Indonesian Journal of Computing, Engineering, and Design 1 (2) (2019) 99-105

Indonesian Journal of Computing, Engineering, and Design

Journal homepage: http://ojs.sampoernauniversity.ac.id/index.php/IJOCED

Decomposition of Nitrous Oxide over Cu/TiO₂ Catalysts: The Effect of Cu Loading, TiO₂ Structure, and Reaction Conditions

K. Yanagida[1], W. Kurniawan [2], C. Salim[3], H. Hinode [2]*

[1] Departement of International Development Engineering, Tokyo Institute of Technology
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan
[2] Department of Transdisciplinary Science and Engineering, School of Environment and Society, Tokyo Institute of Technology
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan
[3] Department of Environmental Engineering, Surya University
Jl. MH. Thamrin, Panunggangan Utara, Kec. Pinang, Kota Tangerang, Banten 15143, Indonesia
Correspondence: E-mail: kurniawan.w.ab@m.titech.ac.jp

ABSTRACT

Decomposition of nitrous oxide (N_2O) over titania (TiO_2) supported copper (Cu) catalyst was investigated with the existence of oxygen and water vapor. The catalytic activity of TiO_2 was promoted by copper loading. It was found that there are optimum levels of copper loading on TiO_2, and these values are correlated to the specific surface area of TiO_2 support being used. The relationship between the catalytic activity for decomposition of N_2O and the crystal structure of TiO_2 was also investigated. The result revealed that Cu/TiO_2 catalysts with the rutile structure has a higher activity toward N_2O decomposition than those with the anatase structure. In this research, Cu(5wt%)/TiO_2 prepared from TiO_2 JRC-TIO-4 (reference catalyst provided by Catalysis Society of Japan) which was mainly constituted of rutile showed the highest activity for N_2O decomposition and it could decompose N_2O completely at 650°C. The catalytic activity was inhibited by the existence of oxygen. However, there was no influence of water vapor to the catalytic activity of Cu/TiO_2 for N_2O decomposition.

ARTICLE INFO

Article History:
Received 04 Jul 2019
Revised 11 Aug 2019
Accepted 27 Aug 2019
Available online 30 Sep 2019

Keywords:
Decomposition of N_2O,
Cu/TiO_2,
Rutile,
Cu loading,
Catalyst.

1. INTRODUCTION

Nitrous oxide (N_2O) is one of the powerful greenhouse gases with a global warming potential per molecule of about 300 times higher than that of carbon dioxide (CO_2). N_2O is also identified as a contributor to the destruction of ozone layer in the stratosphere. Therefore, from the environmental point of view, it is important to investigate the decomposition of N_2O to minimize its adverse effect on the environment. A considerable number of studies have been conducted on the catalytic decomposition and the selective catalytic reduction of N_2O (Haber et al., 2004; Dandekar & Vannice, 1999; Lin et al., 1996; Triawan et al., 2018; Tanaka et al., 2000; Chaki et al., 2003; Pophal et al., 1998; Yan et al., 2003; Sunnardianto et al., 2019).

Selective catalytic reduction of NO to N_2 over TiO_2-supported metal catalysts in the presence of hydrocarbon had been studied by Mitadera and Hinode (2002), and the results showed that TiO_2-supported metal catalysts had good activity for NO reduction (Mitadera & Hinode, 2002). The mechanism of NO reduction to N_2 involves the production of N_2O which occurs at low temperature region. From this result, it could be interpreted that N_2O produced from NO reduction was completely decomposed at high temperature region. Therefore, it was assumed that TiO_2-supported metal catalysts would also show a good activity for N_2O decomposition.

Furthermore, TiO_2 as a support also possesses advantages such as high tolerance to water vapor, which is an important property for N_2O decomposition catalyst in practical use, where oxygen and water vapor often exist in the N_2O containing stream. Therefore, it is desirable to investigate the activity of TiO_2-supported metal catalysts for decomposition of N_2O. In this study, the direct decomposition of N_2O to N_2 by various Cu/TiO_2 catalysts was investigated to understand the influences of Cu loading, TiO_2 structure, as well as oxygen and water vapor on the catalytic activity of the catalyst.

