

Propylene Epoxidation: High-Throughput Screening of Supported Metal Catalysts Combinatorially Prepared by Rapid Sol–Gel Method

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Abstract The gas phase oxidation of propylene using molecular oxygen was studied on a variety of supported metal catalysts. The most promising PO activity was obtained for Cu supported on high surface area SiO₂ and the multimetallic systems exhibit synergistic effects that increased the desired PO yield by several folds for Ag promoted with Cu on SiO₂ after screening a large number of catalysts by a high throughput testing technique.

Keywords Propylene · Epoxidation · Sol–gel · High-throughput

1 Introduction

Propylene oxide (PO) is an important raw material for the chemical industry. PO is produced commercially by the chlorohydrin and hydroperoxide processes. Because of the environmental impacts of the chlorohydrin process, the most recently built plants are all using hydroperoxide process technologies. However, a disadvantage of hydroperoxide process is the production of co-products produced in a volume that is ~3 times larger than that of PO; hence, the

economy of the process is primarily dominated by the market of the co-product [1].

The direct synthesis of PO by O₂ or air in the gas phase has been under intense research due to environmentally friendly catalytic process and its relative simplicity. Among many catalyst formulation, Au and Ag on different support materials are the most widely investigated metals. Since Haruta et al. showed Au on titanium catalyst was very active for certain reactions, many researches based on Au supported on different support, e.g. TS-1, Ti-MCM-41, Ti-MCM-48 etc., have been performed to better understand the activity toward direct PO formation [2–9]. Despite high PO selectivity (~99%) of the catalyst, propylene conversion is a very low; e.g. a few percent. Nevertheless, the addition of H₂ as a co-reactant renders a requirement of extra treatment to separate the product which makes it less desirable for industrial application. Ag also is the most explored catalysts because of its success in EO synthesis reaction. Several supported and unsupported Ag catalysts modified with various promoters were tested to improve selectivity to PO at high propylene conversions [9–19]. The best modifier for Ag catalysts, e.g. for Ag/CO₃, were determined as NaCl which increase the PO selectivity to a maximum of 40% at 1–3% conversion. Similarly, 31.6% PO selectivity at 12.4% conversion and 33.4% PO selectivity at 18.6% conversion were obtained for unsupported Ag catalysts modified with NaCl [10–12]. In contrast, when Ag is loaded in titanium containing silicate support, 91.21% PO selectivity were obtained at 0.92% conversion [13, 14].

Most recently Mo and Cu were reported to be effective in the production of PO. 43.6% PO selectivity at 17.6% propylene conversion obtained over Mo/SiO₂ catalysts under a relatively higher pressure of 5 atm. were determined due to the post-catalytic volume effect [20]. Cu has also been reported as an active catalyst in the direct production of PO

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without H₂ although the initial yields (0.12%) were much lower than those required for commercial interest [21–25]. Hexagonal mesoporous silicas (HMS) containing transition metals such as Ti- and Al-synthesized with sol–gel method showed 47.8% of propylene conversion and 30.6% of selectivity of PO. However deactivation of the catalysts during the reaction is very high and not suppressed completely by the addition of H₂ [26].

The lack of a breakthrough in propylene epoxidation catalysis, in spite of world-wide efforts, clearly suggests the need to develop novel approaches for catalyst research and development. This fact, coupled with the abundance of catalytic materials that must be explored to discover new leads, e.g. binary, ternary and higher order combinations of metals as well as a large variety of support materials, call for the application of combinatorial or high throughput heterogeneous catalysis tools and methods. Senkan and co-workers made pioneering contributions to this field through the development of novel high-throughput catalyst preparation and screening tools [27–31]. In particular, they developed array channel micro-reactors to rapidly screen a large numbers of catalytic materials in parallel [27, 28]. Recently, they developed a high-throughput pulsed laser ablation (HT-PLA) system for the synthesis of uniformly sized single- and multi-metallic nanoparticles for catalytic applications [31].

