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Article

Ozone catalytic oxidation of benzene over AgMn/HZSM-5 catalysts at room temperature: Effects of Mn loading and water content

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ARTICLE INFO

Article history:

Received 22 January 2014

Accepted 3 March 2014

Published 20 September 2014

Keywords:

Catalytic oxidation of benzene

Ozone

AgMn/HZSM-5 catalyst

Mn loading

Water vapor

ABSTRACT

The effects of Mn loading and water content on AgMn/HZSM-5 (AgMn/HZ) catalysts were investigated in the ozone catalytic oxidation (OZCO) of benzene in a continuous air flow at room temperature. The catalytic activity is closely related to the Mn loading, and the AgMn/HZ catalyst with 2.4 wt% Mn (AgMn/HZ(2.4)) had the highest activity and stability in benzene oxidation as a result of its large surface area and high MnO_x dispersion. Temperature-programmed desorption of the used catalysts demonstrated that 2.4 wt% was also the optimal Mn loading for suppressing the accumulation of benzene and HCOOH over the catalyst surface after benzene oxidation. For AgMn/HZ catalysts with Mn loadings ≤ 2.4 wt%, O₃ decomposition to active oxygen species (O*) plays the most important role in benzene oxidation; however, benzene activation is the crucial step for benzene oxidation by O₃ over AgMn/HZ catalysts with Mn loadings > 2.4 wt%. The AgMn/HZ(2.4) catalyst was then used to perform OZCO of benzene in a humid stream. Compared with dry gas, water vapor greatly enhanced the activity and stability of the AgMn/HZ(2.4) catalyst, and 0.1–0.2 vol% was the optimal water content for benzene oxidation.

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1. Introduction

Benzene, a typical volatile organic compound (VOC), has mutagenic, teratogenic, and carcinogenic activities and is known to contribute to poor air quality and to impose serious threats to human health. It is therefore important to strip flues of residual benzene to ensure safety [1].

O₃, which is a strong oxidant, has been widely used for the purification of gaseous and aqueous wastes [2–5]. O₃ has attracted extensive attention and is now being widely investigated in the catalytic removal of toxic substances from polluted gases because its performance in such reactions is superior to those of O₂. It should be noted that there are two factors that regulate catalytic processes: low reaction temperatures and high activities [6]. A Bulgarian group showed that using O₃ as

the oxidant guaranteed high catalytic activity and enabled the reaction to proceed at low temperatures [7–10]. Specifically, the data obtained using manganese oxide as the catalyst demonstrated that the activation energy in catalytic benzene oxidation using O₃ was three times lower than that using O₂ [7].

Several excellent reports on ozone catalytic oxidation (OZCO) of gaseous benzene have been published. Einaga and coworkers [11] mainly investigated the catalytic activities of manganese oxides supported on Al₂O₃ in benzene oxidation with O₃ and clarified the relationship between the behavior of benzene, CO_x, and O₃. They also studied the effects of the catalyst supports (SiO₂, Al₂O₃, TiO₂, and ZrO₂) on benzene oxidation by O₃ over supported Mn catalysts in detail and found a good positive linear correlation between the reaction rate and the catalyst surface area [12]. The activities in benzene oxidation of

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This work was supported by the National Natural Science Foundation of China (U1201231, 11175036).

DOI: 10.1016/S1872-2067(14)60070-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 9, September 2014

various catalyst components (Mn, Ag, Co, Ni, Fe, and Cu) on Al_2O_3 have been studied, and it was found that an Fe sample had the highest activity for O_3 decomposition in the absence of organic substrates, and an Mn sample was most suitable for benzene oxidation and O_3 decomposition in the presence of organic compounds [13]. The effects of catalyst loading were also studied, and it was found that lower Mn loadings were more favorable in OZCO of benzene because of the higher dispersion of Mn [14]. Mehandjiev and coworkers [15,16] prepared several types of highly active samples such as ilmenite-type NiMnO_3 , Al_2O_3 -supported Cu-Cr and Co-Cr [8], and furnace-slag-supported Cu, Co, Mn, and Ni [9] and investigated their activities in O_3 decomposition and benzene oxidation. It has also been established that the oxygen species formed during O_3 decomposition at the active sites contribute greatly to accelerating the reaction rate and decreasing the reaction temperature [8,17].

As mentioned above, OZCO generally proceeds at lower temperatures compared with conventional catalytic oxidation processes, but the catalysts usually suffer from gradual deactivation because of the accumulation of less-reactive byproducts on the catalyst surface [11,13,18–21]; catalyst stability under mild conditions is therefore a problem. Catalyst heating is one of the methods frequently used to overcome this problem [19], but this consumes large amounts of energy. It has been demonstrated that the addition of water vapor can improve the catalytic activity and suppress catalyst deactivation by inhibiting the accumulation of organic intermediates on catalysts [22,23]. In addition, we reported that about 100% of formaldehyde could be oxidized to CO_2 by O_3 in humid air streams [24].

Manganese oxide has frequently been used as one of the catalytically active constituents for OZCO of benzene and O_3 decomposition [7,11,23,25–27] because of its excellent O_3 -decomposing ability and high oxidation rate. It was also clearly shown that an Al_2O_3 -supported Ag catalyst was another potential candidate for this process because it promoted oxidation of intermediates on the catalyst [18].

In our previous study, we investigated the catalytic oxidation of adsorbed benzene by O_3 over AgMn/HZ (HZ = HZSM-5) catalysts for the first time. We found that Ag played an important role in promoting the complete oxidation of benzene and that MnO_x addition not only facilitated O_3 decomposition but also accelerated the oxidation of benzene adsorbed on Ag sites. However, the effects of Mn loading need to be thoroughly investigated for catalyst optimization, and the optimal water content for suppressing catalyst deactivation is also an important issue.

