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Research Note

Effect of water vapor on catalytic oxidation of benzene with ozone on alumina-supported manganese oxides

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Abstract

The effect of water vapor on catalytic oxidation of benzene with ozone was studied over alumina-supported manganese oxides. Water vapor suppressed catalyst deactivation by inhibiting the build-up of organic byproducts on the catalyst surface, including formic acid and strongly bound surface formates. FTIR spectroscopic studies revealed that the surface formates were not completely oxidized with ozone in the absence of water vapor, whereas their oxidation with ozone was promoted by addition of water vapor.

Keywords: Catalytic oxidation; Ozone; Alumina-supported manganese oxides; Catalyst deactivation; Effect of water vapor

1. Introduction

Catalytic oxidation by using ozone (catalytic ozonation) is an effective method for the oxidation of volatile organic compounds (VOCs) in the gas phase at low concentration levels [1]. The use of ozone can lower the reaction temperature for catalytic oxidation of VOCs compared with catalytic combustion. Hitherto, it has been reported that various types of compounds are oxidized on metal oxide catalysts under relatively mild conditions [2–8]. Supported and unsupported manganese oxides have been used for the catalytic ozonation, because Mn is an effective constituent for ozone decomposition [9,10].

One major problem in catalytic ozonation is catalyst deactivation. We have reported that alumina-supported manganese oxide (MnO_x/γ-Al_2O_3) catalysts suffer from deactivation in the VOC oxidation at room temperature due to the build-up of organic byproducts on the catalyst surface [11,15]. For instance, benzene is oxidized on MnO_x/γ-Al_2O_3 catalyst with ozone to form two types of partially oxidized byproducts: weakly bound compounds and strongly bound surface species [11]. The build-up of these compounds inhibits the adsorption and decomposition of ozone on the manganese oxides, the key step in the formation of oxygen species active for benzene oxidation [5–7, 12–14]. Therefore, removal of these compounds is necessary to maintain catalytic activity.

In this paper, we report that water vapor suppresses the deactivation of MnO_x/γ-Al_2O_3 catalyst in benzene oxidation, by promoting the oxidation of organic byproducts on the catalyst surface. Formic acid and surface formates on the catalyst surface, major byproducts in benzene oxidation, are readily oxidized with ozone in the presence of water vapor. To the best of our knowledge, this is the first report on the promoting effect of water vapor on catalytic ozonation reactions.

2. Experimental

Alumina-supported manganese oxide catalyst with 5 wt% Mn loading was obtained by the impregnation of γ-Al_2O_3 (Catalysis Society of Japan, JRC-ALO-8, $S_{BET} = 168\ m^2\,g^{-1}$) with an aqueous solution containing appropriate amount of $Mn(CH_3COO)_2{\cdot}4H_2O$ (Wako Pure Chemical, >99.9%). The catalyst was dried at 383 K and then calcined at 773 K for 3 h in air.

Catalytic ozonation was carried out in a fixed-bed flow reactor modified for reactions with water vapor from the reaction system as reported previously [11]. The reaction gases were

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prepared from N_2 (>99.9999%, total hydrocarbon <0.5 ppm), O_2 (>99.999%, total hydrocarbon <0.5 ppm), and formic acid in N_2 in cylinders. Water vapor was supplied by a water bubbler thermostatted at 295 K. The concentration of water vapor in the reaction gas was measured by a dew point hygrometer (General Eastern HYGRO M4). Ozone was synthesized from O_2 by a silent discharge ozone generator (Ebara Jitsugyo Co., Ltd. OZSD-3000A). Before the reaction, the catalyst was heated at 723 K in O_2 flow. The feed of ozone to the catalyst without organic substrates did not form CO_x, indicating the absence of CO_x species and organic impurities on the catalyst surface. Then the catalyst was thermostatted with a water bath. Analysis of gas sample was performed with a Fourier transform infrared spectrophotometer (Perkin–Elmer Spectrum One) equipped with a 2.4-m optical length gas cell (volume, 100 ml).

FTIR spectra were recorded with a Perkin–Elmer Spectrum One spectrometer equipped with a TGS detector with a resolution of 4 cm^{-1}. Samples were pressed into thin, 20 mm-diameter, self-supporting wafers (ca. 30 mg) and set in an IR cell with KBr windows, which was connected to the reaction system. Before the measurements, the sample was preheated at 723 K in O_2. FTIR spectra confirmed that the catalyst surface did not contain CO_x species after the pretreatment.