In order to be able to synthesize catalysts in a much faster combinatorial fashion, a commercial synthesis apparatus was adapted to prepare catalysts with a sol–gel method in our laboratory. The synthesis apparatus was for high-throughput application where 24 catalysts can be simultaneously synthesized. The reactor block provides a reflux capability by the circulation of cold water. Magnetic stirring is also provided for each tube where a catalyst is synthesized. Reflux capability is an advantage during synthesis of the catalysts, such as silica and alumina that require high temperature conditions. Also, inert gas atmosphere conditions can be provided if required during catalyst synthesis.

In this study, a large number of catalysts were synthesized with sol–gel method and screened to determine active catalysts for propylene epoxidation reaction. In this respect, various metals were loaded into the various support materials by a single step sol–gel method and incipient wetness method to investigate the effect of metal loading and metal-support interaction on the conversion and selectivity.

2 Experimental

2.1 Catalyst Preparation

All catalyst candidates supported on various support materials containing silica, alumina and titania were

prepared combinatorially by using a single step sol–gel method in a magnetically stirred, constant temperature reactor block with 24 tubes and by incipient wetness method.

Silica supported catalysts were prepared with the following precursors; tetraethyl orthosilicate (TEOS) as silica source, ethanol (EtOH) as a solvent, deionized water, 1 M of HNO₃, 0.5 M of NH₄OH and copper (Cu), silver (Ag) and manganese (Mn) nitrate as a metal source (Cu(NO₃)₂, AgNO₃ and Mn(NO₃)₂). The corresponding molar ratio of TEOS:EtOH:HNO₃:H₂O:NH₄OH were 1:(10,20,30):1:13:0.5 and metal precursors were loaded in the range of from 0.5 to 20 weight ratio. First, TEOS, the corresponding amount of EtOH, 1 M of HNO₃, and water were mixed by stirring at room temperature and heated to 80 °C. Then, the metal precursor was added under vigorous stirring and reflux condition. Finally, NH₄OH was added to the clear solution and stirred for few minutes more before gelling. The obtained gel was aged at room temperature, then dried at 120 °C and calcined at 550 °C in air.

The precursors for alumina supported catalysts were aluminum isopropoxide (AIP), concentrated HNO₃ and deionized water in the molar ratio of 1:0.195:(30,60,90) and the same weight ratios for the metal precursors was also used. The necessary amount of water was heated to 85 °C and the corresponding amount of AIP was added to water at 85 °C under vigorous stirring for one hour. To obtain clear solution, the necessary amount of concentrated HNO₃ acid was added to the slurry and kept it stirred for 1 h. The metal precursor was added to this solution and was kept stirred for additional 1 h and then the heater was switched off but the solution was kept stirred for one day. All the procedures were carried out under total reflux conditions. The clear solution was again heated to evaporate the solvent at low temperature without stirring until gel was obtained. The obtained gel was dried at 120 °C for overnight and calcined at 550 °C for a certain time.

The preparation method of supported TiO₂ was as follows; the corresponding amount of tetrabutyl orthotitanate (TBOT) as a Ti source was added to EtOH with stirring at room temperature. The necessary amount of HNO₃ acid was added to the above mixture. In the other tube the necessary amount of metal precursor was dissolved into the deionized water and added to the clear mixture of TBOT, EtOH and HNO₃. The solution was kept stirred until the gel was obtained. The obtained gel was dried at 100 °C, and calcined at various temperatures.

Meso-type silica (m-SiO₂) was prepared according to the method given in the literature [26]. The basis was taken as 1 g of silica. The corresponding amount of dodecylamine (DDA) as a template, deionized water and the concentrated HNO₃ were mixed in a tube and stirred for 1 h. Then, the clear solution of TEOS and EtOH was added

to this solution and continued to stir for 4 h at ambient temperature and pressure. The resulting mixture was aged for 20 h at room temperature. The obtained solid product was filtered, dried at 100 °C and calcined at 650 °C to remove template. Metal precursor was dissolved in water then other materials were added to this mixture in the same sequence for synthesizing metal containing catalysts. This procedure is similar to what is reported in the literature [26].