2. METHODOLOGY

2.1. Catalyst Preparation

In this research, Cu/TiO_2 catalyst was prepared by impregnation method. Various kinds of TiO_2 (JRC-TIO-1, 2, 4, and 6; reference catalyst provided by Catalysis Society of Japan) were used as supports. The specific surface area of JRC-TIO-1, 2, 4, and 6 are 82.0 m^2/g, 15.9 m^2/g, 52.9 m^2/g, and 73.0 m^2/g, respectively.

Parent TiO_2 was stirred in a aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (99.9%, Wako Co.) at room temperature for one day. Afterwards, the impregnated catalysts were dried up at approximately 60°C for one day, followed by calcination at 600°C for 5 hours under air flow. In order to reduce the pressure drop in the catalytic activity study, catalysts were pelletized, crushed and sieved to between 0.71 mm to 1.00 mm. The catalyst samples were expressed as: Cu(x wt%)/TiO_2 y, where x means Cu loading level, and y represents reference support number (e.g. Cu(1wt%)/TiO_2 ① means JRC-TIO-1 loading by 1 wt% of Cu).

2.2. Experimental procedure and characterizations

The catalytic reaction was carried out in a fixed-bed flow reactor under atmospheric pressure. A 1.0 g sample was packed in a quartz tube with 6 mm inner diameter. The reactant gas was prepared by mixing N_2O, O_2, and He gas. The mixed gas of 1,000 ppm of N_2O and 10% of O_2 (He as balance gas) was fed to the catalyst at a flow rate of 5.0-6.0 ml/s, which corresponded to space velocity of 16,000 h-1. Water vapor was introduced to the reactor by bubbling system with concentration of approximately 5 vol%.

Gas chromatograph (GC323w; GL Science Co., with Porapak N, Porapak Q and Molecular Sieve 13X column) was used to analyze the concentration of N_2O, N_2 and O_2 after leaving the catalyst system. Characterization of catalyst was performed by X-ray Diffraction (XRD) Method (MultiFlex; Rigaku) and N_2 Adsorption-Desorption Method (SA3100; COULTER).

3. RESULT AND DISCUSSION

3.1. The decomposition of N_2O over Cu/TiO_2

The catalytic activities of Cu/TiO_2 catalysts with different TiO_2 support (JRC-TIO-1, 2, 4, and 6) for the decomposition of N_2O were investigated. The experimental results without the presence of water vapor are shown in **Figures 1** to **4**.

Figure 1 shows the effect of Cu loading level of Cu/$TiO_2$① on the decomposition of N_2O to N_2. The catalyst with Cu loading of 10wt% showed the highest catalytic activity, and the decomposition began at the temperature of 400°C. Complete conversion of N_2O to N_2 was obtained in the temperature range of 650 to 700°C.

Figure 2 shows the effect of Cu loading level of Cu/$TiO_2$② on the decomposition of N_2O to N_2. In this case, the catalyst with Cu loading of 5wt% showed the highest catalytic activity. However, the difference of catalytic activity with respect to the change of Cu loading level was not significant.

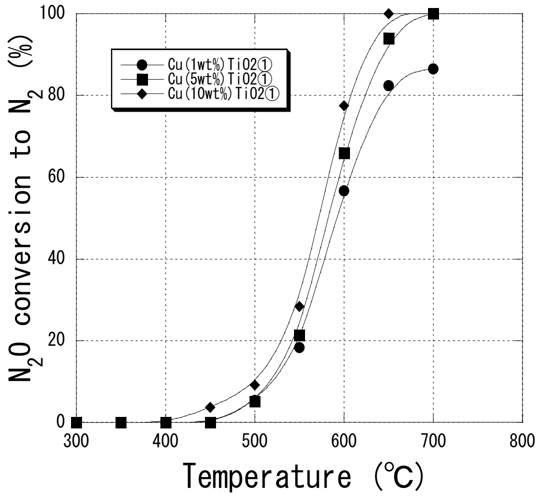

Figure 1. Effect of Cu loading level of Cu/$TiO_2$① on the decomposition of N_2O to N_2

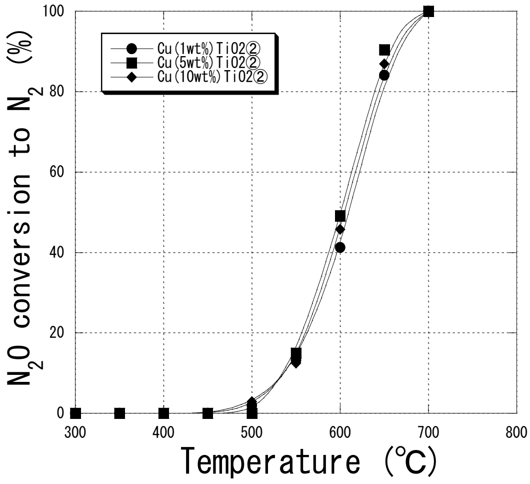

Figure 2. Effect of Cu loading level of Cu/$TiO_2$② on the decomposition of N_2O to N_2.