In this study, we first investigated the effects of Mn loading on the behavior of AgMn/HZ catalysts in OZCO of benzene in a dry continuous air flow and determined the optimal Mn loading. OZCO of gaseous benzene over an AgMn/HZ catalyst with the optimal Mn loading in humid air streams with different water contents was then carried out, and the optimal water content was determined.

2. Experimental

2.1. Catalyst preparation

Ag/HZ and AgMn/HZ catalysts were prepared using an incipient wetness impregnation method. AgNO_3 and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were used as Ag and Mn precursors, respectively. The impregnated samples were stirred for 30 min, aged overnight at ambient temperature in darkness, dried at 110°C for 6 h and calcined at 450°C for 3 h. The obtained powders were grounded, tableted, crushed and sieved to 20–40 mesh. The nominal Ag loading of all the samples was fixed at 1 wt% based on our previous study, which showed that the 0.8 wt% Ag/HZ catalyst gave an excellent performance in plasma catalytic oxidation of stored benzene [28,29]. For the AgMn/HZ catalysts, the Mn loading was varied and seven samples were prepared.

2.2. Catalyst characterization

The elemental compositions of Ag and Mn in the catalysts were analyzed using inductively coupled plasma-atomic emission spectroscopy (Optima 2000DV, Perkin Elmer, USA). The Ag loading of the Ag/HZ catalyst was 0.7 wt%, and the Ag and Mn loadings of the seven AgMn/HZ catalysts were 0.8 wt% and 0.8 wt%, 0.8 wt% and 1.7 wt%, 0.7 wt% and 2.4 wt%, 0.7 wt% and 3.2 wt%, 0.7 wt% and 4.3 wt%, 0.7 wt% and 5.1 wt%, and 0.7 wt% and 6.4 wt%. The AgMn/HZ catalysts were named based on the Mn loadings, i.e., AgMn/HZ(*a*) refers to a catalyst containing *a* wt% Mn. The specific surface area of the catalysts was measured using the N_2 adsorption BET method at -196°C (Autosorb-1, Quantachrome, USA). Diffuse reflectance spectra (DRS) of the catalysts were recorded in the range 200–800 nm at room temperature using a UV-vis spectrophotometer (Cary 5000, Agilent, USA). The spectra were obtained by subtraction of the HZSM-5 support spectrum from those of the Ag/HZ or AgMn/HZ catalysts. The redox behavior was evaluated by temperature-programmed reduction (TPR) using a chemisorption analyzer (Autochem II 2920, Micromeritics, USA). The sample (100 mg) was pretreated in a 50 SCCM (standard cubic centimeters per minute) dry simulated air stream at 450°C for 1 h and then cooled to room temperature in a N_2 stream. The TPR experiments were performed using 5% H_2 in Ar at a flow rate of 50 SCCM. The temperature was increased to 450°C at a heating rate of $10^\circ\text{C}/\text{min}$.

2.3. OZCO reactions

The catalytic reactions were carried out using a fixed-bed flow reactor. Figure 1 shows a schematic diagram of the experimental setup. A quartz U-tube reactor (i.d. 4 mm) containing about 53 mg of catalyst (20–40 mesh particles) was immersed in a water bath at 25°C . O_3 was generated from O_2 using a laboratory-made O_3 generator and monitored online using Fourier-transform infrared (FT-IR) spectroscopy (Nicolet-Antaris IGS Analyzer, Thermo, USA). Water vapor was carried by N_2 and O_2 flowing through a bubbler placed in a water bath at 25°C , and the water concentration was measured online using a dew point hygrometer (635-2, Testo, Germany).

Fig. 1. Schematic diagram of experimental setup.

The desired water content was adjusted by varying the carrier gas flow rates. Prior to the reactions, all catalysts were pretreated in a dry simulated air stream at 450 °C for 1 h and then cooled to room temperature in a N₂ stream. The reaction gas mixture, dry or humid simulated air containing benzene and O₃, was flowed through the catalyst bed at a total flow rate of 250 SCCM, corresponding to a gas hourly space velocity of 170609 h⁻¹. The initial benzene concentration was measured based on its conversion to CO₂ using a laboratory-made VOC-to-CO₂ converter (10% Cu/10% Mn/γ-Al₂O₃ catalyst) at 400 °C, and the concentration of CO₂ was monitored online using a CO_x analyzer [S710, Sick-Maihak, Germany] [30]. The following conditions were used for the oxidation: 862–901 mg/m³ O₃ and 143–153 mg/m³ benzene. Gas samples in the outlet were analyzed using the CO_x analyzer and FT-IR spectrometer. The catalyst deactivation rate (DR) was defined as follows:

$$\text{DR-C}_6\text{H}_6 \text{ (}\mu\text{mol g}^{-1} \text{ min}^{-2}\text{)} = \left[\frac{C_{\text{in}}^{\text{C}_6\text{H}_6} \times (X_{\text{C}_6\text{H}_6}^0 - X_{\text{TOS}=60 \text{ min}}^{\text{C}_6\text{H}_6})}{F_1 / (V_m \times m_{\text{cat}} \times 60)} \right] \quad (1)$$

$$\text{DR-O}_3 \text{ (}\mu\text{mol g}^{-1} \text{ min}^{-2}\text{)} = \left[\frac{C_{\text{in}}^{\text{O}_3} \times (X_{\text{O}_3}^0 - X_{\text{TOS}=60 \text{ min}}^{\text{O}_3})}{F_1 / (V_m \times m_{\text{cat}} \times 60)} \right] \quad (2)$$

