Design of Ag/silica materials for sorption and catalytic removal of volatile organic compounds

N.N. Mikheeva[a], A.S. Gorbunova[a], E.V. Vishegorodtseva[a], V.I. Zaikovskii[b], G.V. Mamontov*[a]
[a] *Tomsk State University, Tomsk, 634050, Russia*
[b] *Boreskov Institute of Catalysis, Novosibirsk, 630090, Russia*
**GrigoriyMamontov@mail.ru*

Abstract: The series of Ag/SiO_2 catalysts on the basis of MCM-41, SBA-15 and commercial silica were prepared by impregnation techniques. The prepared materials were characterized by complex of methods. The sorption and catalytic properties of materials toward volatile organic compounds (VOCs) were studied by TPD and TPR, respectively. It was found that sorption capacity toward C_6 hydrocarbons strongly depends on the S_{BET}. The high catalytic activity of Ag/silica materials in deep oxidation of VOCs is caused by small size of Ag nanoparticles mainly located inside the pores of silica supports. Ag/silica materials are promising for combined sorption and catalytic purification of air from VOCs.

Keywords: silver, silica, VOCs, sorption and catalytic air purification

1. Introduction

High research interest toward Ag/SiO_2 catalysts is connected with their high activity in low-temperature CO oxidation [1, 2], deep oxidation of formaldehyde [3], toluene [4], etc. Silver-based catalysts are promising due to relatively low cost and high stability in comparison with other noble metals. The problem of low-temperature CO oxidation and oxidation of VOCs has high importance for purification of air in industrial space, parking zones, offices and living quarters. The creation of devices with sorbents and/or catalysts working at relatively low temperatures is one of the promising solutions of this challenge. The present work is devoted to design of Ag/SiO_2 sorbent–catalysts for sorption of VOCs at room temperature followed by deep oxidation at relatively low temperatures. Different types of silica were used for materials preparation to control both sorption and catalytic properties.

2. Experimental

To design Ag/SiO_2 catalysts with controllable sorption and catalytic properties a series of silicas was used as supports, including mesoporous ordered silica SBA-15 (S_{BET}=717 m^2/g) and MCM-41 (1222 m^2/g), commercial microporous silica ASM (670 m^2/g) and mesoporous silica KSKG (420 m^2/g). SBA-15 and MCM-41 were prepared by template synthesis using Pluronic P123 and CTAB as templates, respectively. The series of Ag/SiO_2 catalysts were prepared by impregnation techniques. The prepared supports and catalysts were characterized by low-temperature N_2 sorption, powder XRD and XRD small angles, TPR-H_2, TEM HR, FTIR, UV-vis and Raman spectroscopy. The sorption properties of silica supports and Ag catalysts toward different volatile organic compounds (VOCs: n-hexane, cyclohexane, benzene, methanol, etc.) were studied in a dynamic mode at atmospheric pressure and room temperature by TPD method. The catalytic activity of Ag catalysts in deep oxidation of VOCs was studied by TPR method with MS control of the reagents and reaction products.

3. Results and discussion

The silica supports have different porous structure (Fig. 1a). Thus, MCM-41 and SBA-15 are characterized by ordered porous structure with average diameter of cylindrical pores of 3.3 and 6.8 nm, respectively. The pores with sizes below 5 nm are observed for microporous silica ASM, while those of 4-10 nm were found for mesoporous silica KSKG (Fig. 1a). It was found that sorption capacity toward n-hexane depends linearly on the specific surface area of silica. Thus, sorption capacity of MCM-41 achieves 0.5 g/g. Also, it was shown by TPD that n-hexane desorption depends on porous structure of silica. The TPD spectra for MCM-41 are characterized by two peaks of hexane desorption that may be associated with diffusion limitation of hexane transport from thin cylindrical pores. Total desorption of n-hexane from silica in TPD is achieved below 200 °C.

