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DECOMPOSITION OF GAS-PHASE OZONE USING NATURAL MANGANESE ORE AS A CATALYST AT ROOM TEMPERATURE

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ABSTRACT

This paper examines the catalytic decomposition of gas-phase ozone over natural manganese ore (NMO) as a catalyst at room temperature. It is known that NMO mainly consists of γMnO_2, which plays an important role in decomposition of ozone. For the practical application of ozone removal processes, an investigation was conducted for the pretreatment influence of catalyst on decomposition of ozone, especially calcination temperature. NMO was compared with pure MnO_2 and $MnO_2/\gamma\text{-}Al_2O_3$ as reference catalysts. It is found that the optimum calcination temperature is 400 C since MnO_2 is converted to Mn_2O_3 above 500 □. For space velocity below 25,000 hr^{-1}, NMO and pure MnO_2 are known to have the same activities, and their conversions of ozone decomposition, and are higher than that of $MnO_2/\gamma\text{-}Al_2O_3$. The temperature-programmed reduction (TPR) experiments show that NMO has lattice oxygen as many as MnO_2 and more than $MnO_2/\gamma\text{-}Al_2O_3$ on initial temperature of reduction. Also the long-term test confirms that NMO is completely performed in redox cycle.

Key Words: Decomposition of ozone; Catalytic oxidation; Natural manganese ore (NMO); Manganese oxides

1. INTRODUCTION

Gaseous ozone is a chemical compound that has gained a lot of attention in the past years. The ozone layer in the stratosphere is formed through the solar radiation on molecular oxygen, and it protects biological organisms from harmful ultra-violet radiation (Cotton and Wilkinson, 1998). However, ozone in the troposphere is emitted from copiers, printers and water purification system, and is responsible for nausea, headaches and other respiratory illness especially in work environments (Naydenov and Mehandjiev, 1993). Also it enhances photochemical smog formed from reactions between VOCs and nitrogen oxides (Yamashita and Vannice, 1996). Because of its toxicity, the Occupational Safety and Health Administration has declared a permissible exposure limit of 0.1 ppm ozone for a period of eight hours at ground level (Nebel, 1978).

The technology of ozone decomposition is utilized in a number of applications. In airplane cabins, exterior air must be purged of ozone before it can be circulated (Dhandapani and Oyama, 1997). In office environments, cooling air from photocopiers and laser printers carries large amounts of ozone generated by corona discharge processes, and it must be treated before being released, and exhausted gas from deodorization and waste water systems must have its ozone levels reduced (Kent and Fein, 1987; tatsushima and Sakura, 1989).

Most of the works on gas-phase ozone decomposition are catalytically designed to destroy ozone in the air. The active components of the catalysts are noble metals such as Pt, Pd, Rh, etc. (Carr and Junction, 1982; Galligan and Dettling, 1995). But high price of the noble metal has encouraged the use of transition metals such as Mn, Co, Cu, Fe, Ni and Ag (Dhandapani and Oyama, 1997). Catalyst supports used are γ-Al_2O_3, SiO_2, TiO_2, zeolites and activated carbon (Heisig et al., 1997). Supported manganese oxides among oxides used in ozone decomposition have been identified as active oxide (Li et al., 1998; Radhakrishnan et al., 2001). Thus supported manganese oxides are known to be interesting catalysts because they have various types of labile oxygen that are necessary to complete a catalytic cycle. It is for this reason that supported manganese oxides have been used for catalyzing several chemical reactions including the reduction of nitric oxide, oxidation of CO, NH_3, methanol and ethanol (Kanungo, 1979; Stobbe et al., 1999).

In this paper, we report studies of the performance of NMO in ozone decomposition. NMO is composed of various metal oxides, mainly manganese oxides, and has the potential to be used as a catalyst for ozone decomposition. Furthermore, it is low-priced and is prepared by simply methods. The purpose of this paper is to examine the potentiality of NMO as ozone decomposition catalyst.

2. EXPERIMENTAL

The catalyst used in this study is NMO, which is mined in Australia. The NMO is crushed by a jaw crusher and ball mill and then separated to a mean particle diameter of 3 µm. MnO_2 and $MnO_2/\gamma\text{-}Al_2O_3$ are used for the activity of ozone decomposition and as the references for TPR. MnO_2 is a commercial product (Merck Co., Rahway, NJ), and $MnO_2/\gamma\text{-}Al_2O_3$ is prepared by the impregnation method. Impregnated catalysts are dried at 100 □ overnight. The dried material is then placed in a crucible for calcination. The material is heated to 400 C, calcined for 4 hr in air. Mn content of the MnO_2/□-Al_2O_3 is 2 wt.%. Also, NMO is calcined at 400, 500, 600 and 700 C for 4 hr in air respectively, to prepare the catalysts with different calcination temperatures.

