Fuel 188 (2017) 121–131

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Low-temperature CO oxidation on Ag/ZSM-5 catalysts: Influence of Si/Al ratio and redox pretreatments on formation of silver active sites

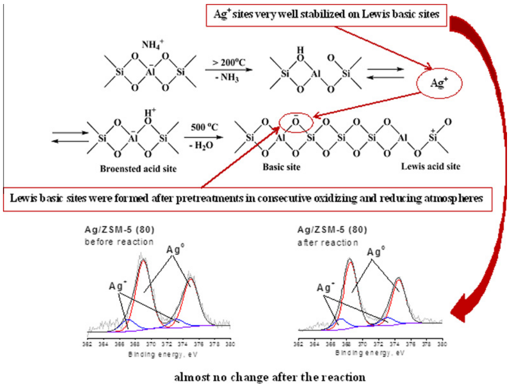
E. Kolobova[a], A. Pestryakov[a,*], G. Mamontov[b], Yu. Kotolevich[c], N. Bogdanchikova[c], M. Farias[c], A. Vosmerikov[d], L. Vosmerikova[d], V. Cortes Corberan[e]

[a] *Tomsk Polytechnic University, Tomsk 634050, Russia*
[b] *Tomsk State University, Tomsk 634050, Russia*
[c] *Centro de Nanociencias y Nanotecnología, UNAM, Ensenada 22860, Mexico*
[d] *Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, Tomsk 634055, Russia*
[e] *Institute of Catalysis and Petroleum Chemistry (ICP), CSIC, 28049 Madrid, Spain*

HIGHLIGHTS

- Cationic Ag^+ and $Ag_n^{\delta+}$ species are active sites in low temperature CO oxidation.
- An appropriate Si/Al ratio is essential for CO oxidation over supported Ag catalyst.
- Broensted acidity of zeolite correlates with the catalyst activity.
- Consecutive oxidizing and reducing pretreatments promote catalytic activity.
- Ag/ZSM-5 (80) catalyst displayed the highest activity in CO oxidation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form 9 September 2016
Accepted 4 October 2016
Available online 11 October 2016

Keywords:
Low temperature CO oxidation
Silver catalysts
ZSM-5
Si/Al ratio
Effect of pretreatments

ABSTRACT

Silver catalysts supported on ZSM-5 (Si/Al = 30, 50 and 80) were investigated for low-temperature CO oxidation to study the nature of the silver active sites and their formation under the influence of the support chemical composition and redox pretreatments. The catalysts were characterized by HRTEM, FTIR, XPS, diffuse reflectance UV–Vis spectroscopy, NH_3 thermodesorption (NH_3 TPD) and temperature-programmed reduction (H_2 TPR). The chemical composition (Si/Al ratio) of the ZSM-5 zeolite support significantly affects catalytic properties of Ag/ZSM-5 samples: the lower the Broensted acidity of the zeolite support, the higher the activity of the catalysts. Interestingly, while oxidizing pretreatment of catalysts led to a significantly better performance than reducing pretreatments, the consecutive reducing treatment of the preoxidized samples significantly promoted the catalytic activity for low-temperature CO oxidation. Thus, Ag/ZMS-5 catalyst with Si/Al = 80, pretreated consecutively in oxidizing and reducing conditions, showed the highest activity, reaching 90% CO conversion at just 40 °C. Comparison of activity and characterization results showed that silver particles with size below 2 nm are the most active; larger particles are just "spectators". The most probable silver active centers in the low-temperature CO oxidation are ionic species, mostly charged clusters $Ag_n^{\delta+}$, strongly interacting with the support. The obtained results in low-temperature CO oxidation might be of particular interest for neutralization of exhaust gases of car engines during "cold start".

---

* Corresponding author.
E-mail address: pestryakov2005@yandex.ru (A. Pestryakov).

http://dx.doi.org/10.1016/j.fuel.2016.10.037
0016-2361/

1. Introduction

The catalytic oxidation of carbon monoxide attracts considerable attention due to its relevance in many industrial sectors, such as gas cleaning in CO_2 lasers, CO sensors, air purification in devices for respiratory protection and protection of the environment from harmful emissions [1]. Development of catalysts of low-temperature CO oxidation is of particular interest for neutralization of exhaust gases of car engines during "cold start". Conventional car catalytic neutralizers based on Pt or Pd start to operate at 130–150 °C; and such differences between environmental and operating temperatures lead to emission of some amount of toxic exhaust gases to atmosphere.

Usually, catalysts containing noble metals (Pt, Pd, Rh, and Au) supported on transition metal oxides (Cr, Co, Cu, Ni, and Mn) [2–8] and hopcalite catalyst [9] are used in this process. The main drawbacks of catalysts containing noble metals are their high cost and the relatively high temperatures, above 100–120 °C, required for their efficient performance. Regarding hopcalite catalysts, their main drawback is deactivation by water vapor. By contrast, nanogold catalysts can operate at low temperatures (below 100 °C), but they are quickly deactivated during reaction or prolonged storage [6–8], and their cost is high. Consequently, there is the need to develop less expensive catalysts which possess both ~~a~~ high activity and stability.

