JCPDS: 78-0424), and ◇: Mn₃O₄ (JCPDS: 80-0382).

catalysts, crystal growth rate and orientation produced different results that were dependent on which reductant was used (Table 1).

Fig. 1 shows the XRD patterns of manganese oxides synthesized using KMnO₄ and C₂–C₅ alcohols as reducing agents andcalcined at 300–500 °C. The crystalline structure of MnO₂ depends on the type of alcohol used and on the calcination temperature used. All samples calcined at 300 °C showed a δ-MnO₂ structure. MnO₂ synthesized with 1° alcohols (1-C_{X=2–5}) underwent a phase

Fig. 2. SEM images of MnO₂ synthesized by the reaction of KMnO₄ with C₂–C₅ alcohols as the reducing agent. The samples were calcined in the range of 300–500 °C.

transition from δ - to α -MnO₂ after calcination at 400 °C. After the calcination of MnO₂ at 500 °C, the highest peaks for MnO₂ synthesized with a short chain alcohol such as a C₂ alcohol were at $2\theta = 37.5^\circ$ (2 1 1). However, the primary peak for MnO₂ synthesized with the 1-C₅ alcohol appeared at $2\theta = 12.6^\circ$ (1 1 0). Particle size

based on the (2 1 1) peak increased in the order of MnO₂ (1-C₅) < 1-C₄ < 1-C₃ < C₂. Meanwhile, in case of MnO₂ produced with isoC₄ and 2-C_{X=3,4}, particle size measured at $2\theta = 12.6^\circ$ (0 0 1), which is the highest peak in the δ -MnO₂ phase, increases in the order of MnO₂ (2-C₄) < isoC₄ < 2-C₃ after calcination in a temperature range

Fig. 3. XP spectra of Mn 2p and O 1s for MnO₂ synthesized by the reaction of KMnO₄ with C₂–C₅ alcohols with different chain lengths and shapes. The samples were calcined at 300 °C.

of 300–500 °C. The crystallinity of δ -MnO₂ (isoC₄ and 2-C₄) also increased after calcination at 400 °C. A mixture of δ - and α -phase was observed after calcination at 500 °C, while pure δ -MnO₂ (2-C₃) was obtained after calcination at 500 °C. The XRD patterns of MnO₂ (C₂) indicated a MnO phase after H₂-TPR at 400 °C, and a mixture of α -MnO₂ and Mn₃O₄ was shown in MnO₂ (1-C₄ and 2-C₄) after CO-TPD to 800 °C.

Fig. 2 shows the evolution of the morphology of MnO₂ catalysts synthesized by the reaction of KMnO₄ with C₂–C₅ alcohols as the reducing agent. The size and shape of MnO₂ particles were dependent on the chain length and shape of the C₂–C₅ alcohols used as reductants. All of the MnO₂ catalysts that were calcined at 300 °C were found to have a low crystalline δ -phase structure by XRD analysis and a similar spherical shape. The short chain length alcohol such as C₂ alcohol is favorable to synthesis of MnO₂ with smaller particles than the C₃–C₅ alcohols. Similarly, 1° alcohols produced smaller particles than 2° or iso alcohols during preparation of MnO₂. The partial morphological transformation to nanorod-shapes was observed for MnO₂ (1-C_{X=2–5}) calcined at 400 °C and MnO₂ (isoC₄ and 2-C₄) calcined at 500 °C. MnO₂

(2-C₃) maintained a primarily spherical shape until a small quantity of plate-shaped MnO₂ appeared after calcination at 500 °C. The observations indicate that smaller particles of MnO₂ promote the phase transformation from δ - to α -phase and have a less thermal stability.

To determine the oxidation states of MnO₂ calcined at 300 °C, XPS analysis was performed. Fig. 3 shows XP spectra of Mn 2p and O 1s, and the binding energies (BEs) of Mn 2p and O 1s are summarized in Table 2. Commonly, Mn 2p_{3/2} has two peaks located at ca. 641 (Mn³⁺) and 642 eV (Mn⁴⁺). Moreover, the satellite peak of Mn 2p_{3/2} appears at ca. 645 eV [17]. Mn³⁺ forms in the presence of labile lattice oxygen, suggesting the formation of non-stoichiometric MnO_{2-x}. The percentage of Mn³⁺ was 15.6% for MnO₂ (1-C_{X=4,5}) and 10% for MnO₂ (2-C₄). For the O 1s peak, BEs existed at ca. 529 and 531 eV representing surface lattice oxygen (Mn–O–Mn) and an adsorbed hydroxyl group (Mn–OH), respectively [18]. The portion of Mn–O–Mn was ca. 66% for MnO₂ (1-C_{X=4,5}) and below 55% for MnO₂ (2-C_{X=3,4}). The abundance of the Mn³⁺ oxidation state and Mn–O–Mn in MnO₂ catalysts is believed to be correlated to their catalytic activity for CO oxidation [18].