The honeycomb catalysts are prepared by wash-coating catalyst powders made by previous processes with silica binder on the cordierite honeycomb (Corning Co., 200 CPSI) with square-shaped cells. The wash-coated honeycomb is blown with compressed air to remove excess slurry on the cordierite off and then is dried at 100 C overnight. These procedures are repeated to increase the amount of catalyst wash-coated on the surface of cordierite, and the honeycomb was calcined at 400 C for 4 hr in air. The active material weight was defined as the weight of all binding materials in each system. The weight of the cordierite is taken before and after impregnation, and the active material weight is 330 g /ℓ.

A schematic of the reactor unit used to test the catalyst activity is given in Fig. 1.

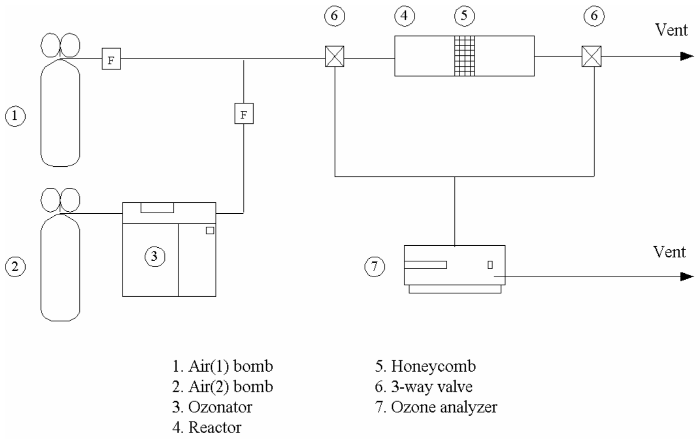

Figure 1. Schematic representation of the experimental apparatus.

A balanced air and air through an ozone generator (OZ BIO Co., Ltd) are used to maintain constant ozone concentration and space velocity. The gas mixture is passed through the honeycomb catalyst, and then vented. Flow rate is controlled by MFC (Mass Flow Controller, Model FC-280S, Tylan). Thermocouples and a pressure transmitter (Dwyer Instrument, Inc., Model 632S-1-LCD) are used to monitor the temperature and pressure drop. Standard conditions are operating temperature of 28 C, the range of linear velocity at the catalyst of 0 ~ 0.4 m/s, inlet ozone concentration of 1.0 ppm, a relative humidity of 60 % and the range of total flow rate of 0 ~ 20,000 cm^3(NTP)/s, corresponding to a space velocity of 0 ~ 68,000 hr^{-1}.

The ozone concentrations at the reactor inlet and outlet are measured using an UV photometric ozone analyzer (Thermo Environmental Instruments Inc. 49C O_3 analyzer) with a sensitivity of 0.001 ppm. The activity is evaluated isothermally at a given condition for at least 10 hr to ensure constant activity and steady-state conditions. Consecutive runs with new samples yield similar results, indicating the reproducibility of the experiments.

Temperature-programmed experiments are performed in a conventional TPR flow apparatus. Samples of 50 mg are heated from room temperature to 900 C in a mixture of 60 vol.% H_2 in Ar (50 ml min^{-1}), with a heating rate of 10 C/min. A cold trap is used for the removal of water. The apparatus is equipped with a thermal conductivity detector (TCD) to determine the hydrogen consumption during the reduction. The concentration of hydrogen is measured by a gas chromatograph (Model HP 6890, Hewlett-Packard). Calibration of the TCD is performed by the injection of known amounts of Ar in the H_2/Ar flow, thus simulating H_2 consumption.

3. RESULTS AND DISCUSSION

The chemical and physical properties of the catalysts used in this study are summarized in Table 1. NMO exists in various forms such as pyrolusite, psilomelane, manganite, braunite and hausmannite in the natural state (Baller et al., 1976). From X-ray photoelectron spectroscopy (XPS) and chemical analysis, the NMO used in this study is found to contain manganese oxides as the main component and Fe_xO_y, CaO, MgO, SiO_2, and Al_2O_3. In more detail, most of the manganese oxide is in the form of β-MnO_2 (pyrolusite). $CaMnSi_4O_{18}$, KMn_8O_{16} (Cryptomelane) and $BaMn_8O_{16}$ (Hollandite) which are formed by the insertion of metal ion into manganese oxides, are present in small quantities. The structure of □MnO_2 is tetragonal.