Silver-containing catalytic systems are inferior in activity of supported gold, but more active than many oxide and metal catalytic systems [10,11]. The most important parameters influencing formation of the active species in silver-based catalysts are synthesis method, character of metal-support interaction, nature of the support, and redox pretreatments at different temperatures. All these factors predetermine the electronic state of supported silver, its dispersion and particle structure, and its catalytic properties. Concerning Ag-containing systems supported on silica and alumina, their thermal or reducing treatment with hydrogen-containing mixtures causes a reduction of silver from the ionic to the metallic state: the dispersed silver particles formed are active in oxidation reactions [12–14]. $[AlO_4]$ tetrahedra are the centers of stabilization of ionic silver species in Ag/zeolite and Ag/aluminosilicate systems [15–18]. The dependence of the silver state on the surface of oxide supports of different nature on the pretreatment conditions and reaction mixtures has been described [19–21]. Silver dispersion on the TiO_2 surface is kept during treatments in inert and reducing atmosphere, whereas for Ag/Al_2O_3 the slight decrease of the metal dispersion is observed. Under the same conditions, aggregation of silver on the surface of SiO_2 is more pronounced; it causes loss of active surface due to dispersion decrease. Zhang et al. [22] discussed the influence of silver concentration on the catalytic activity and Ag particle size, as well as the effect of various pretreatments. Catalyst Ag/SiO_2 (8 wt.% Ag) pretreated with O_2 at 500 °C showed high catalytic activity in the CO oxidation ($T_{98} = 65$ °C). The further treatment with H_2 at 200 °C increased catalytic activity ($T_{98} = 50$ °C).

Catalysts supported on molecular sieves have also been investigated for low-temperature CO oxidation, especially those based on ZSM-5, due to their excellent thermal stability, high surface area and well developed preparation methods [23–26]. ZSM-5 is widely used fora variety of reactions, such as Fischer-Tropsch synthesis, $deNO_x$ process and aromatization of hydrocarbons. Bi and Lu [24] studied catalyst $Pd\text{-}Fe\text{-}O_x/NaZSM\text{-}5$ in the low-temperature CO oxidation ($T_{100} = 47$ °C). Han et al. [25] prepared a series of Pd-Ce/ZSM-5 catalysts and found that the bicomponent Pd-Ce catalyst has higher activity for low-temperature CO oxidation than the Pd or Ce monometallic ones. In general, Pt or Pd-containing zeolites are the most studied for this process, while data on Ag/zeolite systems are much scarce [10]. Oleksenko et al. [26] investigated the catalytic activity of Ag-zeolite (10 wt.% Ag) systems calcined at high temperatures (up to 700 °C) and found that the additional reduction treatment of the samples leads to increase activity of Ag-NaX, Ag-NaA, Ag-NaZSM-5 (37), Ag-NaZSM-5 (47), and Ag-NaMor catalysts. The activity of these zeolite-based systems is largely determined by the number of active sites (Ag^0 clusters and highly dispersed metallic silver particles) which are formed during the preparation of catalysts and during the catalytic reaction.

Han et al. [25] also reported that increasing the Si/Al ratios leads to growth of the catalytic activity, but did not explain why ratio Si/Al influences the activity. Generally, the influence of Si/Al ratio of some zeolites (mordenites, Y, etc.) on physicochemical and catalytic properties of supported metal is caused by the correlation between their Si/Al ratio and surface acidity [8,9,27–31]. However, the mechanism of the effect of Si/Al ratio (and, accordingly, of surface acidity) on catalytic properties of the metals in redox processes remains unclear.

Despite the large number of publications devoted to the study of the mechanism of formation and the nature of active sites in the silver-containing systems, this question is still subject of broad discussion. Some authors suggest that the active sites are metallic silver particles of different sizes, while others prove the activity of ionic states [32–36]. The identification of the nature of the active sites is one of the key aspects of heterogeneous catalysis, because it allows carrying out the directed synthesis of highly efficient catalysts with desired properties.

In our previous study [37] we investigated and discussed the influence of the silver content and the synthesis conditions on the activity of zeolite supported silver catalysts for CO oxidation using a ZSM-5 zeolite with Si/Al = 50 as support. It was found that Ag/ZSM-5 catalysts have a good reproducibility and stability in CO oxidation and their activity depends strongly on Ag loading: the best performance was obtained with among which 7 wt.% Ag. The aim of this work is looking for ways to improve the activity of nanosized Ag catalysts to make them an alternative to nanogold catalysts for low temperature oxidation of CO. For this purpose, we investigated the nature of the silver active sites on the zeolite support surface, and how factors such as the chemical composition of the support (i.e., Si/Al ratio) and the pretreatment atmospheres influence their formation and redox properties.

2. Experimental

2.1. Catalysts preparation

All catalysts were prepared by incipient wetness impregnation of ZSM-5 zeolites in ammonium form with Si/Al ratios of 30, 50 and 80 (Süd-Chemie) with aqueous solution of $AgNO_3$ (0.1103 g/ml), by adding 1 ml of this solution per gram of support (this volume corresponds to internal pore volume of zeolite). Then, the obtained samples were dried at 150 °C for 3 h. Following our previous results [37], silver content in all samples was 7 wt.%. Support and catalyst samples were denoted ZSM-5 (*x*) and Ag/ZSM-5 (*x*), respectively, where *x* is the support Si/Al ratio.

2.2. Catalysts and supports characterization

IR spectra of studied zeolites were recorded on FTIR Nicolet 5700 spectrometer.

The porous structure of zeolites and catalysts was determined by N_2 low-temperature adsorption using 3Flex analyzer (Micromeritics, USA). Specific surface areas were calculated by