Figure 3 shows the effect of Cu loading level of Cu/$TiO_2$④ on the decomposition of N_2O to N_2. It can be seen from Figure 3 that JRC-TIO-4 decomposed only approximately 35% of N_2O to N_2 at 700°C. Supporting copper on JRC-TIO-4 resulted in the improvement of catalytic activity. In this case, the catalyst with Cu loading level of 5wt% showed the highest catalytic activity.

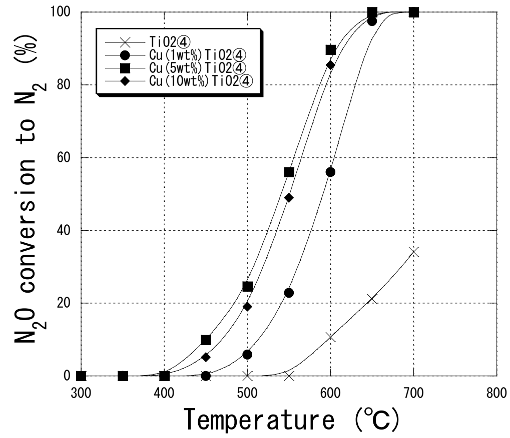

Figure 3. Effect of Cu loading level of Cu/$TiO_2$④ on the decomposition of N_2O to N_2

Figure 4 shows the effect of Cu loading level of Cu/$TiO_2$⑥ on the decomposition of N_2O to N_2. In this case, the catalysts with 5wt% and 10wt% Cu loading levels showed almost the same catalytic activity for the decomposition.

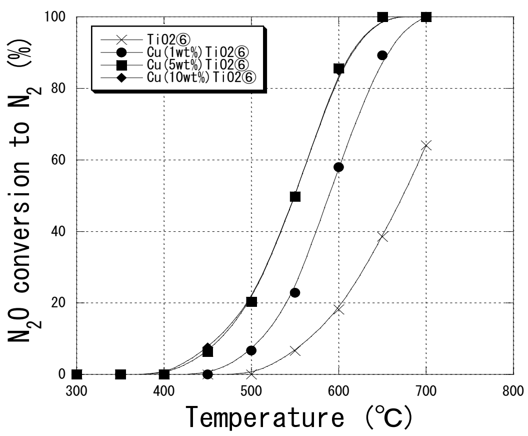

Figure 4. Effect of Cu loading level of Cu/$TiO_2$⑥ on the decomposition of N_2O to N_2.

3.2. The relationship between the optimum Cu loading level and specific surface area of TiO_2

In Section 3.1, it was observed that the optimum Cu loading levels of Cu/TiO_2 for each TiO_2 support were as followed: JRC-TIO-1; 10wt%, JRC-TIO-2; 1wt%, JRC-TIO-4; 5wt%, and JRC-TIO-6; 5wt%. This difference of the optimum Cu loading level was considered to be correlated with the difference of the specific surface area of each TiO_2 support.

The X-ray Diffraction (XRD) analysis showed CuO was identified as the copper species on TiO_2. Therefore, the projected area of one molecule of CuO on the surface of TiO_2 can be calculated using the radius of Cu^{2+} ion and O^{2-} ion and the bonding distance of Cu-O molecule. The radius of Cu^{2+} ion and O^{2-} ion are 0.69 Å and 1.40 Å respectively, and the bonding distance of Cu-O is 1.95 Å. From these data, the projected area (S) of one molecule of CuO on the surface of TiO_2 can be geometrically calculated by using equation (1) to approximately 7.59 Å^2.

$$S = \int_{-1.40}^{1.355} \sqrt{1.40^2 - x^2}\,dx + \int_{1.355}^{2.64} \sqrt{0.69^2 - (x-1.95)^2}\,dx \quad (1)$$

