Competitive Adsorption of O₂ and Toluene on the Surface of FeOₓ/SBA-15 Catalyst

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ABSTRACT

The adsorption of volatile organic compounds (VOCs) and O₂ on the surface of the catalyst was one of the vital progresses in the plasma-catalytic oxidation of VOCs. In this work the breakthrough curves of toluene adsorption on the 3%FeOₓ/SBA-15 were measured under the various O₂ concentrations. The results showed that the breakthrough time of toluene reduced with increasing O₂. Competitive adsorption was observed on the catalyst surface between O₂ and toluene. The catalysts adsorbed the toluene under the various O₂ concentrations were characterized by O₂ temperature-programmed desorption (O₂-TPD), and X-ray photoelectron spectroscopy (XPS). The desorption amounts of O₂ and the Fe percentage on the catalyst surface were dependent on the O₂ concentration during toluene adsorption. The experimental results of pure SBA-15 and 5%MnOₓ/SBA-15 indicated the competitive adsorption site of O₂ and toluene was FeOₓ. In situ FTIR data of toluene adsorption on the catalyst surface indicated that the adsorption state of toluene could not be impacted by the competitive adsorption of O₂, and the O₂ adsorbed on the catalyst could oxidize toluene.

Keywords: O₂ adsorption; Toluene adsorption; Competitive adsorption; Oxygen source.

INTRODUCTION

VOCs are one of the most common precursors of dust-haze (Huang et al., 2015; Vullo, 2016), and have adverse effects on the environment and human health (Sultana et al., 2015; Wu et al., 2015; Zhu et al., 2016). Consequently, considerable attention has been paid to develop methods for removing VOCs. The non-thermal plasma (NTP) combined with the catalyst technology emerged as a promising method in recent years (Lee et al., 2015; Trinh et al., 2015a, b; Stasiulaitiene et al., 2016). In this system, VOCs adsorption on the catalyst is a very important factor because VOCs residual time and reaction with active plasma species in the discharge region will be increased as a result of the catalyst appeared (Sultana et al., 2015). Many researchers observe a positive relationship between catalyst adsorption ability and VOCs degradation. As catalyst adsorption performance increase, so will get the better VOCs degradation (Lu et al., 2015; Pangilinan et al., 2016; Wang et al., 2016). O₂ as an essential for VOCs complete oxidation (Vandenbroucke et al., 2011) can be adsorbed by the catalyst (Chen et al., 2004). In this co-adsorption system, Zhang et al. (2011) reported the competitive adsorption phenomena between O₂ and toluene on the catalyst surface. Nevertheless, this phenomenon is very important to explain the VOCs removal mechanism in the system of NTP assisted catalyst. However, there is little research on this problem. Therefore, the present study was conducted to investigate the competitive adsorption between O₂ and toluene on the catalyst surface.

To explore the competitive adsorption between O₂ and toluene, 3% iron loading on SBA-15 was selected as a catalyst because it showed a good performance for toluene and O₂ adsorption (Lu et al., 2015; Zeng and Bai, 2016). The adsorption breakthrough curves of toluene were measured under the condition of various O₂ concentrations. In order to identify the adsorption site, the catalysts after the toluene adsorption in various O₂ concentrations were characterized by O₂-TPD, XPS. Moreover, in situ FTIR of toluene adsorption under different O₂ concentrations was applied to investigate the effect of O₂ adsorption on the toluene adsorption and oxidation.

EXPERIMENTAL

Catalyst Preparation

<table>
<thead>
<tr>
<th>3% FeOₓ/SBA-15 (wt. %)</th>
<th>5% MnOₓ/SBA-15 (wt. %)</th>
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catalysts were prepared via an impregnation method using SBA-15 (Nanjing XFNANO Materials Tech Co., Ltd) as support. Iron nitrate and manganese acetate ethanol solution of desired concentration were used as Fe and Mn precursors, respectively. The impregnated sample was stirred for 24 h at room temperature, and the solvent was then removed by evaporation at 60°C. The residue was dried in an oven at 120°C for 12 h, followed by calcination at 500°C for 4 h. Pure SBA-15 support was treated in the same way for comparison in this study.

