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Low-temperature oxidation of volatile organic compounds by ozone on Mn-promoted W/Al_2O_3

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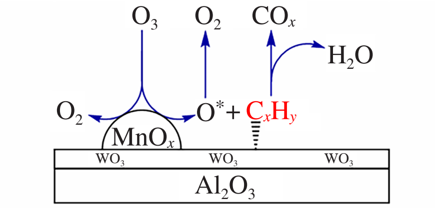
The possibility of combining the catalytic properties of W and Mn to increase the activity of supported catalysts in the ozone catalytic oxidation of volatile organic compounds (VOCs) was studied. The promotion of 8% W/Al_2O_3 by 1 wt% Mn led to a significant increase in conversion of *n*-butane compared to that on reference 8% W/Al_2O_3 and 1% Mn/Al_2O_3 even at ambient temperature.



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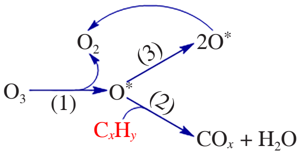
The ozone catalytic oxidation (OZCO) is currently one of the most promising methods for cleaning industrial waste gases within a temperature range of 50–150 °C. Due to the oxidative activity of ozone, this process enables the removal of a wide range of volatile organic compounds[1] (VOCs) and other ecotoxicants[2] at temperatures below 100 °C.

The ozone catalytic oxidation of VOCs can be described by reactions presented in Scheme 1. The key step of the OZCO is the formation of atomic oxygen species O* upon ozone decomposition on the catalyst surface (1). The resulting O* species enables oxidation of volatile organic compounds (2). Transition metal oxides are typically used as OZCO catalysts. As found previously,[3] catalysts based on supported Mn, Co, Ni and Fe oxides exhibit the highest activity in ozone decomposition. However, excessive ozone decomposition activity can decrease the target hydrocarbon oxidation reaction due to the high rate of competitive O* recombination to molecular oxygen (3).



Sheme 1 Ozone catalytic oxidation of VOCs.

In this study, we applied a bifunctional design of OZCO catalysts for minimizing the contribution of the recombination reaction. The bifunctional design implies the separation of ozone decomposition and VOC activation functions between different components of the OZCO catalyst.

Cobalt- or manganese-containing zeolites[4,5] and oxide systems are examples of bifunctional catalysts. Thus, cobalt oxide as a source of atomic oxygen O* and vanadium oxide for activation of VOC molecules were components of an effective OZCO catalyst.[6] Alternatively to V_2O_5, tungsten oxide can also be used for activation of VOCs due to a high concentration of acid sites responsible for the adsorption of hydrocarbons.[7] Note that the largest number of acid sites was observed in monolayer WO_3 supported systems,[8] which are used in various hydrocarbon conversion processes (metathesis, hydrogenolysis, *etc.*).[7] Therefore, we focused on a bifunctional catalytic system based on Mn and W oxides, which were responsible for ozone decomposition and hydrocarbon activation, respectively.

Here, we used γ-Al_2O_3 with a surface area of 76 $m^2\,g^{-1}$ as a carrier. The following manganese and tungsten oxide catalysts were prepared: (*1*) W/Al_2O_3 containing 8 wt% W, which corresponded to four tungsten atoms per nm^2, providing a monolayer coverage of the Al_2O_3 surface with W oxide to a support of a monolayer;[9] (*2*) bifunctional 1% Mn–8% W/Al_2O_3; and (*3*) 1% Mn/Al_2O_3 as a reference sample. The resulting catalysts were investigated by hydrogen temperature-programmed reduction (H_2-TPR) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and tested in OZCO processes (see Online Supplementary Materials for details).