3. Results and discussion

Fig. 1 shows the effect of water vapor on time courses for benzene oxidation with 5 wt% MnO_x/γ-Al_2O_3 catalyst. After the adsorption–desorption equilibrium for benzene was achieved, ozone was fed to the reactor to start the reaction. In the benzene oxidation without water vapor, the catalyst was gradually deactivated with time on stream (stage I in Fig. 1a) due to the build-up of partially oxidized byproducts on the catalyst surface. Although benzene conversion also decreased with time on stream with water vapor, the decrement of benzene conversion became smaller (stage I in Fig. 1b). In addition, the rate for CO_2 formation was enhanced. When the ozone feed was started again without benzene after the benzene oxidation, the byproducts on catalyst surface were oxidized to CO_2 and CO (stage II in Figs. 1a and 1b). It is clearly seen that water vapor greatly promoted oxidation of the byproducts to CO_x. These findings indicate that water vapor suppressed catalyst deactivation by inhibiting the build-up of organic byproducts on the catalyst surface.

TPO measurements were conducted with the used catalysts to investigate the residual species on their surfaces. Fig. 2 shows the TPO profiles for the catalysts used for the oxidation reactions described above. For the catalyst after the reaction without water vapor (Fig. 2a), the profiles show two peaks for CO_x formation. The peak for CO_x evolution at low temperature (403 K) corresponds mainly to the oxidation of weakly bound byproducts on catalyst surface, whereas that at high temperature (626 K) is due to the oxidation of strongly bound surface species including surface formates and carboxylates [11]. Formic acid, one of the major byproducts on catalyst surface, was also observed. In contrast, the amount of products in TPO was much lower for the catalyst after the reaction with water

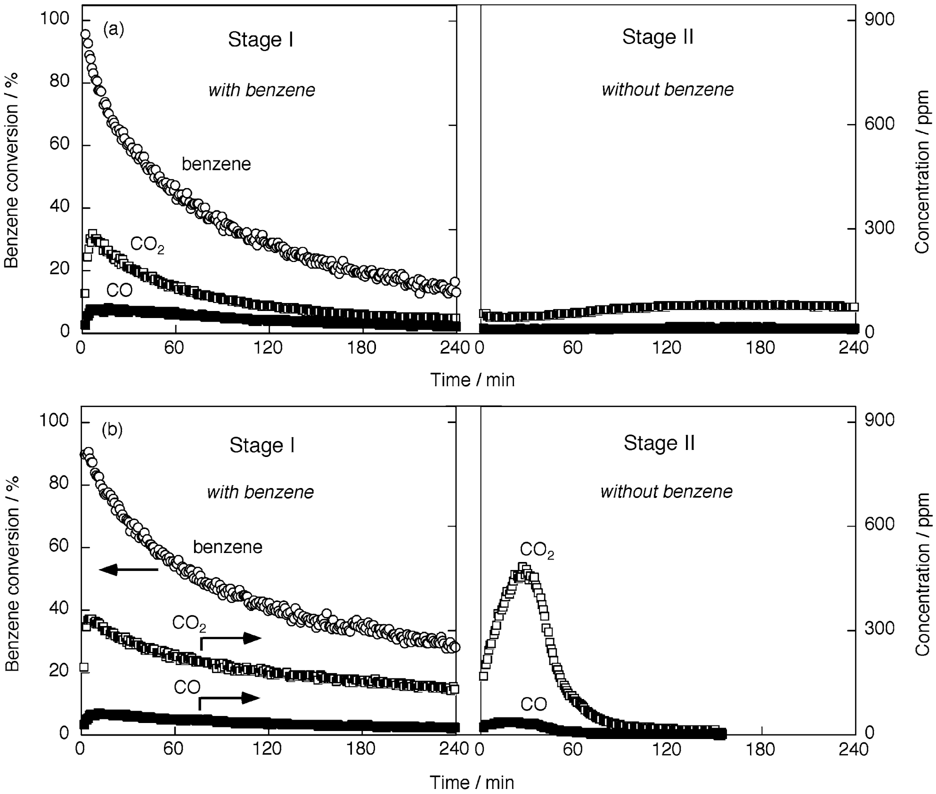

Fig. 1. Time course for benzene oxidation with ozone over 5 wt%-MnO_x/γ-Al_2O_3 catalyst. Catalyst 0.10 g, benzene 150 ppm, O_3 1500 ppm, O_2 10%, N_2 balance, flow rate 1000 ml min^{-1}, reaction temperature 313 K. (a) Without water vapor and (b) with water vapor (0.7%).