where $C_{\text{in}}^{\text{C}_6\text{H}_6}$ and $C_{\text{in}}^{\text{O}_3}$ are the benzene and O₃ concentrations (ppm), respectively, in the reactor inlet gas; $C_{\text{out}}^{\text{C}_6\text{H}_6}$, $C_{\text{out}}^{\text{O}_3}$, $C_{\text{out}}^{\text{CO}_2}$, $C_{\text{out}}^{\text{CO}}$, and $C_{\text{out}}^{\text{HCOOH}}$ are the benzene, O₃, CO₂, CO, and HCOOH concentrations (ppm), respectively, in the reactor outlet gas; $X_{\text{C}_6\text{H}_6}^0$ and $X_{\text{O}_3}^0$ are the benzene and O₃ conversions (%), respectively, when the OZCO reaction starts; $X_{\text{TOS}=60 \text{ min}}^{\text{C}_6\text{H}_6}$ and $X_{\text{TOS}=60 \text{ min}}^{\text{O}_3}$ are the benzene and O₃ conversions (%), respectively, at time-on-stream (TOS) = 60 min; V_m is the molar volume (22400 ml/mol), m_{cat} is the mass of catalyst (g), and F_1 is the total flow rate (SCCM) during OZCO.

CO_x and HCOOH were the only carbon-containing products detected by FT-IR spectroscopy in all cases, so the carbon balance for OZCO ($B^{\text{OZCO}}_{\text{C}}$, %) is defined as follows:

$$B^{\text{OZCO}}_{\text{C}} = S_{\text{CO}_2} + S_{\text{CO}} + S_{\text{HCOOH}} \quad (3)$$

where S_{CO_2} , S_{CO} , and S_{HCOOH} are the selectivities (%) of CO₂, CO, and HCOOH, respectively.

Neither benzene oxidation nor O₃ decomposition was observed without a catalyst; therefore homogeneous gaseous reactions of benzene with O₃ can be neglected.

2.4. Temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO) of used catalysts

TPD and TPO analyses were performed on the catalysts that had been used in the OZCO process. The reactor system was the same as that described above. After OZCO, the reaction gas was switched to N₂ (for TPD) or dry simulated air (for TPO), with a flow rate of 90 SCCM. After purging for over 40 min at room temperature, the catalyst was heated at a rate of 10 °C/min to 450 °C and then the temperature was kept constant for 30 min. The products in the effluent gas were detected by the CO_x analyzer and FT-IR spectrometer. The percentages of desorbed benzene and HCOOH detected by TPD were defined as follows:

$$\text{Benzene desorbed (\%)} = \left[\frac{\int_{t_1}^{t_2} F_2 C_{\text{C}_6\text{H}_6}^{\text{des}} dt}{\int_0^{120} F_1 C_{\text{in}}^{\text{C}_6\text{H}_6} X_{\text{C}_6\text{H}_6}^{\text{des}} dt} \right] \times 100\% \quad (4)$$

$$\text{HCOOH desorbed (\%)} = \left[\frac{\int_{t_1}^{t_2} F_2 C_{\text{HCOOH}}^{\text{des}} dt}{\int_0^{120} F_1 C_{\text{in}}^{\text{C}_6\text{H}_6} X_{\text{C}_6\text{H}_6}^{\text{des}} dt} \right] \times 100\% \quad (5)$$

where $C_{\text{C}_6\text{H}_6}^{\text{des}}$ and $C_{\text{HCOOH}}^{\text{des}}$ are the benzene and HCOOH concentrations (ppm) evolved at t min in the TPD process, respectively; $X_{\text{C}_6\text{H}_6}^{\text{des}}$ is the benzene conversion (%) at TOS = t min during OZCO; F_2 , t_1 , and t_2 are the total flow rate (SCCM), and any moment ($t_1 < t_2$) (min), respectively, during TPD.

2.5. O₃ decomposition measurements without benzene

O₃ decomposition in the absence of benzene was also carried out over the catalysts in the reactor system described above. O₃/O₂ at 100 SCCM was flowed through the reactor, containing about 27 mg of catalyst, and the inlet O₃ concentration was in the range 862–921 mg/m³. The outlet O₃ was quantified using FT-IR spectroscopy.

3. Results and discussion

3.1. Physicochemical properties of catalysts

The BET surface areas were 341, 340, 326, 336, 299, 268, 278, and 274 m²/g, respectively, for Ag/HZ, AgMn/HZ(0.8), AgMn/HZ(1.7), AgMn/HZ(2.4), AgMn/HZ(3.2), AgMn/HZ(4.3), AgMn/HZ(5.1), and AgMn/HZ(6.4). The Ag loading did not decrease the surface area of Ag/HZ compared with the bare HZ support (341 m²/g) [28,29] because the loading was very low. For the AgMn/HZ catalysts, almost no changes were observed in the surface area when the Mn loading was ≤ 2.4 wt%. However, further increasing the Mn loading to 3.2 wt% significantly decreased the AgMn/HZ surface area to 299 m²/g; this could be ascribed to the formation of large MnO_x particles over the catalyst surface, which would block the pores of the HZ support [31]. When the Mn loading was ≥ 4.3 wt%, the surface areas remained nearly unchanged at around 270 m²/g. Based on the BET data, it can be deduced that the 2.4 wt% Mn loading was a turning point, above which large MnO_x particles were formed, resulting in observable decreases in the surface areas of the AgMn/HZ catalysts.

