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The effect of copper valence on catalytic combustion of styrene over the copper based catalysts in the absence and presence of water vapor☆

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ABSTRACT

Catalysts CuO_x/γ-Al_2O_3-IH and CuO_x/γ-Al_2O_3-IM were prepared, characterized, and tested for styrene combustion in the absence and presence of water vapor. The effect of copper valence of the catalysts on the catalytic activity for styrene combustion was discussed using the theory of hard soft acids and bases (HSAB). The results showed that the existence of water vapor in feed stream inhibited the catalytic activity for styrene combustion due to the competition adsorption of water molecule. HSAB theory confirmed that the local soft acidity of the catalyst CuO_x/γ-Al_2O_3-IH was much stronger than that of the catalyst CuO_x/γ-Al_2O_3-IM because of the higher content of soft acid Cu^+ on its surface, which increased the adsorption ability toward soft base of styrene and reduced the adsorption toward hard base of water vapor, and thus increased the catalytic activity for styrene combustion and weakened the negative influence of water vapor.

1. Introduction

Styrene is an important aromatic compound and widely used as a raw material for the production of plastics, rubbers, insulation, pharmaceuticals, dyes, and pesticides [1]. Due to its high volatility at ambient condition, styrene can easily emit into atmosphere from manufacturing units. And it can be absorbed through the human's respiratory tract, skin and digestive tract for a long exposure to styrene [2], which is harmful to the respiratory system and central nervous system even at low concentrations. Thus it is regarded as one kind of the volatile organic compounds (VOCs). Therefore it is necessary to remove styrene for legislation and human health.

In comparison with conventional treatment methods such as thermal destruction and adsorption [3], catalytic combustion is an important method to remove VOCs due to its final disposal and energy saving process [4,5]. The catalyst plays an important role in the catalytic combustion technology. Noble metal based catalysts and transitional metal based catalysts are usually used for VOC combustion. Noble metal based catalysts show higher catalytic activity and stability compared with transitional metal based catalysts, whereas, their application in industry is limited due to its rarity and valuableness. Therefore, many researchers devoted to designing transitional metal based catalysts with higher catalytic activity. Among them, copper based catalysts were reported to show higher activity for VOC combustion [6]. However, its catalytic activity was affected by water vapor of the feed stream in practical applications. The water vapor mainly came from many off-gases such as previous combustions and water-contact operations. For example, Pan *et al.* [7] reported that water vapor had a negative effect on the activity of the copper based catalysts for styrene combustion, and the styrene conversion of the catalyst CuO/γ-Al_2O_3 decreased from 90% to 70% when the water vapor volume concentration increased from 0.21% to 2.1% at 300 °C, which was due to the competitive adsorption of styrene and water on the active sites of the catalysts. Wang *et al.* [8] reported that the conversion of toluene on the catalyst CuO/γ-Al_2O_3 decreased from 85 to 62% when the water vapor concentration increased from 0 to 10 vol.% at 300 °C, which was also due to the competitive adsorption of toluene and water vapor. Similar results were reported by Li [9], who prepared copper–manganese catalysts for toluene combustion in the presence of water vapor. Thus, in order to ensure the copper based catalysts with high activity and durability to water vapor, it is necessary to suppress the adsorption of water vapor and promote the adsorption of styrene on the active sites of the catalysts.

In our previous researches, it was reported that when Ag^+ was loaded on AC, it could enhance the adsorption ability to dibenzothiophene because Ag^+ was a soft acid and dibenzothiophene was a soft base [10], whereas, it could weaken the adsorption ability to dichloromethane because dichloromethane was a hard base [11]. The above

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presentation was supported by Hard and soft acids and bases (HSAB) principle, which shows that soft acids like to bond to soft bases and hard acids like to bond to hard bases. According to the classification of Pearson, Cu^+ belongs to the soft acid, styrene and water belong to the base [12,13]. Thus, if the more content of soft acid Cu^+ on the copper based catalysts is, the stronger the adsorption ability to styrene will be because styrene is a kind of soft base, instead, the weaker the adsorption ability to water will be because water is a kind of hard base. Therefore, raising the Cu^+ content can improve its catalytic activity of the copper based catalysts and inhibit the negative influence of water vapor.