Table 2

Binding energies of MnO₂ synthesized by reacting KMnO₄ with C₂–C₅ alcohols with different chain length and shape and calcined at 300 °C for 2 h.

Alcohol	Binding energies (eV)			
	Mn 2p _{3/2}		O 1s	
	Mn ³⁺	Mn ⁴⁺	Mn—O—Mn	Mn—OH
C ₂	641.4 (12.9) ^a	642.5 (87.1)	529.6 (65.4)	530.9 (34.6)
1-C ₃	641.1 (11.5)	642.3 (88.5)	529.7 (65.0)	530.9 (35.0)
2-C ₃	641.4 (10.8)	642.2 (89.2)	529.5 (54.6)	530.8 (45.4)
1-C ₄	641.2 (15.6)	642.1 (84.4)	529.7 (66.1)	530.8 (33.9)
isoC ₄	641.0 (11.0)	642.1 (89.0)	529.5 (63.8)	530.7 (36.2)
2-C ₄	641.4 (10.0)	642.2 (90.0)	529.5 (46.2)	531.0 (53.8)
1-C ₅	641.2 (15.6)	642.1 (84.4)	529.6 (65.8)	531.2 (34.2)

^a The value in parenthesis means the percentage of relative area of Mn 2p in Mn³⁺ and Mn⁴⁺ and O 1s in Mn–O–Mn and Mn–OH.

Table 3
Reduction temperature of MnO₂ to Mn₃O₄ and MnO in H₂-TPR, the relative quantity of lattice oxygen species in MnO₂ detected by CO-TPD, and catalytic activities for CO oxidation over MnO₂ catalysts calcined at 300 °C.

Alcohol	Temperature in H ₂ -TPR (°C) ^a		CO-TPD ^b	Temperature (°C) ^c		
	L	H		T _{20%}	T _{50%}	T _{80%}
C ₂	267	281	3.9	114	132	155
1-C ₃	273	285	4.1	109	132	153
2-C ₃	298	310	1.8	145	174	204
1-C ₄	268	279	6.2	106	121	147
isoC ₄	285	296	3.4	131	157	196
2-C ₄	288	301	2.1	153	182	222
1-C ₅	274	287	6.0	107	124	146

^a Temperature of reduction from MnO₂ to Mn₃O₄ (L), and MnO (H).^b The relative area of •CO₂ signal (*m/z* = 44) obtained between 50 and 150 °C.^c Temperature at 20, 50, and 80% CO conversion.

H₂-TPR was performed to analyze the reducibility of MnO₂ to non-stoichiometric MnO_{2-x}, and the results are shown in Fig. 4 and Table 3. Reduction of MnO₂ by H₂ can proceed as

Theoretically, the reduction of MnO₂ to MnO proceeds in a three-step process, which includes the stepwise formation of Mn₂O₃, Mn₃O₄, and MnO. However, H₂-TPR displayed only two reduction peaks in the temperature range of 265–310 °C. One large peak indicates the reaction of MnO₂ to form Mn₃O₄, and the other small peak is for the formation of MnO. The first large peak might

contain two peaks for the reduction of MnO₂ to Mn₂O₃ and of Mn₂O₃ to Mn₃O₄ [10]. The final MnO phase was verified by XRD analysis as shown in Fig. 1 [10,19]. The reduction of MnO₂ (1-C_{X=2-5}) to non-stoichiometric MnO_{2-x} occurs at relatively lower temperature than that of MnO₂ (2-C_{X=3,4} and isoC₄).

Generally, CO adsorbed on the surface of MnO₂ catalysts reacts with lattice oxygen in the MnO₂ to produce CO₂. Sequential production of CO₂ may be described by

Fig. 5 and Table 3 show the results of CO-TPD analysis. Two •CO₂ (*m/z* = 44) peaks with different shapes appear at 100–150 °C

Fig. 4. H₂-TPR profiles of MnO₂ synthesized with KMnO₄ and C₂–C₅ alcohols. The MS signal of •H₂ (*m/z* = 2) was recorded using a QMS detector. TPR conditions: catalyst weight of 0.03 g; flow rate of 10 vol% H₂-Ar of 30 cm³ min⁻¹; RT to 400 °C with a heating rate of 10 °C min⁻¹. **Fig. 5.** CO-TPD profiles of MnO₂ calcined at 300 °C. The MS signal of •CO₂ (*m/z* = 44) was recorded using a QMS detector. CO was preadsorbed at RT under flowing 5% CO-Ar (30 cm³ min⁻¹) for 1 h. TPD conditions: catalyst weight of 0.03 g; flow rate of Ar of 30 cm³ min⁻¹; RT to 800 °C with a heating rate of 10 °C min⁻¹.