Figure 2 shows the UV-vis DRS of the Ag/HZ and AgMn/HZ catalysts. UV-vis DRS can provide information on the metal oxidation state and its chemical environment. The Ag/HZ sample exhibited two bands centered at 264 and 413 nm, assigned to Ag clusters and Ag⁰, respectively [32,33]. All the Mn-containing samples exhibited two bands at 279 and 499 nm, char-

Fig. 2. UV-vis DRS of Ag/HZ and AgMn/HZ catalysts.

acteristic of Mn^{3+} and Mn^{4+} , respectively [31]. The UV-vis DRS data were consistent with the previous results that Ag was present in the metallic state in the Ag/HZ and AgMn/HZ catalysts, and Mn in the AgMn/HZ catalysts was present as Mn^{3+} and Mn^{4+} .

The H_2 -TPR results are shown in Fig. 3. No reduction peak was observed for Ag/HZ (data not shown), and this result is in good accordance with the UV-vis DRS data, which showed that Ag was present in the metallic state on the zeolite. For all the AgMn/HZ catalysts, two reduction peaks were observed, ascribable to the sequential reduction of MnO_2 to Mn_2O_3 and Mn_2O_3 to MnO , respectively. Because Ag was present in the metallic state, Ag could not be reduced. As shown in Fig. 3, the low-temperature reduction peaks were centered at 158, 157, and 156 °C for the AgMn/HZ(0.8), AgMn/HZ(1.7), and AgMn/HZ(2.4) catalysts, respectively, and at 195, 190, 198, and 194 °C for the AgMn/HZ(3.2), AgMn/HZ(4.3), AgMn/HZ(5.1), and AgMn/HZ(6.4) catalysts, respectively. The high-temperature reduction peaks were located at 217, 211, and 226 °C for the AgMn/HZ(0.8), AgMn/HZ(1.7), and AgMn/HZ(2.4) catalysts, respectively, and at 271, 268, 274, and 285 °C for the AgMn/HZ(3.2), AgMn/HZ(4.3), AgMn/HZ(5.1), and AgMn/HZ(6.4) catalysts, respectively. The reduction temperatures shifted to higher temperatures when the Mn loadings were

Fig. 3. H_2 -TPR profiles of the AgMn/HZ catalysts. Conditions: 100 mg of catalyst, 50 SCCM of 5% H_2/Ar , 10 °C/min.

higher than 2.4 wt%. This indicates that the AgMn/HZ catalysts with Mn loadings ≤ 2.4 wt% were more easily reduced than the AgMn/HZ catalysts with Mn loadings > 2.4 wt%. Moreover, it has been reported that the reduction temperature for a given metal oxide depends on the dispersion of the metal oxide, and highly dispersed metal oxides can be reduced at lower temperatures than their aggregated counterparts [27,34,35]. It is therefore rational to deduce that large MnO_x particles were formed on the AgMn/HZ catalysts when the Mn loadings were higher than 2.4 wt%, which is in good agreement with the BET data.

Based on the sequential reduction steps $\text{MnO}_2 + \frac{1}{2}\text{H}_2 \rightarrow \frac{1}{2}\text{Mn}_2\text{O}_3$ and $\frac{1}{2}\text{Mn}_2\text{O}_3 + \frac{1}{2}\text{H}_2 \rightarrow \text{MnO}$, and the assumption of complete reduction, $\text{Mn}^{3+}/\text{Mn}^{4+}$ atomic ratios of 9.5, 0.5, 3.3, 0.3, 1.0, 0.5, and 0.5 were calculated for the AgMn/HZ(0.8), AgMn/HZ(1.7), AgMn/HZ(2.4), AgMn/HZ(3.2), AgMn/HZ(4.3), AgMn/HZ(5.1), and AgMn/HZ(6.4) catalysts, respectively.

3.2. OZCO of benzene in dry continuous flow

The catalytic performance of the Ag/HZ and AgMn/HZ catalysts was evaluated in the OZCO of gaseous benzene; the results are presented in Fig. 4. Figure 4(a) and (b) show the variations in benzene conversion and O_3 decomposition with Mn loading at different TOS during benzene oxidation in dry air on the Ag/HZ and AgMn/HZ catalysts. Both benzene conversion and O_3 decomposition declined with increasing TOS, indicating catalyst deactivation during benzene oxidation. It was found that the addition of MnO_x to Ag/HZ significantly influenced the catalytic activity, and the catalytic performance of AgMn/HZ strongly depended on the Mn loading. Specifically, the benzene conversion and O_3 decomposition increased with increasing Mn loading when the loading was ≤ 2.4 wt% because of the increasing O_3 decomposition activities of the catalysts as a result of the high O_3 decomposition activity of MnO_x . The AgMn/HZ(2.4) catalyst showed the best benzene conversion and O_3 decomposition. However, when the Mn loading was higher than 2.4 wt%, the benzene conversion and O_3 decomposition decreased with increasing Mn loading; this is ascribed to a decrease in the surface area and poor MnO_x dispersion, as shown by the BET and H_2 -TPR results. Figure 4(c) shows the CO_x selectivity versus Mn loading during benzene oxidation. It can be seen from Fig. 4(c) that the CO_2 selectivities of the AgMn/HZ catalysts were higher than that of Ag/HZ. This is because MnO_x has a high O_3 decomposition activity, which might promote complete oxidation of benzene. Moreover, the CO_2 selectivity did not change much with Mn loading when the Mn loading was higher than 0.8 wt% during the first 60 min, but after 60 min the CO_2 selectivities of the AgMn/HZ catalysts with Mn loadings > 3.2 wt% became higher than those of the catalysts with Mn loadings ≤ 3.2 wt%; this is a result of the fast drop in benzene conversion for the AgMn/HZ catalysts with Mn loadings > 3.2 wt%, as shown in Fig. 4(a). It should also be noted that for the Ag/HZ and AgMn/HZ catalysts, the CO_2 selectivity gradually increased with increasing TOS. This is because the CO_2 concentration did not decrease as much (data not shown) as the benzene conversion did with increasing TOS