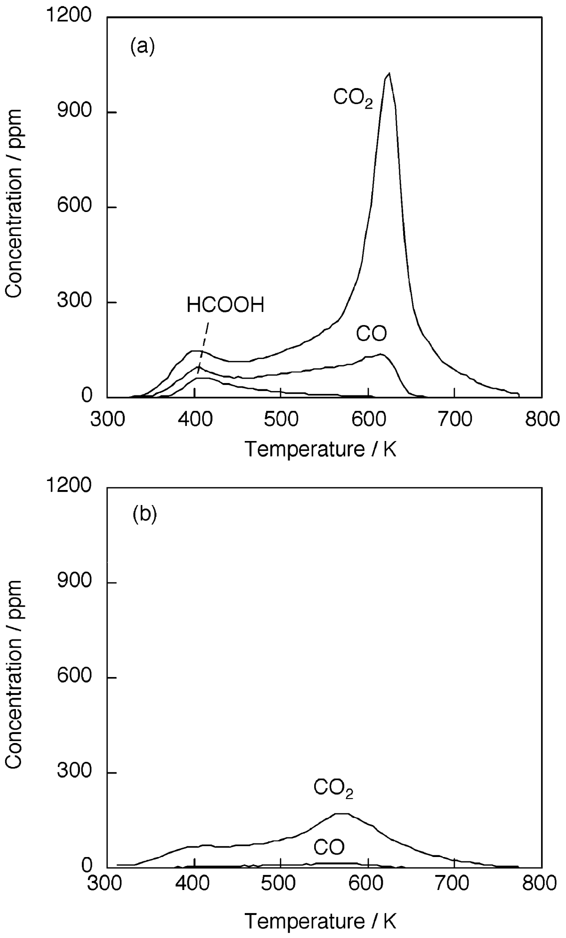

Fig. 2. TPO profiles for 5 wt%-MnO_x/γ-Al_2O_3 catalyst after the use for benzene oxidation with and without water vapor. Heating rate 10 K min^{-1}.

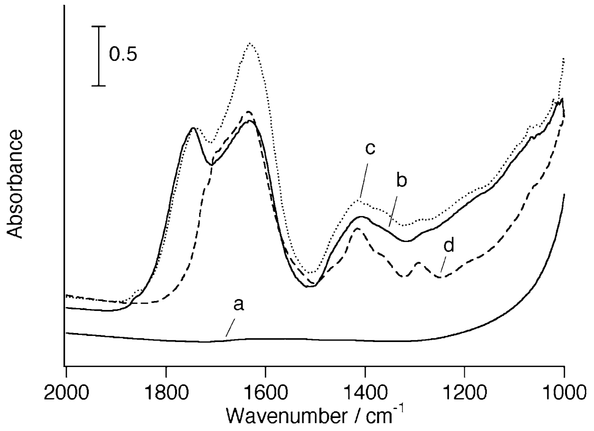

Fig. 3. FTIR spectra of 5 wt%-MnO_x/γ-Al_2O_3 catalyst. Line a: before reaction; b: after benzene oxidation with ozone in the absence of water vapor; c: after the feed of water vapor; d: after oxidation with ozone in the presence of water vapor. Benzene 100 ppm, O_3 1000 ppm, O_2 10%, water vapor 0.6%, N_2 balance, flow rate 200 ml min^{-1}.

vapor (Fig. 2b). In particular, the amount of CO_x at high temperature greatly decreased, and formic acid was not detected, indicating that water vapor inhibited the accumulation of formic acid and strongly bound surface species on the catalyst.

Fig. 3 shows the FTIR spectra of the MnO_x/γ-Al_2O_3 catalyst after benzene oxidation in the absence of water vapor, and that after oxidation with ozone in the presence of water vapor. After the benzene oxidation, absorption bands appeared in the range 1000–1800 cm^{-1} with maximum intensities at 1412, 1630, and 1746 cm^{-1}, indicating the build-up of byproducts on the catalyst. The band at 1746 cm^{-1} was assigned to the C=O stretching vibration of formic acid on the catalyst surface [11]. The bands at around 1630 cm^{-1} and 1412 cm^{-1} were ascribed to other oxygen-containing byproducts. The band at 1630 cm^{-1} was overlapped with that of adsorbed water and increased in intensity due to the water vapor feed. These absorption bands were diminished by ozone feed in the presence of water vapor, revealing that the oxygen-containing byproducts were further oxidized. In particular, the disappearance of the band at 1746 cm^{-1} indicated the complete removal of formic acid.