Previous studies [14] found that the metal dispersion degree of the palladium and platinum-based catalysts can be increased when they were calcined and then reduced. Wang *et al.* [15] reported that the particle size of Co metal of the Co/Mg/Al (10/40/50) is about 14 nm when the catalyst was reduced by H_2. It can be speculated that, the use of H_2 to reduce the copper oxide based catalysts can increase the dispersion degree of copper, and CuO or Cu_2O can be produced when the reduced copper based catalysts were then oxidized under the crystallization temperature.

Based on this perception, in order to raise the content of Cu^+ ion of the copper based catalysts, we used the reduction–oxidation method to prepare the catalyst $CuO_x/\gamma\text{-}Al_2O_3$-IH with different copper loading amounts. By comparison, the catalyst $CuO_x/\gamma\text{-}Al_2O_3$-IM was also prepared by ultrasonic impregnation methods. The copper valence and content of the catalysts were characterized by XRD, TPR, XPS and N2 adsorption. The catalytic activity of the catalysts for styrene combustion was tested in the presence of water vapor whose volume concentration was in the range of 0.21%–3.75%. Moreover, the effect of copper valence and content of the catalysts on the catalytic activity for styrene combustion in the absence and presence of water vapor was also analyzed and discussed here with the help of HSAB theory.

2. Materials and Methods

2.1. Catalysts preparation

Synthesis of $CuO_x/\gamma\text{-}Al_2O_3$-IM: first, the $\gamma\text{-}Al_2O_3$ [(60–80) mesh], obtained from Alfa Aesar company (America), was separately added to aqueous solution of copper nitrate ($Cu(NO_3)_2$, 99%) with different concentrations. The chemical reagent was supplied from Guangzhou Chemical reagent factory (China), and no additional purification was done. Second, the slurry was stirred for 24 h at 30 °C, and then put in an ultrasonic field stirred for 1 h. In this experiment, the ultrasonic sound of frequency was 45 kHz and its power was 185 W. After that the slurry was filtered and then dried at 120 °C for 12 h. Finally, the samples were calcined at 550 °C for 5 h. The obtained catalysts were denoted as $CuO_x/\gamma\text{-}Al_2O_3$-IM with 8.2%–12.3% (by mass) CuO loading.

Synthesis of $CuO_x/\gamma\text{-}Al_2O_3$-IH: About 500 mg catalyst $CuO_x/\gamma\text{-}Al_2O_3$-IM with 8.2%–12.3% (by mass) CuO loading was placed in a stainless steel pipe; both sides of the catalyst bed were sealed with quartz wool. The catalyst was treated by $30\ ml \cdot min^{-1}$ gas flow of H_2 at 350 °C for 2 h, followed by calcination at the same temperature in air for 2 h. Quantitative uptakes of the copper loading on the catalysts were verified by atomic adsorption spectroscopy.

2.2. Characterization of catalysts

X-ray diffraction (XRD) was conducted in a Bruker D8 Advance diffractometer using Cu K_a radiation ($\lambda = 0.15406$ nm). The X-ray tube was operated at 40 kV and 40 mA.

Temperature-programmed reduction of hydrogen (H_2-TPR) was conducted using a Micromeritics Autochem 2920 analyzer. About 100 mg catalyst was placed on a U shape quartz tube and dried at 300 °C for 2 h in a helium flow rate of $40\ ml \cdot min^{-1}$, and then cooled to room temperature. After that, the catalyst was reduced by $30\ ml \cdot min^{-1}$ gas mixture composed of 10% H_2/Ar, and then the catalyst bed temperature was heated to 750 °C at a rate of $10\ °C \cdot min^{-1}$. A thermal conductivity detector (TCD) was used to measure the amount of H_2 consumption.