Fig. 6. CO oxidation over MnO₂ catalysts prepared by the reaction of KMnO₄ with C₂–C₅ alcohols as the reducing agent and calcined at 300 °C. Reaction conditions: molar composition of CO/O₂/Ar/N₂ of 1/4/19/76; catalyst weight of 0.05 g; total flow rate of 200 cm³ min^{−1}; RT to 300 °C with a heating rate of 2 °C min^{−1}.

Fig. 7. Correlation between the catalytic CO oxidation activity and the quantity of lattice oxygen species analyzed by CO-TPD and XPS. $T_{\text{light-off}}$ is the temperature at which a 50% CO conversion is achieved.

and 450–500 °C [20]. The lower temperature peak is attributed to the labile lattice oxygen species of MnO₂. The higher temperature peaks indicate oxygen species produced during the reduction of MnO₂ to Mn₃O₄, which was verified by XRD analysis of sample obtained after CO-TPD (Fig. 1). The relative quantity of lattice oxygen species in MnO₂ detected by CO-TPD is summarized in Table 3. The relative quantity of lattice oxygen species in MnO₂ (1-C_{X=2–5} and isoC₄) was greater than 3.4, which was larger than that in MnO₂ (2-C_{X=3,4}). The relative quantity of lattice oxygen was maximized in MnO₂ (1-C₄) and decreased in the order of MnO₂ (1-C₄) $\approx$ 1-C₅ > 1-C₃ $\approx$ C₂ > isoC₄ > 2-C₄ > 2-C₃. According to this trend, it is believed that the environmental condition of oxygen in MnO₂ mainly depends on the kind of reducing agent used for synthesis.

3.2. Catalytic activities

Temperature-programmed oxidation of CO was performed over MnO₂ catalysts synthesized using C₂–C₅ alcohols with different chain lengths and shapes (Fig. 6 and Table 3). The catalytic activities of MnO₂ catalysts synthesized with 1° alcohols were higher than those synthesized with iso and 2° alcohols. The catalytic activity, which was based on $T_{50\%}$ and $T_{80\%}$ values, depended on the alcohol used in the order of MnO₂ (1-C₄) $\approx$ 1-C₅ > 1-C₃ $\approx$ C₂ > isoC₄ >

2-C₃ > 2-C₄. These results were compared with the presence of lattice oxygen species. Fig. 7 shows the correlations between $T_{50\%}$, which represents catalytic activity, and the relative quantity of lattice oxygen species on the MnO₂ surfaces determined by XPS and CO-TPD analyses. The MnO₂ (1-C₄) catalyst had the highest Mn–O–Mn fraction as detected by XPS and also had the largest quantity of desorbed CO₂ during the reaction between adsorbed CO and lattice oxygen on the MnO₂ surface as measured by CO-TPD.

4. Conclusions

Crystalline MnO₂ catalysts were prepared from KMnO₄ with C₂–C₅ alcohols of different chain lengths and shapes. A simple change to the calcination temperature in the range of 300–500 °C controlled the crystalline structure to be either γ -MnO₂ or α -MnO₂. The physicochemical properties of MnO₂ catalysts were clearly dependent on the chain length and shape of the C₂–C₅ alcohol used as the reducing agent. MnO₂ prepared using 1° alcohols such as 1-C_{X=2–5} alcohol have relatively high S_{BET} compared to those synthesized with iso and 2° alcohols (C₃–C₄ alcohols). MnO₂ catalysts prepared using 1° alcohols (1-C_{X=4,5}) showed better catalytic activity for CO oxidation than those prepared with isoC₄ or 2° alcohols (2-C_{X=3,4}). Improved catalytic activity was correlated with the quantity of lattice oxygen species in the MnO₂, even for MnO₂ catalysts (1-C_{X=4,5}) with a lower S_{BET} . Thus, the availability of labile lattice oxygen species on the MnO₂ surface was determined to be more crucial to improving catalytic oxidation performance than any other physicochemical property.

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