Fig. 4. Dependences of benzene conversion (a), O₃ decomposition (b), and CO_x selectivity (c) on Mn loading at different TOS during OZCO of benzene in dry continuous air flow over Ag/HZ and AgMn/HZ catalysts; (d) HCOOH selectivity versus TOS during OZCO of benzene in dry continuous air flow over Ag/HZ catalyst. Conditions: 53 mg of catalyst, 143–153 mg/m³ benzene in dry simulated air at 250 SCCM, 862–901 mg/m³ O₃.

during OZCO. Furthermore, the addition of MnO_x slightly reduced the CO selectivity, but there were no obvious differences among the AgMn/HZ catalysts with different Mn loadings. The AgMn/HZ(2.4) catalyst showed the best benzene conversion and O₃ decomposition; therefore we also carried out benzene oxidation over Mn/HZ with 2.3 wt% Mn (Mn/HZ(2.3)) for comparison. The benzene conversion and O₃ decomposition at TOS = 60 min for Mn/HZ(2.3) were about 70% and 86% (data not shown), respectively, which were inferior to those for AgMn/HZ(2.4), with 75% benzene conversion. However, more CO was formed over the Mn/HZ(2.3) catalyst and about 12% CO selectivity was achieved at TOS = 60 min (data not shown), which means that the addition of Ag promotes complete oxidation of benzene. The addition of Ag did not greatly affect the CO₂ selectivity, so, in this regard, the Ag component also played an important role in benzene oxidation. A small amount of HCOOH was detected on the Ag/HZ catalyst, and the HCOOH selectivity was plotted against TOS, as shown in Fig. 4(d). No HCOOH was found in the gaseous phase when the AgMn/HZ catalysts were used. The TPD results (discussed later) showed that HCOOH was also formed over the AgMn/HZ catalysts, but the amount was less than that formed over the Ag/HZ catalyst, so HCOOH only accumulated as a byproduct on the AgMn/HZ catalyst surfaces during OZCO. If it is assumed that the OZCO of

benzene proceeded by the steps benzene oxidation to HCOOH, which is then oxidized to CO_x and water, MnO_x could promote the oxidation of HCOOH to CO_x and water.

As mentioned before, the catalysts suffered deactivation during OZCO. The dependence of the catalyst deactivation rate on Mn loading is shown in Fig. 5 to elucidate the effect of Mn loading on catalyst deactivation. The DR-C₆H₆ curve was para-

Fig. 5. Effect of Mn loading on catalyst deactivation rate during OZCO of benzene in dry continuous air flow.

bolic, with a minimum at 2.4 wt% Mn; this catalyst also showed the lowest DR-O₃. A comparison of these two curves gave interesting results. Specifically, the DR-C₆H₆ and DR-O₃ curves showed the same trend up to an Mn loading of 2.4 wt%, but after that point DR-O₃ did not change as much with Mn loading as DR-C₆H₆ did. A plausible explanation is as follows. When the Mn loading was ≤ 2.4 wt%, O₃ decomposition to active oxygen species (O*) was the key step in determining the benzene conversion, and higher benzene conversions were related to better O₃ decomposition. It can be seen from Fig. 4(a) and (b) that both benzene conversion and O₃ decomposition increased with increasing Mn loading when the Mn loading was ≤ 2.4 wt%. The catalyst stability during benzene conversion therefore depended on the O₃ decomposition when the Mn loading was ≤ 2.4 wt%. However, large MnO_x particles were probably formed when the Mn loading was higher than 2.4 wt%, which would result in coverage of Ag sites. As revealed previously, Ag was responsible for benzene activation and O₃ was mainly decomposed on MnO_x to active oxygen species, which could then oxidize benzene. The coverage of Ag would hinder benzene activation. So, the higher the Mn loading was, the faster the DR-C₆H₆ was. It is therefore reasonable to deduce that when the Mn loading was ≤ 2.4 wt%, O₃ decomposition to O* played the most important role in benzene oxidation, whereas benzene activation was the crucial step for benzene oxidation by O₃ when the Mn loading was higher than 2.4 wt%.

Based on the above results, it is reasonable to suggest that the AgMn/HZ(2.4) catalyst has high activity and stability during OZCO of benzene and is promising for benzene removal.

The $B_{\text{OZCO}}^{\text{OZCO}}$ values for Ag/HZ and AgMn/HZ(2.4) are compared in Fig. 6. The $B_{\text{OZCO}}^{\text{OZCO}}$ of AgMn/HZ(2.4) was higher than that of Ag/HZ during the entire reaction, but neither of them reached 100%. The addition of MnO_x facilitated benzene oxidation, and the imperfect $B_{\text{OZCO}}^{\text{OZCO}}$ showed the formation of organic byproducts on the catalyst surface, and the build-up of byproducts was the main cause of catalyst deactivation [11].

The TPO profiles of the used AgMn/HZ(2.4) catalyst are shown in Fig. 7. In addition to desorbed benzene and HCOOH (Fig. 7(a)), CO₂ and CO were formed as primary products. Two peaks were observed, for the formation of CO₂ and CO (Fig.

Fig. 6. $B_{\text{OZCO}}^{\text{OZCO}}$ values for Ag/HZ and AgMn/HZ(2.4) catalysts during OZCO of benzene in dry continuous air flow.