X-ray photoelectron spectra (XPS) was used to analyze the photoelectronic signals of Cu 2p by a Physical Electronics PHI 300 spectrometer with nonmonochromatic AlKa (1486.6 eV). Collected data were corrected for charge shifting using standard C1s binding energy of 284.6 eV. Data analysis with background subtraction and curve fitting was done on XPS Peak 4.1.

The surface area and pore structures of catalysts were measured by nitrogen adsorption at 196 °C using a Micromeritics ASAP-2020 analyzer. The BET surface area was calculated using standard Brunauer–Emmett–Teller equation, and the total pore volume was estimated on the basis of the volume adsorbed when $p / p_0 = 0.99$. Average pore diameter was calculated through $4\ V \cdot A^{-1}$.

2.3. Catalytic activity of catalysts

Catalytic activated tests for styrene combustion in the presence of different water vapor concentrations were conducted in a fixed bed reactor with an internal catalyst bed at atmospheric pressure.

Before the catalytic experiment, about 100 mg catalyst sample was placed in the center of the stainless steel reactor tube, and both sides of the catalyst bed were filled with quartz wool. The reactant gas mixture of styrene vapor, water vapor and pure air gas (Air, 0.9999) was continuously delivered to the catalyst bed. Reactant gas flow-rate through the catalyst bed was controlled by mass flow controllers (MFC) (BJQXHC Electron Company, China). Temperature of the catalyst bed was controlled by a temperature controller (XMYD Electron Company, China), and a K-type thermocouple was used to measure the upstream side temperature of the catalyst bed. The effluent of styrene was analyzed by on line gas chromatography (Hua'ai GC 9160 chromatograph equipped with a FID detector). In this work, the reactant gas flow rate was $180\ ml \cdot min^{-1}$, and the concentration of styrene was $5.17\ g \cdot m^{-3}$ at the gas hourly space velocity (GHSV) of $54000\ h^{-1}$. The controlled volume concentration of water vapor in reactant gas stream was 0.21%, 2.1%, 2.94% and 3.78% separately, which was measured by hygrometers. The relative standard uncertainty of the MFC controllers and temperature controller was to be 1% and ±0.2 °C respectively in this work.

3. Results and Discussion

3.1. Characterization of catalysts

3.1.1. X-ray diffraction (XRD)

Fig. 1 presents the XRD patterns of the two catalysts $CuO_x/\gamma\text{-}Al_2O_3$-IM, $CuO_x/\gamma\text{-}Al_2O_3$-IH and the support $\gamma\text{-}Al_2O_3$ respectively. Both $\gamma\text{-}Al_2O_3$ and the two copper based catalysts show three main diffraction peaks at 2θ values of 36, 46 and 66°, which represent typical characteristic diffraction peaks of $\gamma\text{-}Al_2O_3$. When 10.1% of copper oxide (by mass) is loaded on $\gamma\text{-}Al_2O_3$, the two catalysts display some new diffraction peaks besides the same structure of $\gamma\text{-}Al_2O_3$. It is can be seen easily that these additional new diffraction peaks appear at 2θ value of 35.3, 38.8 and 48.7° (form CuO (JCPDS45-0937)), and 36.2, 42.2 and 61.2° (form Cu_2O (JCPDS78-2076)) respectively, which indicates that both CuO and Cu_2O coexist on the surface of the two catalysts. The mean diameter of CuO and Cu_2O crystallites is calculated by the Scherrer equation, and the data are shown in Table 1. The data in Table 1 show that the crystallite sizes of CuO and Cu_2O are 33.66 and 20.23 nm on the catalyst $CuO_x/\gamma\text{-}Al_2O_3$-IM, and 20.23 and 22.69 nm on the catalyst $CuO_x/\gamma\text{-}Al_2O_3$-IH, separately. It can be seen that the crystallite size of CuO on the catalyst $CuO_x/\gamma\text{-}Al_2O_3$-IM is much higher than that on the catalyst $CuO_x/\gamma\text{-}Al_2O_3$-IH, whereas, there is a small difference in the crystallite size of Cu_2O between the two catalysts. The larger the crystallite sizes of CuO of the catalyst $CuO_x/\gamma\text{-}Al_2O_3$-IM is, the lower the