

Ethylene Epoxidation by Highly Active Nano-Silver (Ag) Catalysts Supported on Ordered Mesoporous Silicas

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Introduction

The selective oxidation of ethylene to ethylene oxide (EO) is probably one of the most important catalytic processes for the production of high added-value petrochemicals [1]. The epoxidation reaction under industrial conditions is usually carried out at elevated pressure over silver catalysts supported on low surface area α -Al₂O₃ (SSA: 0.1–1 m²/g). High ethylene oxide selectivity (up to 80%) can be achieved by introducing alkali (such as Cs) and halide (such as vinyl chloride) promoters to the pure supported silver catalysts, which otherwise give selectivity of 30–50%. The development of high-surface area ordered mesoporous silicas (or metal-substituted silicas) over the last 20 years has provided the opportunity of supporting relatively large amounts of active metal phases with a fairly homogeneous dispersion and significantly smaller particle size compared to metal particles supported on low surface area oxides. In this work, we have studied the activity, selectivity and stability of Ag-catalysts supported on high surface area (600–1000 m²/g) mesoporous silicas with varying mesopore size (2–20 nm) and pore structure (hexagonal/MCM-41 or SBA-15, wormhole/HMS, and cellular/MCF).

Experimental

Metallic silver nanoparticles were supported on MCM-41, HMS, SBA-15 and MCF ordered mesoporous silicas, which have been synthesized in the laboratory [2]. Silver was loaded via typical incipient wetness method using aqueous solutions of AgNO₃, and the Ag content of the final reduced catalysts (at 350°C in H₂ flow) ranged from 10 to 40 wt.%. Low-surface area supports (α -Al₂O₃, SiO₂) were also used for comparison. All the supports and catalysts before and after reaction were characterized by ICP-AES, XRD, SEM, HRTEM, TPD/TPR-H₂, and XPS. The catalytic experiments for ethylene epoxidation were carried out in a fixed-bed flow reactor with feed mixture of 2% C₂H₄, 6% O₂ in He, in the temperature range of 150 to 350°C.

Results/Discussion

Ag loadings as high as 40 wt.% could be achieved in the high surface area mesoporous silicas with relatively homogeneous particle size distribution (average size \leq 50 nm), in comparison with the non-porous SiO₂ or α -Al₂O₃ on which Ag particles exhibited irregular shape and were in some cases even larger than ca. 90 nm (see TEM images, Fig.1). As a result, highly active catalysts based on mesoporous silicas were produced with respect to C₂H₄ conversion. Interestingly, selectivity to ethylene oxide (EO) was similar to that with the low surface area

oxide catalysts and consequently the highly loaded (40 wt.% Ag) mesoporous silica based catalysts provided significantly higher EO yields, as can be seen in Fig. 2a. These results show that neither the long-straight channels of MCM or SBA-15 type mesoporous materials or the tortuous pathways of the 3-D wormhole-like mesostructures (HMS) could induce undesirable effects, mainly in selectivity, by enhancing secondary reactions leading to overoxidation towards CO₂. In addition, it appears that surface hydroxyls of mesoporous silicas do not induce sufficient acidity capable of decreasing the selectivity towards ethylene oxide. However, the mesoporous silica supported catalysts are not stable over time, in contrast to the low surface area supported catalysts, as can be seen in Fig. 2b. Detailed characterization of the used catalysts by XRD, XPS, TEM, N₂ porosimetry and other methods is expected to elucidate the cause of changes in the performance of the otherwise highly active Ag/mesoporous silica epoxidation catalysts.

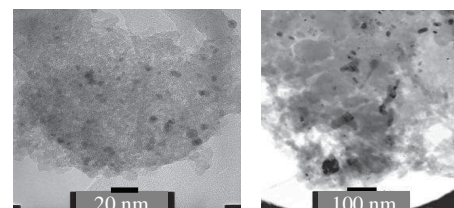


Figure 1. TEM images of metallic nano-Ag (10 wt.%) supported on high surface area HMS mesoporous silica (left) and low surface area α -Al₂O₃ (right).

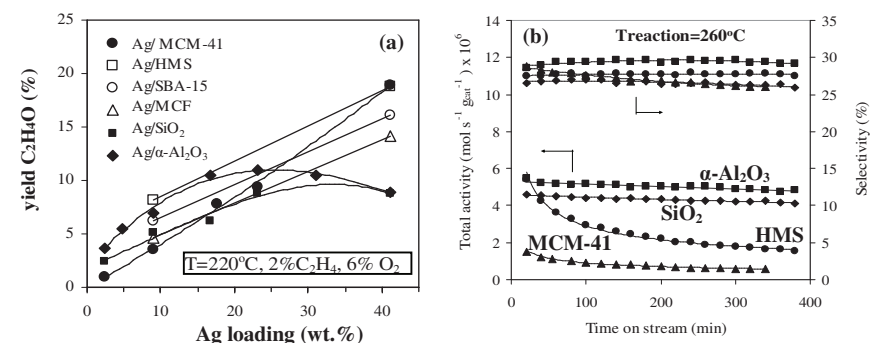


Figure 2. (a) Yield of ethylene oxide vs. Ag loading, and (b) stability of Ag catalysts.

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References

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