However, during impregnation, $Cu(NO_3)_2$ was dispersed rather than CuO and loaded on the surface of TiO_2. Therefore the projected area of $Cu(NO_3)_2$ on TiO_2 surface was also calculated. The necessary amount of CuO or $Cu(NO_3)_2$ molecule to make the monolayer on the surface of TiO_2 can be calculated by assuming the TiO_2 surface was uniform and the molecules of CuO or $Cu(NO_3)_2$ composed the first monolayer on the surface of TiO_2. **Table 1** shows the relationship between the specific surface area of TiO_2 and the optimum Cu loading level of Cu/TiO_2 from the catalytic activity experiments and from the geometrical calculation of CuO and $Cu(NO_3)_2$ projected area.

Table 1. Relationship between the specific surface area of TiO_2 and ideal Cu loading level for the decomposition of N_2O

Support	Specific surface area [m^2/g]	Optimum Cu loading level [wt%]		
		Experimental data	Geometrical calculation of CuO	Geometrical calculation of $Cu(NO_3)_2$
JRC-TiO-1	82.0	10	11.4	2.25
JRC-TIO-2	15.9	1	2.21	0.436
JRC-TIO-4	52.9	5	7.35	1.45
JRC-TIO-6	73.0	5	10.1	2.00

The results from **Table 1** indicated that the optimum Cu loading level of Cu/TiO$_2$ obtained by the catalytic activity experiments showed a good correlation with the calculated value from the projected area of CuO. This finding suggested that when the TiO$_2$ surface was completely covered with CuO, the catalytic activity for the decomposition of N$_2$O reached maximum. If the amount of CuO loading exceeded the optimum loading, the catalytic activity remained the same or declined because of sintering of copper.

3.3. The relationship between crystal structure of TiO$_2$ and catalytic activity

Figure 5 shows the comparison of the catalytic activities of catalyst prepared from JRC-TIO-1, 2, 4, and 6. The Cu loading level for each sample was selected from loading level of the sample with the best result presented in section 3.1.

The specific surface area of JRC-TIO-2 was 15.9m^2/g, and this value was evidently smaller than other samples. Optimum Cu loading level of Cu/TiO$_2$ prepared from JRC-TIO-2 was 1wt% which was also lower than other samples. This low loading level was considered as the cause of the low activity of Cu(1wt%)/TiO$_2$②.

The Cu(5wt%)/TiO$_2$④ and Cu(5wt%)/TiO$_2$⑥ showed higher catalytic activity than Cu(10wt%)/TiO$_2$①, even though the optimum Cu loading levels of Cu/TiO$_2$ prepared from JRC-TIO-4 and JRC-TIO-6 were lower than that prepared from JRC-TIO-1. This result can be explained using the results of XRD analysis (**Figure 6**). The crystal structure of JRC-TIO-1 and JRC-TIO-2 was anatase and remained as anatase after the preparation of Cu/TiO$_2$. The crystal structure of JRC-TIO-6 was rutile, and it remained rutile structure after the preparation of Cu/TiO$_2$. Moreover, the main crystal structure of JRC-TIO-4 was anatase, and it changed to rutile after the preparation of Cu/TiO$_2$. Therefore, the crystal structure of Cu(5wt%)/TiO2④ and Cu(5wt%)/TiO$_2$⑥ was rutile, and the crystal structure of Cu(10wt%)/TiO$_2$① and Cu(1wt%)/TiO$_2$② was anatase.

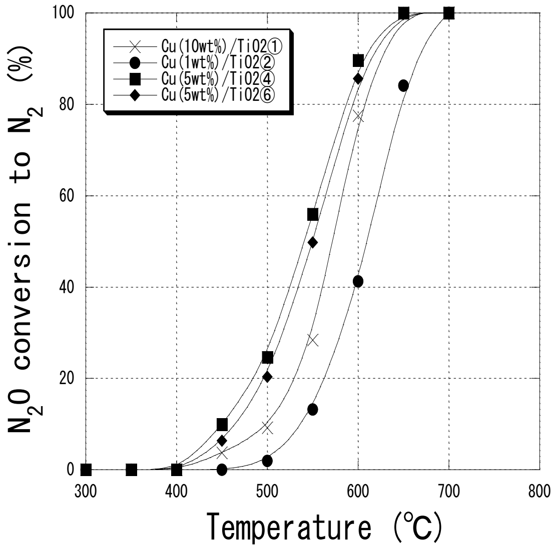

Figure 5. The decomposition of N$_2$O to N$_2$ over Cu/TiO$_2$ prepared from each TiO$_2$