In the benzene oxidation with ozone on the MnO_x/γ-Al_2O_3 catalyst, formic acid is one of the major byproducts on the catalyst surface [11]. Formic acid is transformed on the catalyst surface to strongly bound surface formates, leading to deactivation of MnO_x/γ-Al_2O_3 catalyst [11]. Therefore, our finding that water vapor inhibited the build-up of organic byproducts on the catalyst spurred us to investigate the oxidation behavior of surface formates with and without water vapor.

Fig. 4 shows the FTIR spectra of 5 wt% MnO_x/γ-Al_2O_3 during the adsorption of formic acid without water vapor (Fig. 3a). New bands appeared in the range of 1000–2000 cm^{-1}, which were assignable to the surface formates on the catalyst; the bands at 1596 and 1628 cm^{-1} were due to the asymmetric stretching of COO–, and the bands at 1324 and 1374 cm^{-1} were the COO– symmetric stretching overlapped with C–H stretching. In the higher vibration region, the band of C–H stretching and OH stretching appeared, along with the disappearance of surface OH groups of γ-Al_2O_3 due to hydrogen bonding to surface formates (data not shown). The formation of strongly bound surface formates was confirmed by TPD measurements; heating the MnO_x/γ-Al_2O_3 catalyst resulted in the formation of CO_2 and CO, which was ascribed to the decomposition of strongly bound surface formates. During the adsorption of formic acid with water vapor, the bands of surface formates were also observed on the catalyst surface, overlapped with the band of adsorbed water at 1638 cm^{-1}. The band of COO– asymmetric stretching was shifted to 1590 cm^{-1} by the addition of water vapor.

The surface formates on the catalysts were oxidized by the reaction with ozone, and water vapor promoted the oxidation of surface formates to CO_2. Fig. 4 also shows the FTIR spectra of MnO_x/γ-Al_2O_3 obtained when ozone was contacted with the catalyst after formic acid was adsorbed on the catalyst surface. When water vapor was absent, the band intensity of adsorbed species decreased (Fig. 4b). However, the disappearance of surface formates stopped, and the band due to residual surface formates remained after a prolonged ozone feed. In contrast, the band of adsorbed species completely disappeared in the oxidation with water vapor (Fig. 4c), giving rise to the spectrum showing only the band of adsorbed water on the catalyst surface. Fig. 5 shows the profiles for product formation and