7(b)). The peaks at low temperatures corresponded to the desorption of CO₂ and CO formed in OZCO; the peaks at higher temperatures were assigned to oxidation of residual benzene and intermediate products such as formates and carboxylates. The TPO results confirm that the $B_{\text{OZCO}}^{\text{OZCO}}$ was imperfect because of residual benzene or its derivatives on the catalysts after OZCO of benzene.

3.3. TPD investigation of surface species after OZCO of gaseous benzene

To identify the surface species present after OZCO, TPD investigations were carried out on the used catalysts after OZCO of benzene. Figure 8 shows the TPD results for the used Ag/HZ and AgMn/HZ catalysts. Two benzene evolution peaks were observed for the Ag/HZ and AgMn/HZ catalysts (Fig. 8(a)). The low-temperature peaks correspond to desorption of benzene from the HZ support, and the high-temperature peaks are assigned to desorption of benzene from Ag, as discovered by our previous study. The benzene desorption was plotted against Mn loading for quantification; the results are shown in Fig. 8(c). The benzene desorption did not vary much at high temperatures (Fig. 8(c)). However, the benzene desorption at low temperatures decreased significantly from Ag/HZ to AgMn/HZ(2.4)

Fig. 7. TPO profiles of used AgMn/HZ(2.4) catalyst after OZCO for 120 min. (a) Benzene and HCOOH concentrations; (b) CO_x concentration. TPO conditions: 90 SCCM of dry simulated air, 10 °C/min.

Fig. 8. TPD profiles of used catalysts after OZCO of benzene for 120 min in dry continuous air flow. (a) Benzene concentration; (b) HCOOH concentration; (c) Dependence of benzene desorption on Mn loading; (d) Dependence of HCOOH desorption on Mn loading. TPD conditions: 90 SCCM of N_2 , 10 $^{\circ}C/min$.

and then remained almost constant with increasing Mn loading. In addition to benzene, HCOOH was detected during TPD, and the time courses for HCOOH concentration are shown in Fig. 8(b). HCOOH was evolved as a result of desorption of HCOOH formed during OZCO. Quantification of desorbed HCOOH was also carried out, and the results are displayed in Fig. 8(d). The trend in the dependence of desorbed HCOOH on Mn loading was the same as that for the dependence of desorbed benzene on Mn loading. The TPD results reveal that 2.4 wt% is the minimum Mn loading for suppressing the accumulation of benzene and HCOOH on the catalyst surface during benzene oxidation.

3.4. O_3 decomposition without benzene

Figure 9(a) shows the time profiles for O_3 decomposition in the absence of benzene over the Ag/HZ and AgMn/HZ catalysts. The decomposition behavior was very different from that for O_3 decomposition with benzene (Fig. 4(b)); this might be caused by the different reaction atmospheres. It can be seen from Fig. 9(a) that the AgMn/HZ catalysts performed better than the Ag/HZ catalyst; this can be ascribed to the very high activities of manganese oxides in O_3 decomposition [11,19,20,36–38]. For AgMn/HZ catalysts with different Mn loadings, the O_3 decomposition did not change regularly with

Mn loading. However, if the mechanism of O_3 decomposition is taken into consideration, a linear correlation between O_3 decomposition and Mn^{3+} content (wt%) is found. O_3 decomposition is a redox process, and Oyama and coworkers [39] have reported that O_3 decomposition on MnO_x/Al_2O_3 catalysts proceeded by electron transfer from Mn sites to O_3 , and Mn was reduced by desorption of oxygen species. Based on this assumption, it is reasonable to suppose that MnO_x with low Mn valence is favorable for O_3 decomposition. Based on the Mn^{3+}/Mn^{4+} atomic ratios obtained in H_2 -TPR experiments, the Mn loading, the mass of catalyst used, the Mn^{3+} content for each AgMn/HZ catalyst could therefore be calculated. Figure 9(b) shows the effects of the Mn^{3+} contents of the AgMn/HZ catalysts on O_3 decomposition at TOS = 120 min. A good linear relationship between O_3 decomposition and Mn^{3+} content was observed. These findings show that the Mn^{3+} content is the key parameter in determining the O_3 decomposition activities of the AgMn/HZ catalysts, and that AgMn/HZ catalysts with high Mn^{3+} contents are effective for O_3 decomposition. Similar results were also obtained by Rezaei et al. [20], who found that the lower oxidation states of Mn were more favorable in O_3 decomposition. It should be specifically pointed out that although the AgMn/HZ(4.3) catalyst gave the best O_3 decomposition without benzene, it did not show the highest benzene conversion during OZCO (Fig. 4(a)); this was a result of its poor

Fig. 9. (a) Time courses for O_3 decomposition without benzene over Ag/HZ and AgMn/HZ catalysts; (b) Effect of Mn^{3+} content on O_3 decomposition at TOS = 120 min. O_3 decomposition conditions: 27 mg of catalyst, 100 SCCM of O_3/O_2 , and 862–921 mg/m^3 O_3 . Numbers in (b) represent the Mn loadings (wt%) of AgMn/HZ catalysts.

Fig. 10. Effects of water content on benzene conversion (a), CO_x selectivity (c), and O_3 decomposition (d) at different TOS and dependence of catalyst deactivation rate on water content (b) for OZCO of benzene in humid continuous air flow over AgMn/HZ(2.4) catalyst. OZCO conditions: 53 mg of catalyst, 143–153 mg/m^3 benzene in dry simulated air at 250 SCCM, and 862–901 mg/m^3 O_3 .

benzene activation ability because benzene activation was crucial when the Mn loading was higher than 2.4 wt%.

3.5. Effect of water vapor on OZCO over AgMn/HZ(2.4) catalyst

The above results show that the AgMn/HZ(2.4) catalyst is promising for benzene oxidation using O_3 . However, the pres-

ence of water vapor is inevitable under real conditions. The effects of water vapor over the AgMn/HZ(2.4) catalyst for five water contents, i.e., 0.1, 0.2, 0.4, 0.8, and 1.5 vol%, were investigated.