Mesosilicate containing 2 and 4 mol.% of titanium was prepared as follows: the clear solution of TEOS in EtOH and TBOT in butanol (BA) were added to DDA, H₂O and HNO₃ mixture with vigorous stirring at ambient temperature for 4 h and aged for 20 h. The resultant mixture was filtered, dried at 80 °C and calcined at 650 °C.

In addition to the direct sol–gel method, α -Al₂O₃ supported metal catalysts were prepared by use of incipient wetness method.

2.2 Activity Tests

Catalyst evaluations were performed using computer controlled array channel microreactor system described previously [27] in which up to 80 catalysts can be screened in parallel. In the array microreactors, reactant gases flow over the flat surfaces of catalyst powder which are individually isolated within reactor channels; the flow regime is similar to that of a monolithic reactor [30]. All experiments were performed under atmospheric pressure and at a gas hourly space velocity (GHSV) of 20,000 h⁻¹, representing differential reactor conditions. Initial screening experiments were performed at temperatures of 300 °C using a feed gas composition of 20 vol% O₂, 20 vol% C₃H₆ and balance He. Reactor effluent gases were analyzed by withdrawing the products using a heated capillary sampling probe followed by on-line gas chromatography (Varian CP-4900 Micro GC with thermal conductivity detector, Porapak Q (10 m) and Molecular sieve 13X (10 m) columns). The selectivity of PO is defined as the percent of carbon in PO among all the products.

2.3 Characterization

Powder X-ray diffraction (XRD) analysis was performed using Philips X'pert Pro XRD operated at 40 kV and 45 mA. The surface area of catalysts was obtained from Brunauer-Emmett-Teller (BET) plot and the pore size was obtained from Barrett-Joyner-Halenda (BJH) analysis by Micromeritics Gemini V and Micromeritics ASAP 2010 apparatus. X-ray photoelectron spectroscopy was performed to determine the oxidation state of the selected metals. The X-ray photoelectron spectra were obtained

using Mg K α ($h\nu = 1253.6$ eV) unmonochromatized radiation with SPECS spectrometer.