For Ag/SiO_2 it was found that the silver distribution mainly depends on both preparation conditions and porous structure of silica. Thus, silver particle size distribution for catalysts prepared on the basis of mesoporous silica KSKG is characterized by relatively wide distribution from 1 to 10 nm. Two types of silver nanoparticles were observed for Ag/MCM-41 and Ag/SBA-15 catalysts (Fig. 1b). Small silver particles with sizes below 3 nm were observed inside pores of support, while large particles (4-8 nm) are located on the external surface of the support. Thus, unique porous structure of MCM-41 and SBA-15 may be used to prepare small Ag nanoparticles.

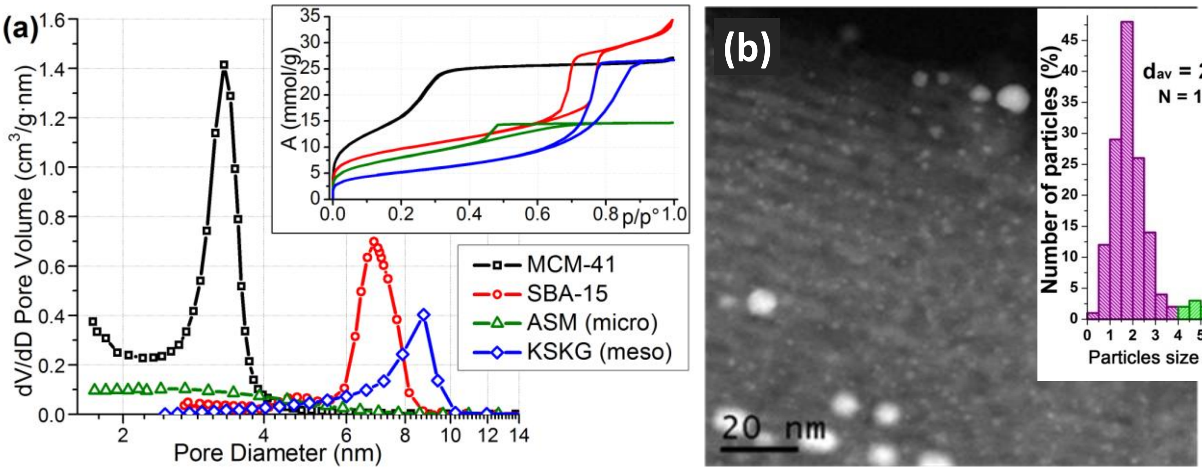

Figure 1. Pore size distributions and isotherms of N_2 adsorption–desorption for silica supports (a) and HAADF-STEM image of Ag/SBA-15 catalyst and corresponding particles size distribution (b)

Catalytic properties of Ag catalysts were studied in deep oxidation of methanol and other VOCs. It was found that oxidation of methanol (2000 ppm) over Ag/SBA-15 catalyst started at 70-80 °C simultaneously with desorption of methanol from the catalyst surface. Total conversion of methanol was achieved at 105-110 °C. Addition of ceria into Ag/SBA-15 catalyst increased its activity. Thus, a combination of high sorption capacity of silica-based materials at room temperature with high activity at relatively low temperature may be used for sorption of small amount of VOCs followed by deep oxidation.

4. Conclusions

Thus, Ag/SiO_2 composites are promising materials for sorption and/or catalytic removal of VOCs from air. The high sorption capacity toward both non-polar (C_6 hydrocarbons) and polar (alcohols, aldehydes) VOCs is an advantage of such silica-based materials. The unique porous structure of MCM-41 and SBA-15 may used for both high sorption capacity and stabilization of small nanoparticles of silver. The combination of high sorption and catalytic properties of Ag/SiO_2 materials may be used for air purification from different VOCs, including methanol, formaldehyde and hydrocarbons.

References

1. Z. Qu, M. Cheng, W. Huang, X. Bao, J. Catal. 229 (2005) 446.
2. V.V. Dutov, G.V. Mamontov, V.I. Zaikovskii, L.F. Liotta, O.V. Vodyankina, Appl. Catal. B. 221 (2018) 598.
3. T. Kharlamova, G. Mamontov, M. Salaev, et al. Appl. Catal. A. 467 (2013) 519.
4. Y. Qin, Z. Qu, C. Dong, N. Huang. Chin. J. Catal.38 (2017) 1603.