Adsorption Breakthrough Curves of Toluene

Experiments of toluene adsorption were carried out at room temperature and atmospheric pressure. Toluene vapor was produced by passing dry N2 through pure liquid toluene kept in ice/water (0°C). The adsorption gas was mixed by N2 and O2, and their rates were adjusted by mass flow controllers. At last, the adsorption gas containing 100 ppm toluene passed through catalyst bed at a rate of 300 mL min⁻¹. Concentrations of toluene in the outlet gas were recorded using an online gas chromatograph (GC-2014C, Shimadzu).

O2-TPD

Initial, the catalyst adsorbed toluene in various O2 concentrations at room temperature and atmospheric pressure, until adsorption saturation. The O2-TPD performance was measured using Micromeritics AutoChem 2920 equipment. The analysis procedure was as follows: 100 mg sample was pretreated at 300°C using high-purity He (30 mL min⁻¹) for 30 min, and then cooled down to 60°C. Subsequently, the flow of O2-He mixture (5% O2 by volume) was switched on for 60 min. High-purity He was then switched on and waited until the system stabilized. Then the sample was heated up to 800°C at a rate of 10°C min⁻¹.

XPS

The catalyst adsorbed toluene in various O2 concentrations at room temperature and atmospheric pressure. Until adsorption saturation, the XPS performance was measured using an ESCALAB 250 spectrometer (Thermo Fisher Scientific, USA) equipped with a hemispherical electron analyzer, employing an Mg Kα radiation source (1253.6 eV) of 25 W. All binding energies were referenced to the C 1s line at 284.6 eV, which provided an accuracy of ± 0.48 eV within the full scanning range of 0 to 1100 eV. XPS peak 4.1 software was used for curve fitting.

In Situ FTIR

In situ FTIR spectra were recorded using a Nicolet 6700 spectrometer equipped with a mercury-cadmium-telluride (MCT) detector cooled by liquid nitro-gen. The catalyst was pretreated at 300°C using high-purity Ar (100 mL min⁻¹) for 60 min, and then cooled down to the room temperature. Subsequently, toluene-N2-O2 mixture (100 ppm toluene) was introduced into the IR cell. Until toluene adsorbed saturation, the high-purity Ar was introduced for 20 min, and then the sample was heated up to 150°C. The infrared spectra were collected with a resolution of 2 cm⁻¹ and 64 scans in the region of 650–4000 cm⁻¹.

RESULTS AND DISCUSSION

Adsorption Breakthrough Curve of Toluene

The adsorption breakthrough curves of toluene on the 3%FeOx/SBA-15 catalyst were presented in Fig. 1. The outlet toluene concentration was very low and the breakthrough curves were close to a straight line at first. Then the outlet toluene concentration was significant increased with the extension of adsorption time, finally reached a value of steady state (Fig. 1). The time that the toluene concentration increased was defined as the breakthrough time (Zhao et al., 2011). The breakthrough time of toluene displayed an obvious difference at the different O2 concentration streams, the following sequence was 100%N2 (36 min) > 95%N2 + 5%O2 (24 min) > 90%N2 + 10%O2 (24 min) > 80%N2 + 20%O2 (18 min). Our previous work found that the 3%-Fe-loading catalyst could adsorb O2 on the surface and oxidize Fe²⁺ into Fe³⁺ (Lu et al., 2015). This type of O2 could quickly occupy the adsorption site, reduced the amount of toluene adsorption, so that the breakthrough time decreased when O2 concentration increased. Those results indicated that O2 provided competitive adsorption with toluene on the 3%FeOx/SBA-15 catalyst.