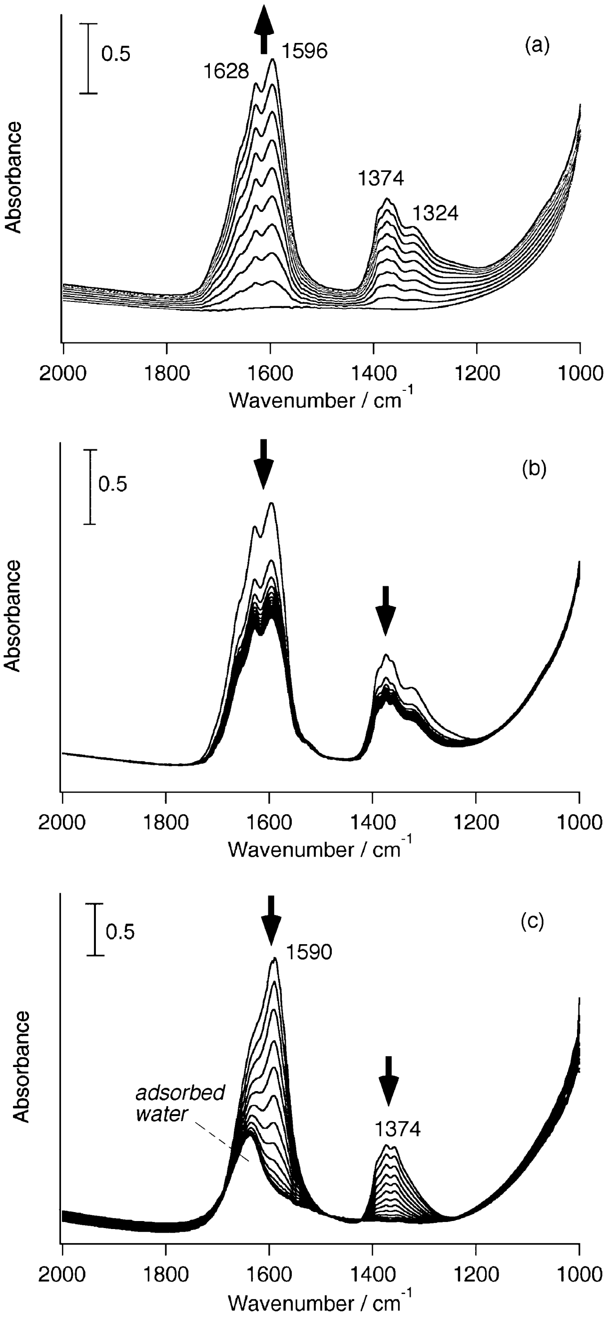

Fig. 4. FTIR spectra of 5 wt%-MnO_x/γ-Al_2O_3 catalyst during adsorption of (a) formic acid, (b) decomposition of formic acid without water vapor, and (c) with water vapor.

ozone decomposition when ozone was contacted with the catalyst after the adsorption of formic acid. Only CO_2 was observed as the product, and its amount monotonically decreased with time. Ozone was completely consumed during the reaction. The profiles with water vapor (Fig. 5b) show that the rate for CO_2 formation and the total amount of CO_2 formed increased due to the addition of water vapor. The profile of ozone consumption resembled that for CO_2 formation; the amount of ozone consumed decreased with time on stream and reached nearly zero after the surface formates were completely oxidized.

