

# Propylene epoxidation by molecular oxygen with supported silver catalysts: Effect of preparation method and silver size/morphology

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## Introduction

Propylene oxide is a valuable chemical intermediate in the petrochemical industry that is mainly produced by the chlorohydrin and the hydroperoxide process [1]. The gas-phase epoxidation of propylene with Au nanoparticles on TiO<sub>2</sub> or various titano-silicate materials [2] using *in situ* formed H<sub>2</sub>O<sub>2</sub> as oxidant, has been proposed as a promising alternative with very high propylene oxide selectivity (as high as 99%) but at very low conversion levels (less than ca. 5%). Still however, economic and process safety issues make the direct gas-phase epoxidation of propylene by molecular oxygen even more attractive compared to the gas-phase/H<sub>2</sub>O<sub>2</sub> method [3]. In this work, we focused on silver-based catalysts and we studied the effect of support type, preparation method and use of alkali chloride promoters.

## Experimental

The supports used for the preparation of the catalysts were  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> (rutile and anatase), ZrO<sub>2</sub> and CaCO<sub>3</sub>, which exhibit varying porosity, acidic and redox characteristics. Two methods were applied for loading Ag (50 wt.%) on the supports: a) wet impregnation with aqueous solutions of AgNO<sub>3</sub>, and b) deposition from aqueous solution via *in situ* reduction of Ag-oxalate in ethylene diamine/ethanolamine mixture. The Ag catalysts were reduced at 350°C in H<sub>2</sub> prior to characterization and testing. Promotion of the catalysts was conducted via wet impregnation with aqueous solution of NaCl (2 wt.%). The catalysts were characterized by ICP-AES, XRD, Raman, TEM, TPR-TPO, TPD-NH<sub>3</sub> and XPS. The catalytic tests were conducted in a fixed-bed reactor using a 5% C<sub>3</sub>H<sub>6</sub>/10% O<sub>2</sub> mixture (v/v) in He, at the temperature range of 180 to 300°C. The reaction products were analyzed by on-line GC –FID/TCD.

## Results/Discussion

The high Ag content (50 wt.%) and the relatively low surface area (< 50 m<sup>2</sup>/g) of the supports used, resulted in catalysts with similar size of metallic Ag particles (ca. 70-110 nm, Table 1). The catalysts prepared by the Ag-oxalate/amines method provided slightly larger Ag crystals compared to the wet impregnation method. The catalysts supported on SiO<sub>2</sub>, TiO<sub>2</sub>/anatase and ZrO<sub>2</sub> were very active for the conversion of propylene but not selective towards propylene oxide (PO), leading mainly to the production of CO<sub>2</sub>, due to their relative acidic nature, at least compared to the rest of the supports used in the present work (Figure 1). The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>/rutile based catalysts were also quite active but were more selective towards PO formation, especially the rutile supported catalysts which kept a constant PO selectivity over a wide range of conversion degree (up to 50%). The conversion activities of the Ag/CaCO<sub>3</sub>-

oxalate and the AgNO<sub>3</sub> impregnated CaCO<sub>3</sub> catalyst were similar but the selectivity of the former one towards PO was slightly higher (Fig. 1), due mainly to the more uniform shape and size of Ag nanocrystals in that catalyst (TEM results, not shown here). Promotion of the CaCO<sub>3</sub> based catalysts with NaCl suppressed the conversion activity but favored PO selectivity. The detailed characterization of the catalysts before and after reaction with all the techniques described in the experimental section will provide further insight in the reaction mechanism, the effect of Ag crystal size and morphology, and the effect of metal-support interactions.

Table 1. Physical properties of supports and silver (Ag) catalysts prepared by wet impregnation

Catalysts	Surface Area (m <sup>2</sup> /gr)	Ag Crystallite Size (nm)
50% Ag/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	2.1	73 / 105 <sup>(*)</sup>
50% Ag/CaCO <sub>3</sub>	6.8	86 / 103 <sup>(*)</sup>
50% Ag/TiO <sub>2</sub> rutile / anatase	0.8 / 50	95 / 86
50% Ag/ZrO <sub>2</sub> / 50% Ag/SiO <sub>2</sub>	5.5 / 6.5	93 / 116

<sup>(\*)</sup> Size of Ag in catalyst prepared via the silver oxalate/amines method.

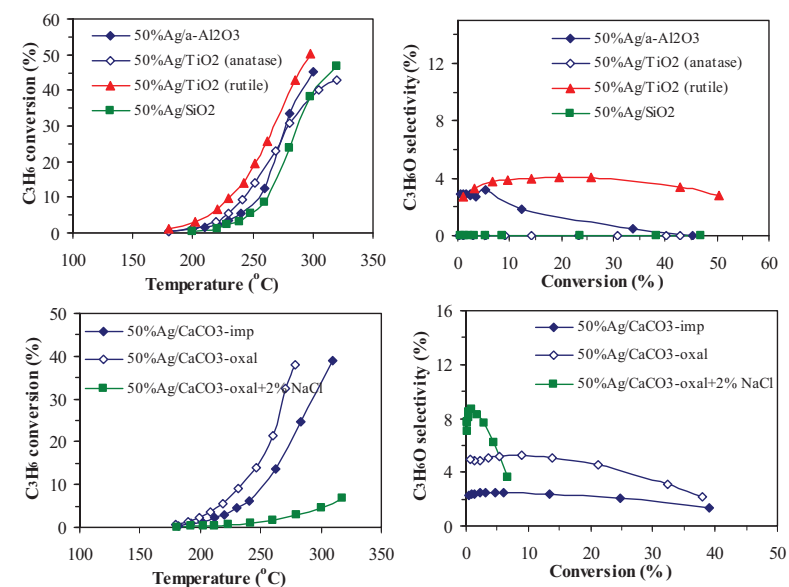


Figure 1. Propylene epoxidation with various supported silver (Ag) catalysts.

## References

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