3 Results and Discussion

3.1 Activity Test Results of Supported Ag Catalysts

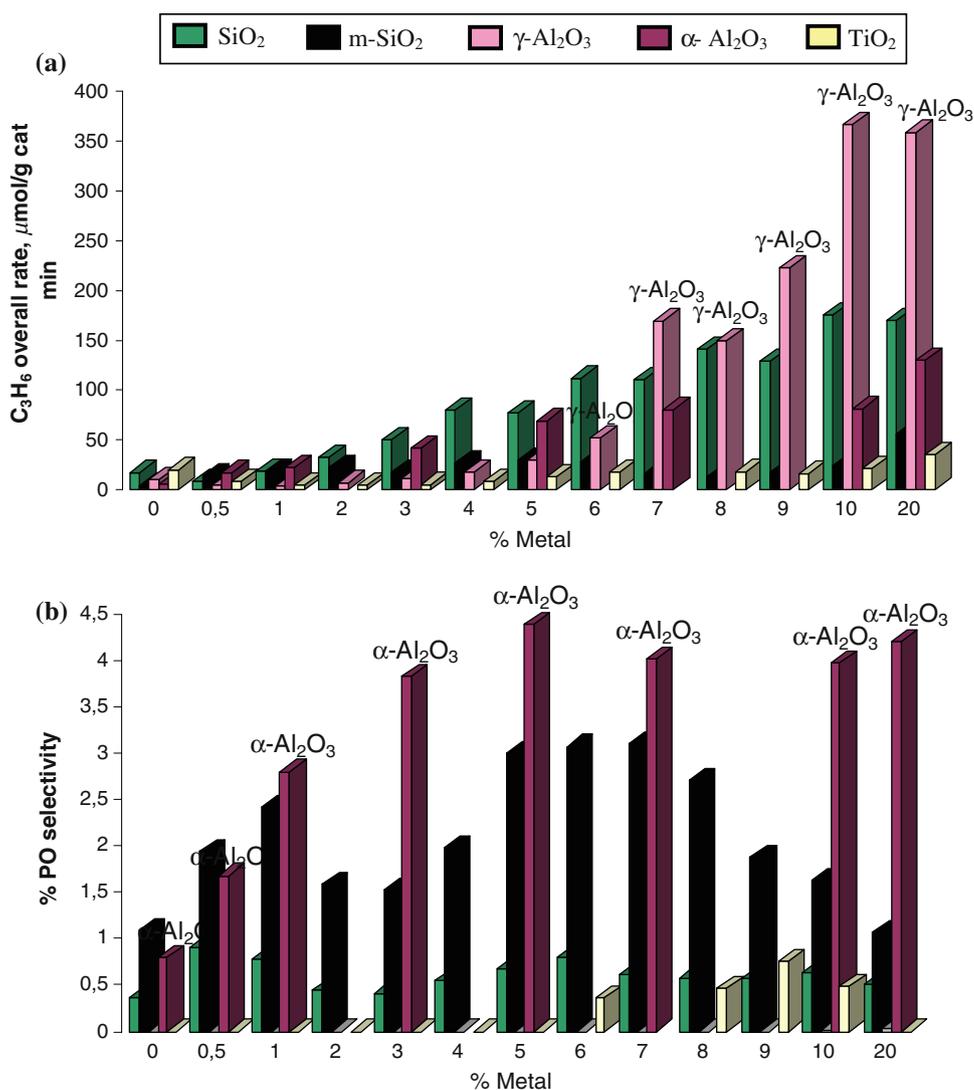
The propylene consumption rate and PO selectivity results as a function of Ag loading supported on five support materials (γ -Al₂O₃, α -Al₂O₃, TiO₂, SiO₂ and m-SiO₂) are shown in Fig. 1a and b, respectively. As shown in the figures, propylene consumption rate increases with the metal loading and it reaches a maximum value of 367 μ mol/g cat-min for γ -Al₂O₃ supported catalysts. The lowest propylene consumption rate was obtained over m-SiO₂ and TiO₂. The Ag catalysts supported on silica synthesized with a DDA as a template and also Ag catalysts supported on commercial alumina did not improve propylene consumption rate but they improved the PO selectivity. Maximum PO production rate was 5.5 μ mol/g cat-min over 20 wt% Ag on commercial α -Al₂O₃ (at 3.2% conversion and 4.2% PO selectivity). The supported Ag catalysts in general mainly produced CO₂. However, the maximum the maximum propionaldehyde plus acrolein (PaL + AC) selectivity as a major C₃ product reached 30% over Ag/m-SiO₂ and the maximum acetone (AT) selectivity as a second major C₃ product was 5% over Ag/ γ -Al₂O₃.

According to the XRD results, a small peak belonging to Ag(111) was observed when 1 wt% Ag was loaded into SiO₂ synthesized by direct sol–gel method, and an increasing the Ag amount to 10 wt% caused an appreciable increase in the peak intensity. This trend was also confirmed by XPS analysis for high and low Ag loadings. The intensity of Ag 3d_{5/2} peak is higher for 10%Ag/SiO₂ than for 1%Ag/SiO₂ catalyst and the Ag was metallic form regardless of Ag loading. We found that the PO production rate and propylene conversion rate increased with the metal amount for Ag/ α -Al₂O₃ catalyst (Fig. 1a and b). It seems that the large Ag particles are desirable for PO production for α -Al₂O₃. However, this may not be true for other support materials as can be seen in activity test results given in Fig. 1a and b.