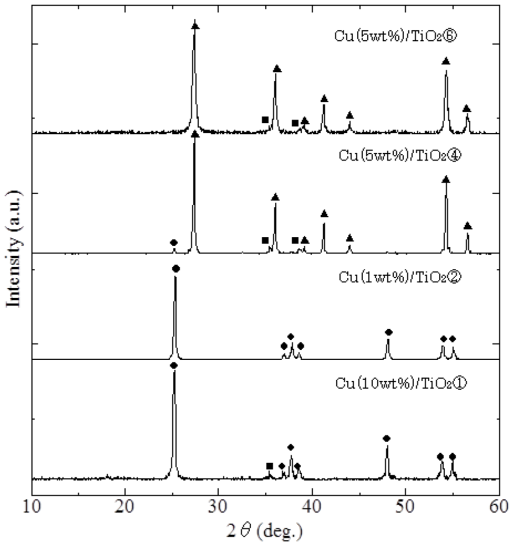

Figure 6. XRD pattern of Cu/TiO$_2$ prepared from each TiO$_2$ (anatase:●, rutile:▲, CuO:■)

In **Figure 5**, Cu(5wt%)/TiO$_2$④ and Cu(5wt%)/TiO$_2$⑥ (rutile) exhibited higher catalytic activity for N$_2$O decomposition than Cu(10wt%)/TiO$_2$① and Cu(1wt%)/TiO$_2$② (anatase). This result suggested that the crystalline structure of the support contributed to the catalytic activity of samples, and rutile is considered to be more effective than anatase for the decomposition of N_2O.

3.4. The influence of oxygen and water vapor on the N_2O decomposition to N_2

Figure 7 shows the influence of oxygen and water vapor on the decomposition of N_2O to N_2 over Cu(5wt%)/$TiO_2$④. In the absence of oxygen and water vapor, the decomposition of N_2O to N_2 over Cu(5wt%)/$TiO_2$④ began from the temperature of 400°C, and the conversion of N_2O to N_2 reached 100% at the temperature of 550°C. However, in the presence of oxygen, N_2O decomposition shifted to higher temperature. The temperature for 100% decomposition of N_2O to N_2 was higher than non-existent case.

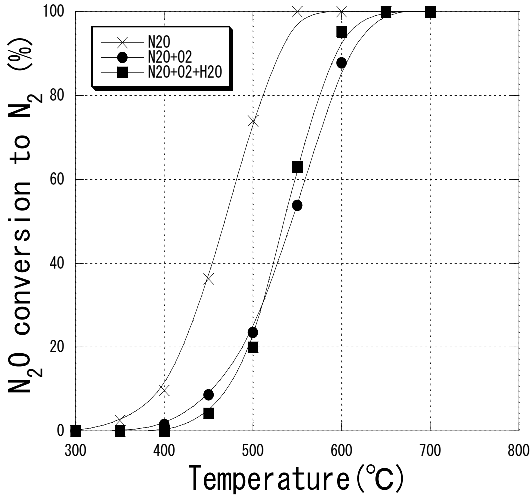

Figure 7. Influence of oxygen and water vapor on the catalytic activity of Cu/TiO_2 for the decomposition of N_2O

N_2O+O_2 system and N_2O+O_2+H_2O system in **Figure 7** showed no difference of the catalytic activity for N_2O decomposition. Previous research reported that the catalytic activity for the decomposition of N_2O increased because of the existence of water vapor. However, our result in **Figure 7** showed that no difference of the catalytic activity for N_2O decomposition in N_2O+O_2 system and N_2O+O_2+H_2O system. This indicates that the existence of water vapor does not influence this catalytic system, and the catalyst could be used in the water treatment process.