Figure 10(a) shows the effect of water content on benzene conversion over the AgMn/HZ(2.4) catalyst. Compared with a dry air stream, water vapor greatly enhanced the catalytic ac-

tivity. Figure 10(a) also shows that 0.1–0.2 vol% water in the reaction gas resulted in higher activity, but further increases in the water content gradually decreased the catalytic activity, as a result of blockage of the active catalytic sites by excess water molecules. Figure 10(b) shows the dependence of DR-C₆H₆ on the water content. Water vapor significantly improved the catalyst stability, and 0.1–0.2 vol% water gave the best stability. Several authors have reported positive effects of water vapor on OZCO [22–24,40], and these findings indicate that water vapor could suppress catalyst deactivation by inhibiting the build-up of organic byproducts on the catalyst surface. The CO₂ selectivity (Fig. 10(c)) was also promoted by water addition when the water contents were ≤ 0.8 vol%, and similar CO₂ selectivities were obtained when the water contents were ≤ 0.4 vol%. When the water content was increased to 1.5 vol%, the CO₂ selectivity dropped below that in a dry stream. It should be noted that during reaction for 90–120 min, the CO₂ selectivity in a dry air stream became higher than those in humid streams. This is because in a dry stream the benzene conversion decreased sharply with increasing TOS, as shown in Fig. 10(a), but the CO₂ concentration did not decrease much (data not shown). Although water vapor has a clear effect on CO₂ selectivity, the CO selectivity was almost the same in dry and humid streams (Fig. 10(c)). Figure 10(d) shows the variations in O₃ decomposition with Mn loading at different TOS over the AgMn/HZ(2.4) catalyst in dry and humid air streams. Different water contents affected O₃ decomposition to different extents. When 0.1–0.4 vol% of water was added, the decomposition behavior was similar to that in a dry air stream, but the percentage of O₃ decomposition was much lower in the cases of 0.8 vol% and 1.5 vol% water. Water addition did not promote O₃ decomposition, so why did water vapor enhance benzene removal (Fig. 10(a))? There are two possible reasons. One is that the formation of byproducts on the catalyst surface was crucial for benzene oxidation with O₃ [27]. It is therefore likely that suppression of

the formation of organic byproducts by water vapor played an important role in benzene oxidation in a humid stream. The other is that more-active oxygen species (such as hydroxyl radicals) were formed on the catalyst surface in a humid stream [24], and this would promote benzene oxidation.

4. Conclusions

The effects of Mn loading and water content on OZCO of benzene over AgMn/HZ catalysts were studied in a continuous air flow. The addition of MnO_x not only enhanced benzene conversion and O₃ decomposition compared with those achieved using Ag/HZ but also increased the CO₂ selectivity. The AgMn/HZ catalyst with a 2.4 wt% Mn loading had the highest activity and stability in benzene oxidation, but further increases in the Mn loading decreased the catalytic activity and stability because of the decreased surface area, poor MnO_x dispersion, and the coverage of Ag by MnO_x particles, which would hinder benzene activation. TPD results for the used catalysts showed that 2.4 wt% was also the optimal Mn loading for suppressing the accumulation of benzene and HCOOH on the catalyst surface after benzene oxidation. When the Mn loading was lower than 2.4 wt%, O₃ decomposition to active oxygen species (O*) played the most important role in benzene oxidation, whereas benzene activation was the crucial step for benzene oxidation by O₃ when the Mn loading was higher than 2.4 wt%. Water vapor suppressed catalyst deactivation and greatly enhanced the catalytic activity; 0.1–0.2 vol% water was the optimal water content for benzene oxidation.

References

- [1] Whysner J, Reddy M V, Ross P M, Mohan M, Lax E A. *Mutat Res*, 2004, 566: 99
- [2] Zhao D Z, Ding T Y, Li X S, Liu J L, Shi C, Zhu A M. *Chin J Catal* (赵德

Graphical Abstract

Chin. J. Catal., 2014, 35: 1465–1474 doi: 10.1016/S1872-2067(14)60070-X

Ozone catalytic oxidation of benzene over AgMn/HZSM-5 catalysts at room temperature: Effects of Mn loading and water content

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AgMn/HZSM-5 catalyst with Mn loading of 2.4 wt% has the best activity and stability. O₃ decomposition is crucial for AgMn/HZSM-5 (Mn loading ≤ 2.4 wt%), whereas benzene activation is important for AgMn/HZSM-5 (Mn loading > 2.4 wt%). Water vapor greatly enhances the OZCO reactivity and stability.