Figure 1 shows the results of the temperature-programmed reduction of the test samples. The H_2-TPR profile of the 8% W/Al_2O_3 showed no hydrogen absorption, which was consistent with published data for tungsten-containing systems[10] in the test temperature range. For the 1% Mn/Al_2O_3 sample, one peak of hydrogen consumption at 360 °C was observed. The H_2/Mn ratio was 0.45, which is close to a theoretical value[11] of 0.5, corresponding to the reduction $Mn_2O_3 \rightarrow MnO$.[12,13] For the 1% Mn–8% W/Al_2O_3, the peak maximum shifted to 400 °C compared to that of monometallic 1% Mn/Al_2O_3. The H_2/Mn ratio was 0.22, which was significantly lower than the theoretical

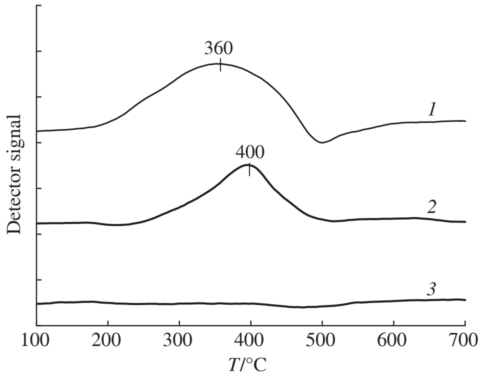


Figure 1 H_2-TPR profiles for (*1*) 1% Mn/Al_2O_3, (*2*) 1% Mn–8% W/Al_2O_3, and (*3*) 8% W/Al_2O_3.

value for MnO_x reduction and typical of Mn–W systems[14] due to a change in the redox properties of manganese.

The SEM-EDS data for the 1% Mn–8% W/Al_2O_3 sample showed a uniform distribution of manganese and tungsten on the carrier surface (see Online Supplementary Materials for details). Table 1 summarizes the chemical composition of the samples.

Because the element contents of the test samples corresponded to the values expected from calculations, we concluded that Mn and W were predominantly located on the surface of the carrier. The activity of the prepared samples was evaluated in ozone decomposition because the decomposition of ozone on the catalyst surface led to the formation of highly active O* species initiating the OZCO process. Figure 2 shows the temperature dependences of O_3 conversion on the studied samples. To evaluate the contribution of ozone decomposition in a gas phase, an additional experiment was carried out in an empty reactor without a catalyst.

Ozone decomposition in a gas phase began at 130 °C and increased with temperature to reach a 100% conversion at 330 °C, which is in good agreement with previously published data.[6] A comparison of the catalytic properties of individual 1% Mn/Al_2O_3 and 8% W/Al_2O_3 in ozone decomposition showed that a sample with deposited tungsten had a significantly lower activity. The O_3 decomposition on 8% W/Al_2O_3 started at 60 °C and slowly increased with temperature; the complete conversion was achieved at 270 °C. On the contrary, 1% Mn/Al_2O_3 demonstrated a high activity, as evidenced by ozone conversion of 15% already at 30 °C, which approached 100% at 150 °C.

Modification of 8% W/Al_2O_3 by 1 wt% Mn significantly accelerated the process of ozone decomposition. Thus, ozone conversion on the bifunctional sample at 30 °C was 55% *versus* 15% on 1% Mn/Al_2O_3. However, at temperatures above 75 °C, the conversion values on both samples became comparable.

To compare the activity of catalyst samples in the OZCO of *n*-butane, the following reaction was carried out under conditions of a stoichiometric excess of ozone (an O_3/*n*-C_4H_{10} ratio of 16):

$$C_4H_{10} + 13O_3 \rightarrow 4CO_2 + 5H_2O + 13O_2.$$

Figure 3 shows the temperature dependences of *n*-butane conversion on the test samples.

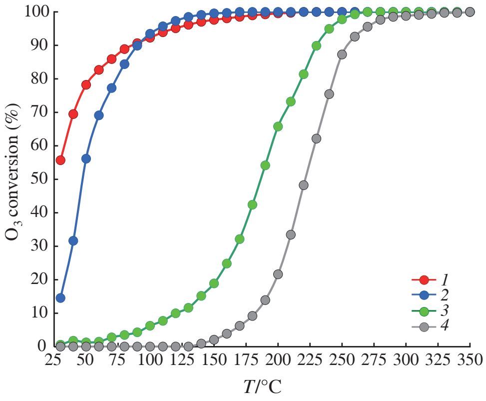


Figure 2 Temperature dependences of ozone conversion in the presence of (*1*) 1% Mn–8% W/Al_2O_3, (*2*) 1% Mn/Al_2O_3, and (*3*) 8% W/Al_2O_3, as well as (*4*) in a gas phase. Conditions: *n*-C_4H_{10}, 100 ppm; O_3, 1600 ppm; O_2, 20%; and GHSV = 150 000 h^{-1}.