3.2 Supported Cu Catalysts

Silica supports containing 2 and 4 mol.% titanium were also synthesized in addition to the five supports used for Ag catalysts to investigate the catalytic activity of Cu containing catalysts. The propylene consumption rate and PO selectivity for various supports and Cu metal loading are given in Figs. 2 and 3.

Fig. 1 **a** C_3H_6 consumption rate and **(b)** PO selectivity for supported Ag catalysts



The maximum propylene consumption rate was obtained on 2% Cu/TiO₂ as 552 μmol/g cat-min. However, it produced the lowest C₃ epoxidation product selectivity (max. PaL + AC selectivity as 11.8% and AT selectivity as 2.2%). Although γ-Al₂O₃ is the least effective support material in terms of PO selectivity, C₃ product selectivities reached 35.8% for PaL + AC and 8.4% for AT over for 2% Cu/γ-Al₂O₃ catalyst. Among the 7 support materials indicated in Figs. 2 and 3, silica materials are the most promising catalysts for PO synthesis. Selectivity toward PO (10.7%) was the highest for 2%Cu/m-SiO₂ at 2% propylene conversion. At the same conversion value, the PO selectivity obtained over SiO₂ is 5 times lower than m-SiO₂. For m-SiO₂, an increase in Cu loading from 1 to 3% results in a slight decrease in PO selectivity. However, a further increase causes a significant decrease in PO selectivity (3.4% PO selectivity for 10 wt% Cu). Similarly, better PO selectivity and propylene conversion was

observed over SiO₂. For SiO₂ and m-SiO₂ supported Cu catalysts, the major product is PaL + AC (60–70%) almost at all metal loadings. AT selectivity is 9.5% for SiO₂ but 1.8% for m-SiO₂ at low metal loading and it falls with an increase of loading.

To improve the activity of m-SiO₂ support material, 2 and 4 mol% titanium was added into the structure in accordance with literature studies [26]. However an expected increase in the performance was not observed for titanium silicate support materials, neither propylene consumption rate nor selectivity to PO was improved by Ti addition.

In order to determine the oxidation state of Cu at high and low metal loadings, XPS analysis was performed on the fresh 0.5 and 9% Cu/SiO₂ as shown in Fig. 4. The binding energy at 937.6 and 935.8 eV indicates the presence of isolated-like ionic Cu⁺² species for the catalyst with low metal loading. However, for 9% Cu/SiO₂

Fig. 2 C₃H₆ consumption rate of supported Cu catalysts SiO₂, γ-Al₂O₃, α-Al₂O₃, TiO₂, m-SiO₂, 2%Ti-Si, 4%Ti-Si

