Journal of Molecular Catalysis A: Chemical 404–405 (2015) 98–105

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Effect of oxygen pretreatment on the surface catalytic oxidation of HCHO on Ag/MCM-41 catalysts

Dan Chen [a], Zhenping Qu [a,*], Yang Lv [b], Xin Lu [a], Weifang Chen [a], Xiangyu Gao [a]

[a] *Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, China*
[b] *School of Civil Engineering, Faculty of Infrastructure Engineering, Dalian University of Technology, Dalian, China*

ARTICLE INFO

Article history:
Received 28 September 2014
Received in revised form 17 April 2015
Accepted 18 April 2015
Available online 20 April 2015

Keywords:
Ag/MCM-41
HCHO
O_2 pretreatment
Particle size
Ag_2O

ABSTRACT

The effect of oxygen pretreatment on HCHO catalytic oxidation of Ag/MCM-41 catalysts has been investigated from 500 °C to 800 °C in this paper. The highest HCHO surface reaction activity is achieved on the silver sample pretreated at 700 °C. The state and the dispersion of silver species on the support are strongly related to the pretreatment temperature. The increase of the O_2 pretreatment temperature for Ag/MCM-41 catalysts results in the diffusion of Ag_2O clusters from outside to inside of the channels. And the amount of Ag_2O clusters inside the channels becomes maximum at 600 °C. Interestingly, it is found that the smaller metallic Ag nanoparticles coexist with large particles when the catalyst is pretreated at 700 °C. It is suggested that Ag_2O clusters inside of MCM-41 pores improves the HCHO adsorption capacity and accelerates the formation of HCHO adsorption intermediates, particularly dioxymethylene(DOM) ad-species. And the formed meallic silver particles with smaller size at 700 °C plays an essential effect on the formation of formate intermediate and the enhancement of surface reaction activity. It is also concluded that CO_2 formation rate from formate is higher than that from DOM species in HCHO oxidation. The decrease of HCHO surface reaction activity after oxygen pretreatment at 800 °C may be due to the decrease of the Ag_2O clusters inside MCM-41 pores and the aggregation of metallic Ag nanoparticles.

1. Introduction

Silver has been widely used in the catalytic oxidation reactions with outstanding activity, such as ethylene epoxidation [1–3], hydrogenation of unsaturated aldehydes [4,5], partial oxidation of methanol to formaldehyde [6,7], oxidative coupling of methane to ethane and ethylene [8–10], selective catalytic reduction of NO_x [11–13], VOCs catalytic oxidation [14,15] and CO oxidation [16–18], and so on.

It is generally accepted that the catalytic activity of Ag depends to a large extent on the size of the Ag particles, the nature of the active sites, which are proved to be of fundamental importance [17,19]. Moreover, different pretreatment atmosphere and temperature not only leads to the geometric structure changes, such as the particle size, the morphology, but also results in the electronic structure changes, for example, surface chemical states, redox properties and so on then affects the catalytic reaction acitivity [18,20,21].

Many researchers have supposed that treating silver catalysts in an oxygen atmosphere may result in different surface structures, comparing with the treatment in vacuum or inert gas [18,22]. Bron et al. [23] suggested that morphological changes and surface restructuring of the Ag nanoparticles occurred during O_2 pretreatment, which might modify the catalytic properties of acrolein hydrogenation in Ag/SiO_2 catalysts. Shimizu et al. [24] suggested that silica-supported silver nanoparticles with the surface oxygen atoms due to O_2 pretreatment acted as an effective heterogeneous catalyst for the alkylation of arens with alcohols and styrenes. Beneficial effects of oxygen pretreatment of Ag/SiO_2 catalysts in the acrolein hydrogenation have been demonstrated by Bron et al. [23]. Gac et al. [25] reported that the catalytic activity of Ag catalyst was strongly related to the pretreatment atmosphere and the dispersion of crystallites or the formation of strong silver-oxygen bounding. Therefore, these Ag–O interaction due to the high-temperature O_2 pretreatment has proved the outstanding activity for many reactions. Our previous studies [22,26] have also reported that pretreatment in oxygen at 500 °C can markedly improve the activity of Ag/SiO_2 catalysts for the low temperature CO oxidation. The oxygen pretreatment at 500 °C redisperses and restructures the metallic Ag particles on the surface, and more interestingly, the

---

* Corresponding author. Tel.: +86 411 84708083; fax: +86 411 84708083.
E-mail address: quzhenping@dlut.edu.cn (Z. Qu).

http://dx.doi.org/10.1016/j.molcata.2015.04.014
1381-1169/

subsurface oxygen species formed during the pretreatment can not only stabilize the active Ag structures but also participate in the CO oxidation. Su et al. [27] have also proved that silver catalysts undergo massive structural change during oxygen pretreatment at high temperatures (>500 °C). In Ag/SBA-15 catalysts, we found that O_2 pretreatment at 900 °C could induce the evaporated silver atoms to be redeposited on the support, and meanwhile diffuse into the channels of SBA-15, forming more highly dispersed small metallic silver particles inside the channels [18]. Therefore, the active species inside or outside mesoporous materials play the different role in the catalytic oxidation activity.