Table 1 Elemental composition of samples according to the EDS data.

Sample	Element concentration (wt%)			
	Mn	W	Al	O
8% W/Al_2O_3	–	8.21	35.68	56.11
1% Mn/Al_2O_3	1.01	–	39.87	59.11
1% Mn–8% W/Al_2O_3	0.92	7.99	35.87	55.22

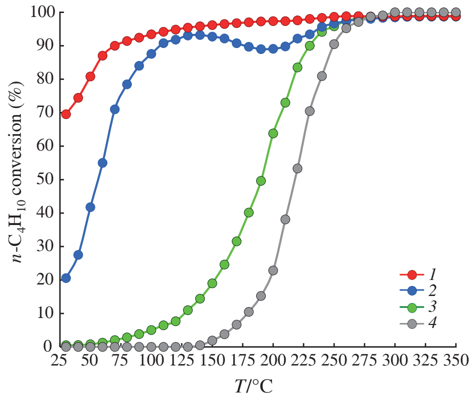


Figure 3 Temperature dependences of *n*-C_4H_{10} conversion in the presence of (*1*) 1% Mn–8% W/Al_2O_3, (*2*) 1% Mn/Al_2O_3, and (*3*) 8% W/Al_2O_3, as well as (*4*) in a gas phase. Conditions: *n*-C_4H_{10}, 100 ppm; O_3, 1600 ppm; O_2, 20%; and GHSV = 150 000 h^{-1}.

The oxidation of *n*-C_4H_{10} by O_3 in a gas phase occurred in parallel with ozone decomposition, as indicated by the coincidence of O_3 and *n*-C_4H_{10} conversion curves (Figures 2 and 3). The OZCO on the 8% W/Al_2O_3 sample also proceeded simultaneously with ozone decomposition. Thus, oxidation of *n*-butane began at 60 °C and approached a 100% conversion at 270 °C. The agreement of the ozone decomposition and *n*-C_4H_{10} oxidation profiles suggests the high efficiency of W in using O_3 in hydrocarbon oxidation. However, high conversion values in the low-temperature region cannot be achieved due to an insufficient activity of 8% W/Al_2O_3 in ozone decomposition.

The sample containing 1 wt% Mn was more active in the OZCO process than that containing 8% W/Al_2O_3. Thus, the hydrocarbon conversion was 20% already at 30 °C, and it increased with temperature to reach a maximum of 93% at 140 °C. However, there was a slight decrease to ~85% at 140–200 °C, which was explained by an insufficient amount of ozone for hydrocarbon oxidation due to its 100% conversion. Further heating led to an increase in conversion, which reached 100% at 290 °C due to the predominance of the gas-phase reaction. The experimental data demonstrated the high activity of manganese both in ozone decomposition and in hydrocarbon oxidation due to an optimal balance of activity in this reaction.[1]

The catalytic activity was significantly improved in the bifunctional 1% Mn–8% W/Al_2O_3 catalyst prepared by deposition of a Mn component onto W/Al_2O_3. Thus, the conversion of *n*-butane at 30 °C was ~70%, which is higher by a factor of 3.5 than that on the 1% Mn/Al_2O_3 catalyst. The conversion increased with temperature to reach 100% at 150 °C. Remarkably, there is no decrease in the values of the degree of conversion for this sample in the temperature range of 140–200 °C compared to that for 1% Mn/Al_2O_3.

Analysis of the reaction products showed that no compounds other than CO and CO_2 were formed. The carbon balance calculated as a concentration ratio of CO_x to reacted *n*-butane in terms of C_1 was 98–99%. It is also important that the selectivity for CO_2 in all catalytic systems was $\geqslant$87%.