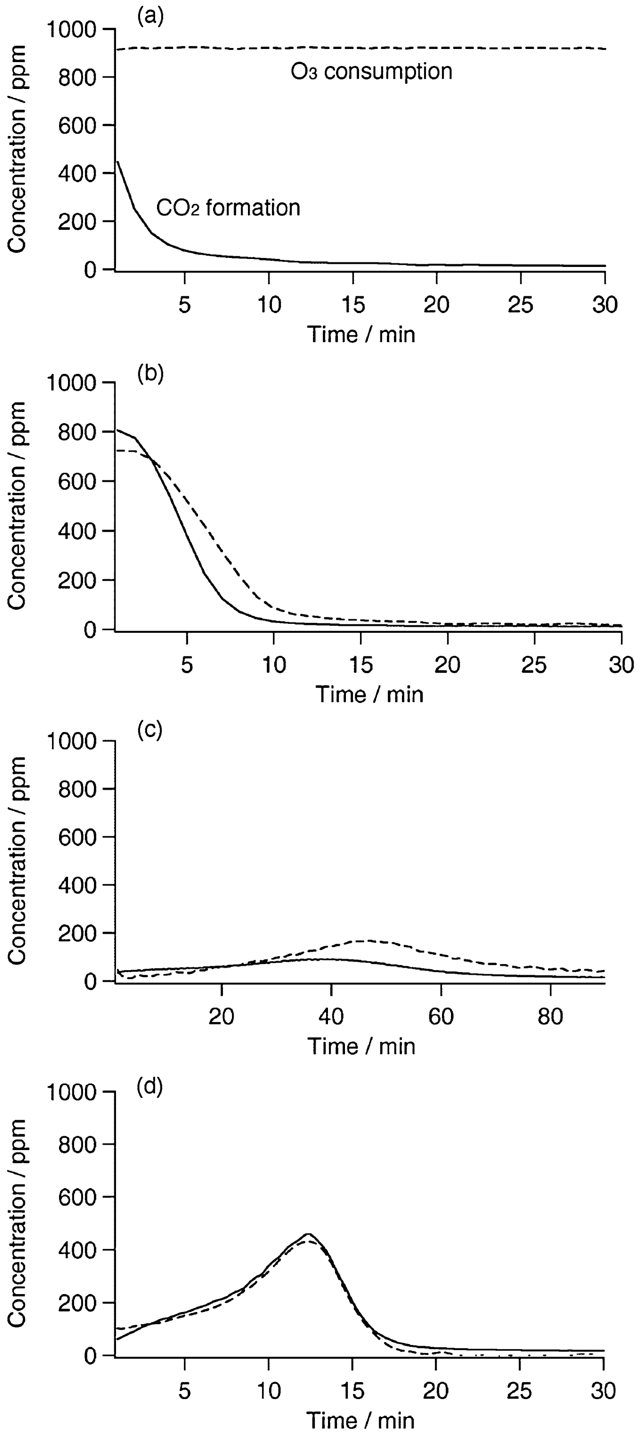

Fig. 5. Time course for oxidation of formic acid and surface formates on 5 wt%-MnO_x/γ-Al_2O_3 and γ-Al_2O_3 with ozone. (a) MnO_x/γ-Al_2O_3 without water vapor, (b) MnO_x/γ-Al_2O_3 with water vapor, (c) γ-Al_2O_3 without water vapor, and (d) γ-Al_2O_3 with water vapor. Solid line: concentration of CO_2 formed; dashed line: concentration of O_3 consumed. Catalyst 0.10 g, O_3 920 ppm, O_2 50%, water vapor 1.0%, N_2 balance.

It has been reported that ozone can oxidize various types of organic compounds [1]. However, ozone itself is not the active species for benzene oxidation under our conditions, because benzene oxidation did not proceed with the support materials Al_2O_3, SiO_2, ZrO_2, and TiO_2, which were inactive for ozone decomposition [6]. Thus, Mn is crucial to obtaining catalytic activity for benzene oxidation, suggesting that the oxygen species formed in ozone decomposition are the active species for benzene oxidation. According to the studies by Oyama et al., ozone is decomposed to O_2 on manganese oxide catalysts as expressed by Eqs. (1)–(3), where $*$ denotes the surface site on the catalyst [5–7,12–14]:

$$O_3 + {}^* \rightarrow O_2 + O^*, \quad (1)$$

$$O^* + O_3 \rightarrow O_2 + O_2^*, \quad (2)$$

$$O_2^* \rightarrow O_2 + {}^*. \quad (3)$$

It is likely that the oxygen species formed in this process are involved in benzene oxidation.

The oxygen species formed in ozone decomposition cannot completely oxidize the surface formates on the MnO_x/γ-Al_2O_3 catalyst. The surface species remained on the catalyst after a prolonged ozone feed, when the oxygen species were continuously supplied by ozone decomposition (Fig. 5a). In contrast, the surface formates were completely oxidized by ozone feed with water vapor, although water vapor inhibits ozone decomposition on the catalyst [11]. This indicates that not only the oxygen species formed in ozone decomposition, but also other species, are active for the oxidation of surface formates.

Here the question is raised as to what kind of oxygen species takes part in the oxidation reaction. The oxidation profiles for the surface formates on pure alumina support provide a clue as to the reaction mechanism, because the alumina support used in this study was inactive for ozone decomposition, preventing the oxidation of surface formates by the oxygen species formed in ozone decomposition. Fig. 5c shows the profile obtained when ozone was contacted with the alumina support without water vapor, on which formic acid was previously adsorbed. Although an induction period was observed, the surface formates were gradually oxidized to CO_2 along with ozone consumption, revealing that ozone itself directly oxidized the surface formates. The oxidation of the surface formates was also promoted by addition of water vapor (Fig. 5d). In this case, the profile of CO_2 formation was followed by that of ozone consumption, and the amount of CO_2 formed was almost the same as that of ozone consumption, indicating that chemical equation can be expressed as follows:

$$HCOOH + O_3 \rightarrow CO_2 + O_2 + H_2O. \quad (4)$$

Water vapor may promote the direct reaction of ozone with the surface species. However, further investigation is needed to clarify the detailed mechanism of the reaction.

The MnO_x/γ-Al_2O_3 catalyst plays important roles in benzene oxidation with ozone in the presence of water vapor. The catalyst decomposes ozone to form oxygen species that are active for benzene oxidation. Benzene is oxidized on the catalyst to form CO_x and oxygen-containing byproducts, including formic acid and surface formates. The catalyst also acts as the adsorption site for water vapor and ozone to further oxidize the byproducts to CO_x. We have reported that manganese oxides are indispensable for ozone decomposition, the key step in benzene oxidation [11]. These oxides also promote oxidation of byproducts on the catalyst in the presence of water vapor.

4. Conclusion

In this paper, we have shown that water vapor plays an important role in benzene oxidation with ozone on MnO_x/γ-Al_2O_3 catalyst. Water vapor suppressed catalyst deactivation by promoting the oxidation of organic byproducts on the catalyst surface. In particular, the accumulation of formic acid and strongly bound surface species was inhibited. The strongly bound surface formates, one of the major byproducts on the catalyst, were readily oxidized to CO_2 with water vapor. Our results suggest that not only oxygen species formed in ozone decomposition, but also ozone itself, are active for the oxidation of surface formates.

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