O2-TPD

O2-TPD profiles could provide useful information on the behavior of oxygen in composite oxide materials. The O2-TPD profiles of fresh 3% FeOx/SBA-15 catalyst and after toluene adsorbed in various background gases were measured. In the TPD curves of various samples (Fig. 2), the peak emerged at 80°C could be ascribed to desorption of weak adsorption molecular oxygen (O2−) from the catalyst surface (Li et al., 2008; Ma et al., 2013). Quantitative evaluation of this desorption peak (Table 1) revealed that desorption amount of O2− from the catalyst, after it adsorbed toluene drastically dropped compared to the fresh catalyst. The degree of reduction depended on the O2 concentrations when toluene adsorbed. Simultaneously, the intensity of
this peak showed the minimum for the sample of toluene adsorption at the pure N2. Whereas, the peak was arising as O2 concentration increased. For this phenomenon, there were two main reasons: (i) Oxygen that adsorbed on the catalyst surface during toluene adsorption desorbed from the catalyst surface; (ii) The adsorbed toluene was oxidized by the adsorbed O2 during the pretreatment procedure (O2-TPD, pretreated at 300°C), so the adsorption sites occupied by the toluene were released. And those sites were re-adsorbed by the O2 which came from O2-He mixture (O2-TPD, O2-He mixture was switched for 60 min). Finally, improved O2 desorption amount. Whatever the results, these indicated that O2 and toluene had the competitive adsorption on the 3%FeOx/SBA-15 catalyst surface. Simultaneously, the temperature of this peak shifted lower compared to the fresh catalyst, and the lowest was observed at the pure N2 as the background gas of toluene adsorption. This implied that the lattice oxygen activity might be improved when the oxygen adsorbed on the catalyst surface. It was beneficial for the complete oxidation of toluene. 

To better understand the competitive adsorption of O2 and toluene on the FeOx/SBA-15 catalyst, an additional experiment was carried out with pure SBA-15 and 5%MnOx/SBA-15 adsorbed toluene in the feed gases of 100%N2 and 80%N2 + 20%O2 (Fig. 3). No significant difference was observed between the spectra acquired with different background gases, suggested that there was no competitive adsorption of O2 and toluene on the pure SBA-15 and 5%MnOx/SBA-15 catalysts surface. This indicated that FeOx was the competitive adsorption site of O2 and toluene.

**Effect of O2 Concentration on the Atomic Surface Compositions of Catalyst**

Atomic surface compositions of catalysts were obtained via XPS (Table 2, Fig. 4). The results showed that the O, Fe, Fe2+ and Fe3+ content had been changed as the toluene adsorbed (Table 2). Compared to the fresh catalyst, the percentage of Fe2+ increased when the adsorbed gas was 100%N2, while decreased as the background gas containing O2. However, Fe3+ content showed the opposite tendency, decreased in the 100%N2, increased as the background gas containing O2, and the 20%O2 showed the maximum. Previous study showed that the toluene could adsorb on the catalyst surface of metal ion (Liu et al., 2005). Therefore, when the background gas was pure N2, the toluene could be adsorbed on the Fe2+ or Fe3+ site, resulting in the decrease of Fe ion concentration on catalyst surface. Subsequently, the Fe2+ and O located on the catalyst subsurface moved to the catalyst surface, and brought out the increase of Fe2+, O and Fe content on the catalyst surface (Table 2). Another hand, O2 had the competitive adsorption with toluene on the 3%FeOx/SBA-15 (Figs. 2 and 3). Therefore, when the background gas contained O2, the O2 could be adsorbed on the Fe2+ and oxidized Fe2+ into Fe3+ (Lu et al., 2015), resulting in the increase of Fe3+ (Table 2). This result further demonstrated that the O2 and toluene appeared the competitive on the FeOx/SBA-15 surface, and the Fe2+ was one of the competitive adsorbed sites.