It has been known that the formation and oxidation of different adsorption intermediates, such as dioxymethylene (DOM), formate, and adsorbed CO, strongly affect the reaction rates in HCHO catalytic oxidation reaction on Ag/MCM-41 catalysts [28,29]. It is reasonable to suggest that, according to the previous reported results, the intermediates formation will be directly related with the different silver states and their dispersion on the support. The investigation about the state and dispersion of silver species and the relationship of silver state with the formation of intermediates and HCHO oxidation activity is rare. Then it is essential to discuss the state of silver species on MCM-41 in HCHO catalytic oxidation reaction because it is very important for the investigation of the reaction mechanism and the activity improvement of silver catalytst. Herein, the influence of oxygen pretreatment temperature in the silver structure and the HCHO catalytic activity of Ag/MCM-41 catalysts was systematically investigated and discussed. In situ FTIR, temperature programmed desorption (TPD) and temperature programmed surface reaction (TPSR) were all used to study the characteristics of HCHO adsorption and reaction on the Ag/MCM-41 catalyst.

2. Experimental

2.1. Catalyst preparation

Commercial porous materials (MCM-41) were used as the supports. To endow the catalytic activity, 8 wt.% silver was introduced into the support using nitrate precursor of silver by incipient-wetness impregnation method. The obtained wet samples were dried at room temperature overnight and then at 100 °C overnight. The catalysts were sieved into 20–40 mesh granules and then pretreated with O_2 atmospheres at different temperatures (500–800 °C) before testing and characterization. And the O500, O600, O700, and O800 stands for the Ag/MCM-41 catalysts pretreated with oxygen at 500, 600, 700, and 800 °C, respectively.

2.2. Catalyst characterization

Specific areas were computed from these isotherms by applying the Brunauer–Emmett–Teller (BET) method in Quantachrom NOVA4200e. Before measurement, the samples were treated by degassing at 300 °C for 4 h. The pore diameter distributions were calculated from desorption branches using the BJH (Barrett–Joyner–Halenda) methods.

Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a Rigaku D/max-γb ($\lambda = 0.1542$ nm) and operating at 40 kV and 200 mA. The patterns were taken over the 2θ range from 10° to 80° and a position-sensitive detector using a step size of 0.02°.

Transmission electron microscopy (Tecnai G^2 Spirit) operated at 120 kV was used to study the morphology and the particle size of catalyst samples. The sample was supported on a copper mesh for the TEM analysis.

UV–vis diffuse reflectance spectra were recorded in air on a SHIMADZU UV-2450 UV–vis spectrophotometer. Reference spectra were collected with pressed $BaSO_4$ disks. The following parameters were used to collect data: 5.0 spectra band width, 0.5 nm data pitch, 800–190 nm measurement range, and 200 nm/min scanning speed.

H_2-TPR (temperature programmed reduction) was carried out in Quantachrom Automated Chemisorption Analyzer. 0.1 g sample after different pretreatment in fixed bed reactors was then pretreated in He at 200 °C for 1 h, cooled to room temperature in He in chemisorption analyzer. For H_2-TPR study, it was exposed to a flow of 30 ml/min H_2/Ar (10 vol.% H_2) mixture. The temperature was programmed with a constant heating rate of 10 °C/min.

2.3. In situ FT-IR

In situ FT-IR spectra were recorded in BRUKER VERTEX 70 using variable-temperature quartz cells. A catalyst wafer (12 mm × 0.1 mm in size and ca. 30 mg in weight) was placed in the flow IR cell-reactor and then pretreated in He flow at 300 °C for 40 min. All spectra were recorded with a resolution of 4 cm^{-1} and accumulating 16 scans. A background spectrum was subtracted from each spectrum, respectively.

2.4. Adsorption/desorption and surface reaction experiments

The adsorption/desorption and surface reaction of HCHO were performed in a fixed catalytic reactor system in the middle of which 0.1 g catalyst (20–40 mesh) was packed. The reaction was performed at temperatures ranged from room temperature (RT) to 500 °C. A thermocouple was placed in the middle of the catalyst bed for the temperature measurement. Gaseous HCHO was generated by flowing He over trioxymethylene (99.5%, Acros Organics) in an incubator kept in an ice water mixture. A HCHO adsorption breakthrough curve was obtained for each run to ensure the saturation of the catalyst surface using the mass spectrum (Ametek, LC-D200M). The catalysts were purged with high purity helium for 1 h to fully remove physically adsorbed HCHO, and then the temperature was ramped at 10 °C/min from RT to 500 °C. The effluent from quartz reactor was analyzed by MS. The exhaust line from the reactor to the mass spectrometer was maintained at ~120 °C to prevent the condensation of the formaldehyde and reaction products. Temperature programmed desorption (TPD) of HCHO was carried out in a continuous flow of helium, and the temperature programmed surface reaction (TPSR) experiments were conducted in flow of O_2/Ar (30 vol.% O_2).

3. Results and discussion

3.1. Catalysts characterization

As we all know, silver will be restricted in the formation of minimum-energy crystal structures during pretreatment. Thus, the silver catalyst will undergo the pronounced geometric and/or electronic structure changes after high-temperature treatments in order to obtain the structure which is most thermodynamically favorable.

3.1.1. Textural properties

To measure the effects of O_2 pretreatment temperature on the textural properties, the N_2 adsorption and distribution of pore diameter curves are presented in Fig. 1. As shown in Fig. 1(a), these samples exhibit the type IV adsorption/desorption isotherms with H1 type hysteresis loop having inflection around $P/P_0 = 0.3–0.45$, which are typical characteristics of mesoporous materials according to the IUPAC classification [28]. The inflection around $P/P_0 = 0.3–0.45$ region indicates the uniformity of the