- 志, 丁天英, 李小松, 刘景林, 石川, 朱爱民. 催化学报, 2012, 33: 396
- [3] Kasprzyk-Hordern B, Ziółek M, Nawrocki J. *Appl Catal B*, 2003, 46: 639
- [4] Xiao H, Liu R P, Zhao X, Qu J H. *Chemosphere*, 2008, 72: 1006
- [5] Long L P, Zhao J G, Yang L X, Fu M L, Wu J L, Huang B C, Ye D Q. *Chin J Catal* (龙丽萍, 赵建国, 杨利娟, 付名利, 吴军良, 黄碧纯, 叶代启. 催化学报), 2011, 32: 904
- [6] Konova P, Stoyanova M, Naydenov A, Christoskova St, Mehandjiev D. *Appl Catal A*, 2006, 298: 109
- [7] Naydenov A, Mehandjiev D. *Appl Catal A*, 1993, 97: 17
- [8] Mehandjiev D, Cheshkova K, Naydenov A, Georgesku V. *React Kinet Catal Lett*, 2002, 76: 287
- [9] Dimitrova S, Ivanov G, Mehandjiev D. *Appl Catal A*, 2004, 266: 81
- [10] Stoyanova M, Konova P, Nikolov P, Naydenov A, Christoskova St, Mehandjiev D. *Chem Eng J*, 2006, 122: 41
- [11] Einaga H, Futamura S. *J Catal*, 2004, 227: 304
- [12] Einaga H, Ogata A. *J Hazard Mater*, 2009, 164: 1236
- [13] Einaga H, Futamura S. *React Kinet Catal Lett*, 2004, 81: 121
- [14] Einaga H, Harada M, Ogata A. *Catal Lett*, 2009, 129: 422
- [15] Mehandjiev D, Zhecheva E, Ivanov G, Ioncheva R. *Appl Catal A*, 1998, 167: 277
- [16] Mehandjiev D, Naydenov A, Ivanov G. *Appl Catal A*, 2001, 206: 13
- [17] Naydenov A, Stoyanova R, Mehandjiev D. *J Mol Catal A*, 1995, 98: 9
- [18] Einaga H, Ogata A. *Environ Sci Technol*, 2010, 44: 2612
- [19] Rezaei E, Soltan J. *Chem Eng J*, 2012, 198-199: 482
- [20] Rezaei E, Soltan J, Chen N. *Appl Catal B*, 2013, 136-137: 239
- [21] Rezaei E, Soltan J, Chen N, Lin J R. *Chem Eng J*, 2013, 214: 219
- [22] Einaga H, Futamura S. *J Catal*, 2006, 243: 446
- [23] Einaga H, Teraoka Y, Ogata A. *Catal Today*, 2011, 164: 571
- [24] Zhao D Z, Shi C, Li X S, Zhu A M, Jang B W L. *J Hazard Mater*, 2012, 239-240: 362
- [25] Wang M X, Zhang P Y, Li J G, Jiang C J. *Chin J Catal* (王鸣晓, 张彭义, 李金格, 姜传佳. 催化学报), 2014, 35: 335
- [26] Wang M Y, Zhu T L, Fan X. *Chin Environ Sci* (王美艳, 朱天乐, 樊星. 中国环境科学), 2009, 29: 806
- [27] Einaga H, Teraoka Y, Ogata A. *J Catal*, 2013, 305: 227
- [28] Fan H Y, Shi C, Li X S, Zhao D Z, Xu Y, Zhu A M. *J Phys D*, 2009, 42: 225105
- [29] Fan H Y, Li X S, Shi C, Zhao D Z, Liu J L, Liu Y X, Zhu A M. *Plasma Chem Plasma Process*, 2011, 31: 799
- [30] Zhao D Z, Li X S, Shi C, Fan H Y, Zhu A M. *Chem Eng Sci*, 2011, 66: 3922
- [31] Qu Z P, Bu Y B, Qin Y, Wang Y, Fu Q. *Appl Catal B*, 2013, 132-133: 353
- [32] Bogdanchikova N, Meunier F C, Avalos-Borja M, Breen J P, Pestryakov A. *Appl Catal B*, 2002, 36: 287
- [33] Shi C, Chen B B, Li X S, Crocker M, Wang Y, Zhu A M. *Chem Eng J*, 2012, 200-202: 729
- [34] Ma F T, Lou H. *Chin J Catal* (马福泰, 楼辉. 催化学报), 1984, 5: 82
- [35] Boot L A, Kerkhoffs M H J V, van der Linden B T, Jos van Dillen A, Geus J W, van Buren F R. *Appl Catal A*, 1996, 137: 69
- [36] Dhandapani B, Oyama S T. *Appl Catal B*, 1997, 11: 129
- [37] Oyama S T. *Catal Rev-Sci Eng*, 2000, 42: 279
- [38] Wang H C, Chang S H, Hung P C, Hwang J F, Chang M B. *J Hazard Mater*, 2009, 164: 1452
- [39] Radhakrishnan R, Oyama S T, Chen J G, Asakura K. *J Phys Chem B*, 2001, 105: 4245
- [40] Wang H C, Chang S H, Hung P C, Hwang J F, Chang M B. *Chemosphere*, 2008, 71: 388

AgMn/HZSM-5催化剂上室温O₃氧化脱除空气中的苯: Mn含量和水含量的影响

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摘要: 考察了Mn含量和水含量对AgMn/HZSM-5(AgMn/HZ)催化剂上室温O₃氧化(OZCO)脱除空气中苯的影响. 研究发现, Mn含量为2.4 wt%的AgMn/HZ催化剂(AgMn/HZ(2.4))具有大的比表面积和高的MnO_x分散度, OZCO活性和稳定性最高. 反应后的程序升温脱附结果表明, 2.4 wt%的Mn含量能有效抑制苯和甲酸在催化剂上的残留. 当Mn含量≤2.4 wt%时, 催化剂分解O₃的活性在苯氧化过程中占主导; 当Mn含量>2.4 wt%时, 苯的活化起主要作用. 基于AgMn/HZ(2.4)催化剂优越的反应活性和稳定性, 进一步研究了湿气流中该催化剂上苯的氧化. 与干气流相比, 水汽的加入能显著提高催化剂的反应活性和稳定性, 且以0.1–0.2 vol%水含量时最优.

关键词: 催化氧化苯; 臭氧; AgMn/HZSM-5催化剂; Mn含量; 水含量

收稿日期: 2014-01-22. 接受日期: 2014-03-03. 出版日期: 2014-09-20.

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基金来源: 国家自然科学基金(U1201231, 11175036).

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