4. CONCLUSION

The decomposition of N_2O over various TiO_2-supported copper catalysts was investigated. Cu/TiO_2 catalyst exhibits catalytic activity for the decomposition of N_2O to N_2. Optimum Cu loading level is related to the specific surface area of TiO_2 support being used. The optimum Cu loading level increases with the specific surface area of TiO_2 support. Furthermore, when the TiO_2 surface is covered with CuO completely, the catalytic activity for the decomposition of N_2O reaches maximum value. On the basis of catalytic activity towards the decomposition of N_2O and XRD pattern of Cu/TiO_2 prepared from each TiO_2, rutile is considered to be more effective than anatase for the decomposition of N_2O. Therefore, Cu(5wt%)/$TiO_2$④ and Cu(5wt%)/$TiO_2$⑥ that constitute of rutile has the highest catalytic activity for the decomposition of N_2O to N_2.

The catalytic activity for N_2O decomposition decreases in the existence of oxygen. However, the catalytic activity of Cu/TiO_2 for the decomposition of N_2O is not affected by water vapor. This water vapor tolerance of Cu/TiO_2 catalyst for the decomposition of N_2O is an advantage in the practical use.

REFERENCES

Chaki, T., Arai, M., Ebina, T., & Shimokawabe, M. (2003). Catalytic reduction of N_2O by C_2H_4 over Fe-ZSM-5: Formation and nature of carbonaceous deposits and influence of the addition of O_2. *Journal of Catalysis - J CATAL*, *218*, 220–226. https://doi.org/10.1016/S0021-9517(03)00121-0

Dandekar, A., & Vannice, M. A. (1999). Decomposition and reduction of N_2O over copper catalysts. *Applied Catalysis B: Environmental*, *22*(3), 179–200. https://doi.org/https://doi.org/10.1016/S0926-3373(99)00049-1

Haber, J., Machej, T., Janas, J., & Nattich, M. (2004). Catalytic decomposition of N_2O. *Catalysis Today*, *90*(1), 15–19. https://doi.org/https://doi.org/10.1016/j.cattod.2004.04.002

Lin, J., Chen, H. Y., Chen, L., Tan, K. L., & Zeng, H. C. (1996). N_2O decomposition over ZrO_2 — an in-situ DRIFT, TPR, TPD and XPS study. *Applied Surface Science*, *103*(3), 307–314. https://doi.org/https://doi.org/10.1016/0169-4332(96)00527-2

Mitadera, J., & Hinode, H. (2002). Catalytic reduction of nitric monoxide by ethene over Nb/TiO_2 in the presence of excess oxygen. *Applied Catalysis B: Environmental*, *39*(3), 205–210. https://doi.org/https://doi.org/10.1016/S0926-3373(02)00084-X

Pophal, C., Yogo, T., Yamada, K., & Segawa, K. (1998). Selective catalytic reduction of nitrous oxide over Fe-MFI in the presence of propene as reductant. *Applied Catalysis B: Environmental*, *16*(2), 177–186. https://doi.org/https://doi.org/10.1016/S0926-3373(97)00071-4

Sunnardianto, G. K., Triawan, F., Aamer, A. M., Hastuty, S., Nandiyanto, A. B. D., & Abdullah, A. G. (2019). Boron and Nitrogen Dopant Atoms Precise Tuning (Increment and Reduction) of Charge-transfer Rates in Hydrogenated Graphene. *Materials Physics & Mechanics*, *42*(2).

Tanaka, S., Yuzaki, K., Ito, S., Uetsuka, H., Kameoka, S., & Kunimori, K. (2000). Mechanism of N_2O decomposition over a Rh black catalyst studied by a tracer method: The reaction of N_2O with $^{18}O(a)$. *Catalysis Today*, *63*(2), 413–418. https://doi.org/https://doi.org/10.1016/S0920-5861(00)00486-7

Triawan, F., Nandiyanto, A., Gafar Abdullah, A., & Aziz, M. (2018). Plasma nitriding time on the hardness and crystal structure/phase of SUS403 and SCS6 martensitic stainless steels: An analytical study. *Journal of Engineering Science and Technology*, *13*, 2369–2378.

Yan, L., Ren, T., Wang, X., Ji, D., & Suo, J. (2003). Catalytic decomposition of N_2O over $M_xCo_{1-x}Co_2O_4$ (M = Ni, Mg) spinel oxides. *Applied Catalysis B: Environmental*, *45*(2), 85–90. https://doi.org/https://doi.org/10.1016/S0926-3373(03)00174-7