Table 1. Chemical properties of NMO (balance oxygen of Mn and Fe: 36.33 wt.%)

Compositions	Mn	SiO_2	Al_2O_3	Fe	CaO	MgO
Wt. %	51.85	3.13	2.51	3.86	0.11	0.25

In order to use NMO as ozone decomposition catalyst, effective calcination conditions must be made as a selection. Fig. 2 is the conversion of ozone decomposition with the space velocity as a function of calcination temperature. The conversion of ozone decomposition can be calculated based on a following formula;

$$\text{Conversion of } O_3 \text{ decomposition (\%)} = \frac{([O_3]_{in} - [O_3]_{out})}{[O_3]_{in}} \times 100 \qquad (1)$$

NMO catalyst calcined at 400 C shows the highest conversion. The dried NMO catalyst has less activity than NMO catalyst calcined at 400 C.

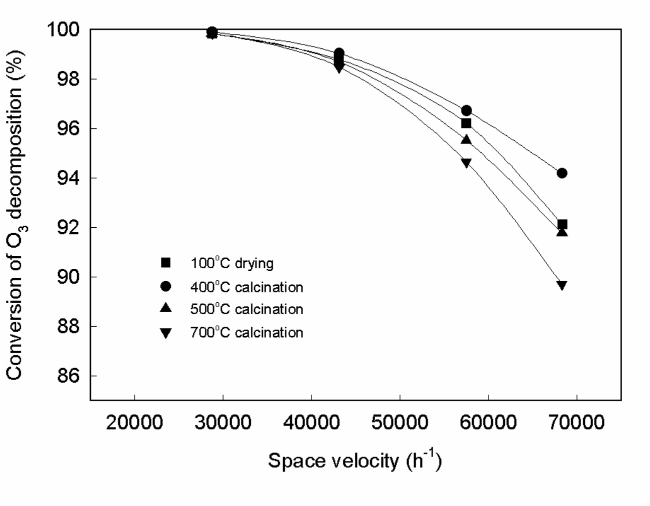

Figure 2. The conversion of ozone decomposition as a function of space velocity for NMO catalysts prepared at different calcination temperatures.

Kanungo (1979) is found that MnO_2 release the physically adsorbed water below 200 C, and chemically adsorbed water and surface hydroxyls are removed beyond 400 C. This result supports that the dried NMO catalysts could remove only the physically adsorbed moisture and the residual hydrated water may deteriorate the catalytic activity. The NMO catalysts calcined over 600 C are transphased by the release of lattice oxygen. According to Li et al. (1998), ozone adsorbs dissociatively on the manganese oxide catalyst to form an oxygen molecule and an atomic oxygen species. The atomic species react with another gaseous ozone to form a peroxide species and a gas-phase oxygen molecule and then the adsorb peroxide species decomposed to form a gas-phase oxygen molecule (Li et al., 1998). Consequently, the mechanism of ozone decomposition must consist of redox mechanism. In the viewpoint of manganese oxidation state, Mn_2O_3 may have less the capacity of redox function than MnO_2.

To inquire into the effect of calcinations temperature on NMO catalyst, the analyses of XRD and BET are investigated. In Fig. 3, the XRD results indicate that main peaks (the angles of 2θ) of NMO catalysts are turned up from 28.7, 37.3 and 56.8 to 23.1, 32.9 and 55.1 at the boundary of 500 C. As seen in TGA experiment, the NMO catalysts calcined beyond 500 C have mainly Mn_2O_3 phase. It is, therefore, considered that this phase-transfer causes NMO catalyst to decrease the activity of ozone decomposition. The specific surface area according to the calcination temperature is presented in table 2. The specific surface areas of NMO catalysts calcined below 500 C is almost identical to dried NMO catalyst. But that of the NMO catalyst calcined at 700 C is deeply decreased. Finally the calcination over 700 □ leads to the release of lattice oxygen and then the shrinkage of micropores, sintering of NMO catalyst, showing remarkable decrease in the ozone decomposition activity.