The experimental data allowed us to conclude that the promotion of W/Al_2O_3 with a minor amount of Mn oxide significantly increased its activity in ozone decomposition and ozone catalytic oxidation of VOCs at ambient temperature. This was achieved due to a combination of ozone decomposition (Mn component) and hydrocarbon activation (W/Al_2O_3 component) functions in the 1% Mn–8% W/Al_2O_3 bifunctional catalyst. Excellent activity of 1% Mn–8% W/Al_2O_3 in the OZCO at nearly ambient temperature can be additionally attributed to the improved activity of a Mn component in O_3 decomposition (Figure 2), which was presumably related to Mn–W mixed oxide formation.

In general, the bifunctional design applied to the preparation of the 1% Mn–8% W/Al_2O_3 catalyst seems to be a promising method for further development of highly effective catalytic systems for VOC abatement by ozone catalytic oxidation.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7854.

References

1 B. Liu, J. Ji, B. Zang, W. Huang, Y. Gan, D. Y. C. Leung and H. Huang, *J. Hazard. Mater.*, 2022, **422**, 126847; https://doi.org/10.1016/j.jhazmat.2021.126847.

2 D. A. Bokarev, I. V. Paramoshin, S. A. Kanaev, G. O. Bragina and A. Yu. Stakheev, *Mendeleev Commun.*, 2023, **33**, 669; https://doi.org/10.1016/j.mencom.2023.09.033.

3 J. Ma, R. Cao, Y. Dang and J. Wang, *Chin. Chem. Lett.*, 2021, **32**, 2985; https://doi.org/10.1016/j.cclet.2021.03.031.

4 D. A. Bokarev, I. V. Paramoshin, S. A. Kanaev, G. N. Baeva, A. V. Rassolov and A. Yu. Stakheev, *Kinet. Catal.*, 2024, **65**, 417; https://doi.org/10.1134/S0023158424601736.

5 D. A. Bokarev, G. O. Bragina, A. R. Kolyadenkov, A. V. Kazakov and A. Yu. Stakheev, *Mendeleev Commun.*, 2024, **34**, 837; https://doi.org/10.1016/j.mencom.2024.10.022.

6 D. A. Bokarev, S. A. Kanaev, G. O. Bragina, A. E. Vaulina, G. N. Baeva and A. Yu. Stakheev, *Russ. Chem. Bull.*, 2024, **73**, 1201; https://doi.org/10.1007/s11172-024-4236-4.

7 F. Can, X. Courtois and D. Duprez, *Catalysts*, 2021, **11**, 703; https://doi.org/10.3390/catal11060703.

8 T. Aihara, H. Miura and T. Shishido, *Catal. Sci. Technol*., 2019, **9**, 5359; https://doi.org/10.1039/c9cy01385g.

9 I. E. Wachs, *Catal. Today*, 1996, **27**, 437; https://doi.org/10.1016/0920-5861(95)00203-0.

10 H. Wang, Y. Wu, Z. Liu, L. He, Z. Yao and W. Zhao, *Fuel*, 2014, **136**, 185; https://doi.org/10.1016/j.fuel.2014.07.034.

11 A. Wōllner, F. Lange, H. Schemels and H. Knōzinger, *Appl. Catal., A*, 1993, **94**, 181; https://doi.org/10.1016/0926-860X(93)85007-C.

12 Y. Liu, M. Luo, Z. Wei, Q. Xin, P. Ying and C. Li, *Appl. Catal., B*, 2001, **29**, 61; https://doi.org/10.1016/S0926-3373(00)00193-4.

13 A. Sorge, M. Turco, G. Pilone and G. Bagnasco, *J. Propul. Power*, 2004, **20**, 1069; https://doi.org/10.2514/1.2490.

14 A. Malekzadeh, A. Khodadadi, A. K. Dalai and M. Abedini, *J. Nat. Gas Chem.*, 2007, **16**, 121; https://doi.org/10.1016/S1003-9953(07)60037-1.

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