At the same time, the XPS spectra for Fe 2p (Fig. 4) shifted lower after adsorbed toluene, especially fit adsorbed toluene in the 90%N2 + 10%O2. This could be attributed to the existence of FeSi or FeSi2 (Li et al., 2015). This indicated that the toluene adsorption could increase the interaction between Fe and supporter, which benefitted the performance of catalyst activity.

Thus, based on those results, the schematic diagram of competitive adsorption of O2 and toluene on FeOx/SBA-15...
was proposed, as shown in Fig. 5. The O₂ and toluene adsorbed on the site of Fe²⁺ loading on the catalyst surface, resulted in the decrease of Fe²⁺ ion concentration on catalyst surface. Consequently, the Fe²⁺ located on the catalyst subsurface moved to the catalyst surface. At the same time, Fe²⁺ could be oxidized into Fe³⁺ as the gas containing O₂.

**In Situ FTIR**

In situ FTIR studies provided real-time monitoring of transient events occurring on the catalyst during toluene adsorption. In this study, a set of FTIR spectra were obtained during toluene adsorption over 3% FeOₓ/SBA-15 in different O₂ concentrations (Fig. 6). Fig. 6(A) was the IR transmittance spectra of toluene adsorption over the catalyst. After adsorption saturation, the catalyst was immersed in pure Ar and purged for 20 min (Fig. 6(B)), then heated under the condition of 150°C (Fig. 6(C)).

During toluene adsorption, strong peaks due to toluene appeared at 1392, 1460, 1495, 1608 (C = C vibrations of an aromatic ring) (Li et al., 2007), 2879, 2928 (C-H vibrations of methyl) (Maira et al., 2001; Eby et al., 2012), and 3031 (C-H vibration of aromatic ring) (Maira et al., 2001). The peaks displayed no significant shift under the different O₂ concentrations, indicated that the O₂ did not influence the toluene adsorption state.

During the Ar purge processing, vibration bands of C =
C (aromatic ring), C-H (methyl), and C-H (aromatic ring) were also observed. This indicated that the toluene could steadily adsorb on the catalyst surface, which agreed with the results of Table 2. After 20 min of Ar purge, the catalyst was heated in the pure Ar stream (Fig. 6(C)). The bands of toluene adsorption disappeared, and some new peaks were formed. Two peaks at 1215 cm\(^{-1}\) and 1296 cm\(^{-1}\) indicated the formation of C-O-C and C-O of ester, respectively (Long et al., 2011). At the same time, the intensity of the band at 1215 cm\(^{-1}\) decreased with increasing O\(_2\) concentration.
This suggested that the O₂ adsorbed on the catalyst surface promoted toluene oxidation and decreased the formation of ester organic by-products. The peaks at 3558 cm⁻¹ and 3718 cm⁻¹ should correspond to the bridging OH groups with toluene and the OH of the catalyst surface, respectively (Maira et al., 2001; Wu et al., 2014). The peak at 3558 cm⁻¹ decreased as the background gas containing O₂, which was due to the reaction of toluene with O₂ adsorbed on the catalyst surface. Those results demonstrated that O₂ adsorbed on the catalyst surface could oxidize toluene.

Additionally, the peaks at 3616 cm⁻¹ should be assigned to a lattice OH stretching mode (Wu et al., 2014), and the intensity was the maximum under the pure N₂. Our previous study found that the 3%-Fe-loading catalyst could oxidize toluene into COₓ in the pure N₂ plasma (Lu et al., 2015), one of the reasons might arise from the oxidation ability of the OH under the pure N₂.

CONCLUSIONS

In the present study, the breakthrough time of toluene in the different background gases indicated that O₂ could competitively adsorb with toluene on the 3%-FeOₓ/SBA-15 catalyst, and the Fe²⁺ was one of the adsorption sites for both O₂ and toluene. In situ FTIR study of toluene adsorption on the catalyst surface showed that the competitive adsorption between O₂ and toluene could not impact the toluene adsorption state on the catalyst surface, and the O₂ adsorbed on the catalyst surface could oxidize toluene.

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REFERENCES