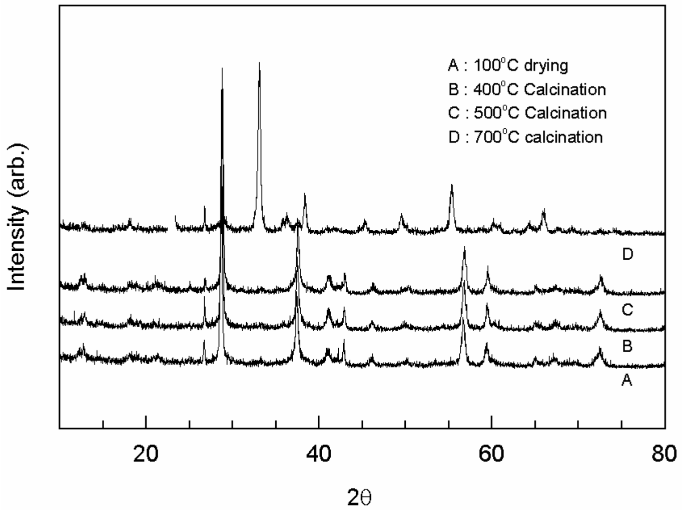

Figure 3. XRD patterns of NMO catalyst prepared at different calcination temperatures.

Table 2. The BET specific surface area of NMO with respect to calcination temperatures

Conditions	Fresh	100 C Drying	400 C Calcination	500 C Calciantion	700 C Calcination
Surface area $(m^2\ g^{-1})$	32.2	31.2	30.2	28.8	14.2

Generally, the reaction of ozone decomposition happens onto the surface of catalysts. Therefore, it is very important to observe the surface composition of NMO catalysts according to the calcination temperatures. Fig. 4 is the result of the wide scan for a variety of calcined NMO catalysts. The analysis reveals the presence of impurities and some metals such as C, Si, Al and Fe. The amount of residual carbons decreases with increased calcination temperature. Specially compared with the intensity of O 1s orbitals, it was remarkably appears in NMO catalyst calcined at 400 C. Since oxygen onto the surface of NMO catalyst participates in redox reaction of ozone decomposition, it is conformed that the optimal calcinations temperature was 400 □.

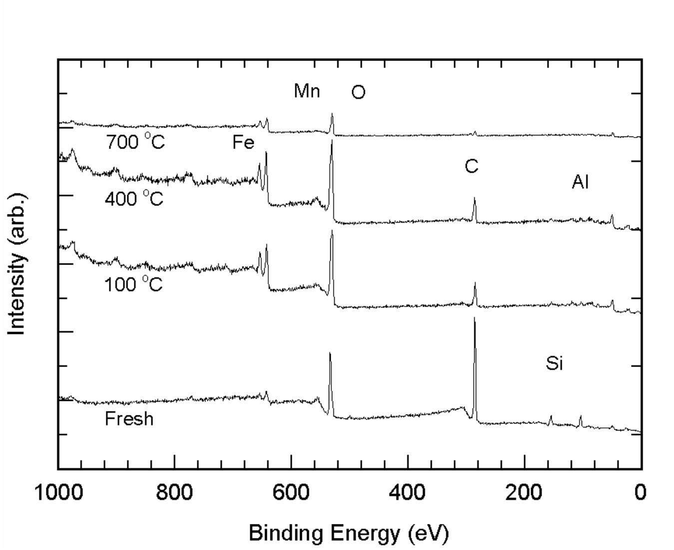

Figure 4. XPS wide scans of NMO catalyst prepared at different calcination temperatures.

Figure 5 shows the XPS patterns of manganese oxides in NMO with different calcination temperature. The typical binding energy of MnO_2 and Mn_2O_3 is indicated in Table 3. The binding energy of Mn $2p_{3/2}$ in fresh NMO appears at 642.3 eV, then being shifted to 641.4 eV as increased calcination temperature and also the binding energy of Mn $2p_{1/2}$ for fresh NMO and calcined NMO at 700 □ is 653.7 and 652.9 eV, respectively. Thus it could be ascertained that the phase change from MnO_2 to Mn_2O_3 occurs as increased calcination temperature and results in low activity of ozone decomposition.

Table 3. The binding energy of manganese oxides

Type	$2p_{1/2}$	$2p_{3/2}$
MnO_2	653.9 eV	642.3 eV
Mn_2O_3	652.9 eV	641.4 eV

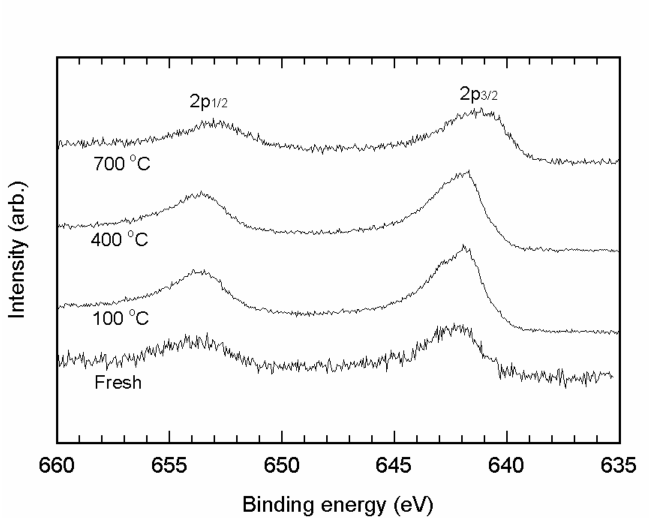

Figure 5. XPS narrow scans of NMO catalyst prepared at different calcination temperatures.

To compare with manganese oxides in NMO, pure MnO_2 and MnO_2/□-Al_2O_3 catalysts are tested and the activities of ozone decomposition are shown in Fig. 6. Physical properties of these manganese oxides are presented in Table 4. The pure MnO_2 catalyst shows the highest ozone decomposition activity. In spite of high surface area, $MnO_2/\gamma\text{-}Al_2O_3$ catalyst has very poor ozone decomposition activity. In the case of space velocity is increased by 25,000 hr^{-1}, the activity of NMO catalyst is similar to pure MnO_2 catalyst. Radhakrishnan, et al. (2001) suggested that the desorption step is a reduction step which proceeds when electrons are transferred to the manganese center by peroxide species to form oxygen. Therefore, it seems that the reducibility of the manganese sites is crucible for the activity of ozone decomposition.

Table 4. Physical properties of NMO and manganese oxides (calcined at 400 C)

Catalysts	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore diameter (Å)
NMO	30.2	0.0398 (> 930 Å)	91.84
MnO_2	22.48	0.0479 (> 1130 Å)	98.41
Mn_2O_3	18.24	0.0404 (> 1040 Å)	95.32

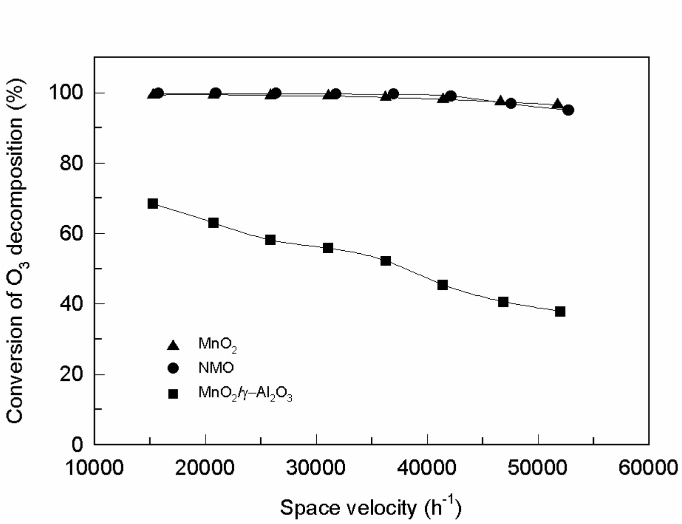

Figure 6. The conversion of ozone decomposition as a function of space velocity for a various manganese oxides (calcination temperature = 400 C; inlet ozone concentration = 4.5 ppm).

TPR profiles of the NMO, MnO_2 and MnO_2/γ-Al_2O_3 catalysts are shown in Fig. 7. Based on the fact that TPR up to 900 C leads to MnO formation, the average oxidation state of the metal could be determined from hydrogen consumption. In this study all samples also show two major peaks but $MnO_2/\gamma Al_2O_3$ exhibits one shoulder on the ending edge. MnO_2 reduces first in one step to Mn_3O_4 and in a second step to MnO.

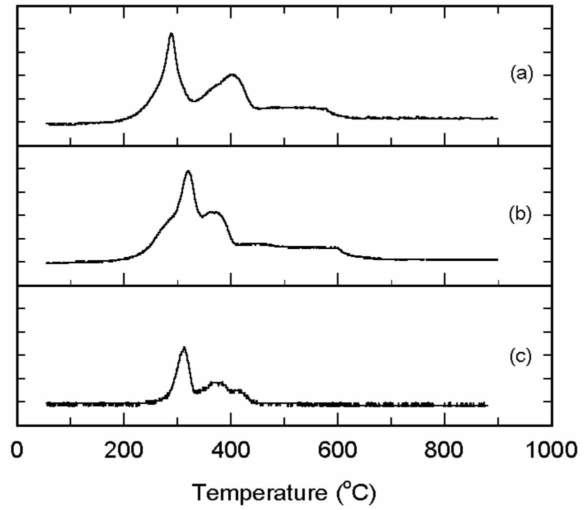

Figure 7. TPR profiles of manganese oxides (reducing gas; Ar 40 vol.% based H_2; gas flow rate = 50 ml min^{-1}; sample wt. = 50 mg, 10 K min^{-1}, (a) MnO_2, (b) NMO and (c) MnO_2/γ-Al_2O_3).

Therefore, the first peak indicates to change from MnO_2 to Mn_3O_4. And second peak indicates to change from Mn_3O_4 to MnO. The reduction ends exhibits green gray color that suggested MnO. The exact estimation of phase change of NMO is difficult because NMO is composed of various metal oxides. It is suggested that the first peak is to change manganese oxides because NMO contained manganese oxides mainly. The onset of reduction in TPR indicates the temperature of desorption of lattice oxygen for redox function. The onset temperature of reduction of MnO_2 and NMO is about 160 C, and that of $MnO_2/\tilde{\gamma}Al_2O_3$ is about 220 □. In accordance with this fact we presume that the activity of MnO_2 and NMO exhibits higher than that of $MnO_2/\tilde{\gamma}Al_2O_3$. The hydrogen consumption ratio of MnO_2, NMO and $MnO_2/\tilde{\gamma}Al_2O_3$ from the first peak area is 1.0 : 0.93 : 0.44. The amount of lattice oxygen of MnO_2 and NMO is similar.

According to the reaction mechanism proposed by the studies of Mehandjiev, et al. (2001) and Rakitskaya, et al (1999), it can be concluded that the reaction intermediates of ozone decomposition should be the electron-rich species such as O^-. Since manganese oxides in NMO catalyst prepared in optimal conditions are almost in the oxidation state of 4, the probable mechanisms as follows:

$$O_3 + Mn^{4+} \rightarrow O^- + Mn^{3+} + O_2 \qquad (2)$$

$$Mn^{3+} + O^- + O_3 \rightarrow Mn^{4+} + 2O_2 . \qquad (3)$$

In the view of electron mobility, manganese oxides in high oxidation state hold a large number of empty d-orbitals which permits greater reducibility.

Presently, some catalysts experience a long-term decline in the activity of ozone decomposition. Higher activity as well as the development of lack deactivation is important goals in catalyst improvement. Heisig, et al (1997) investigated over a series of activated carbon-supported oxide catalyst. The study of binary oxide combinations formed from MnO_2, Co_3O_4, Fe_2O_3 and NiO shows a small decline in activity over time, so a real steady state could not be reached. Also Dhandapani and Oyama (1997) studied the activity over oxides of Mn, Co, Ni, Cr, Ag, Cu, Ce, Fe, V and Mo supported on Al_2O_3. The decline in activity over all catalysts is analogous to that of carbon-supported oxide catalyst.

4. CONCLUSIONS

Natural Manganese Ore (NMO) is found to be very promising catalyst from the viewpoint of activity. The main component of NMO consisted of β-MnO_2 (pyrolusite), which could act as active site of ozone decomposition. The activity of NMO with respect to calcination temperature is observed. The preparation of drying could not remove the residual hydrated water but only remove the physical adsorbed moisture. This reason may deteriorate the catalytic activity and necessitates the preparation of calcinations. Increasing the calcination temperature of 400 □ results in decreasing the ratio of MnO_2 to Mn_2O_3, subsequently the catalytic activity. The activity of pure MnO_2 and $\tilde{\gamma}Al_2O_3$ supported MnO_2 are compared with that of NMO. For space velocity below 25,000 h^{-1}, NMO shows the same activities as pure MnO_2 and the higher than MnO_2/γ-Al_2O_3. It appears to be correlated with the reducibility of lattice oxygen by TPR experiments.

5. ACKNOWLEDGEMENTS

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