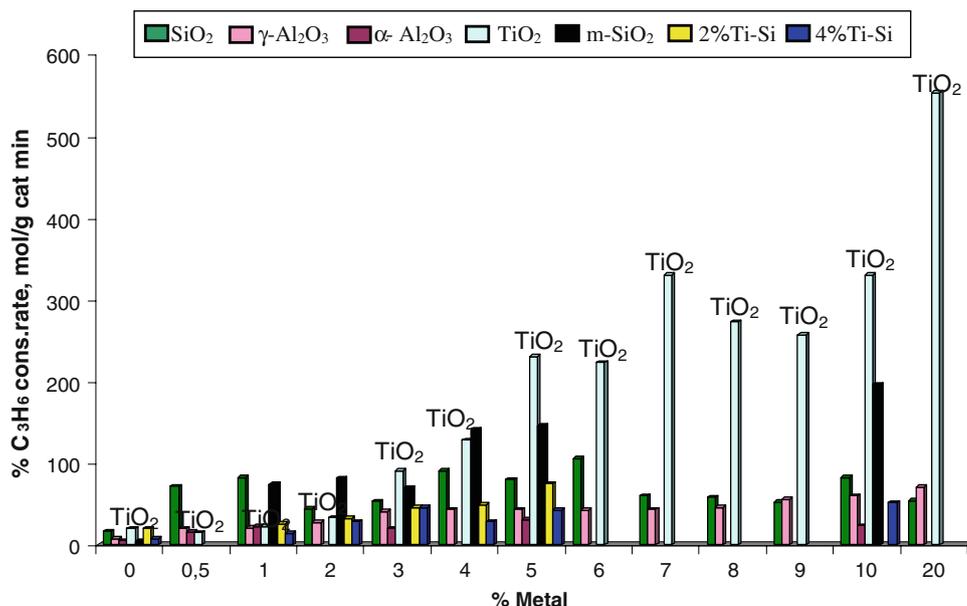
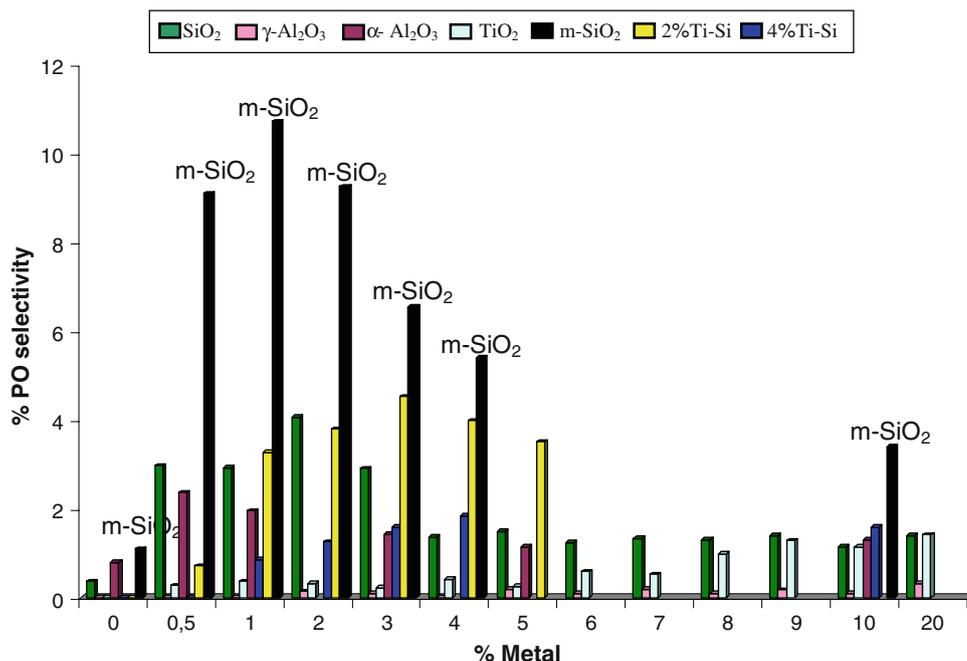


Fig. 3 PO selectivity of supported Cu catalysts SiO₂, γ-Al₂O₃, α-Al₂O₃, TiO₂, m-SiO₂, 2%Ti-Si, 4%Ti-Si



catalysts, the binding energy at 933.7 eV is attributed to the existence of Cu²⁺ species in CuO form and the binding energy at 934.3 and 936.5 eV indicates Cu existing in the isolated-like ionic form. This point seems to be controversial in the literature. For example, Lu and Vaughen state that metallic copper is an active state for propene epoxidation and Cu with high valence causes combustion reaction and acrolein production [21, 22]. In another study, Chu and co-workers state that copper in oxidized state (Cu^I or Cu^{II}) is responsible for epoxidation of C₃H₆ by O₂ [23, 24].

3.3 Activity Test Results of Supported Mn Catalysts

Cu and Ag were previously reported to be active towards PO synthesis from propylene and oxygen especially for promoted catalysts whereas Mn has not been investigated in detail. So, supported Mn catalysts were synthesized and tested in this study too. We found that Mn catalysts generally caused low propylene conversion (<0.1%) and low PO selectivity (<0.5%). Among the seven support materials, the best performance was obtained for m-SiO₂ (4.7%

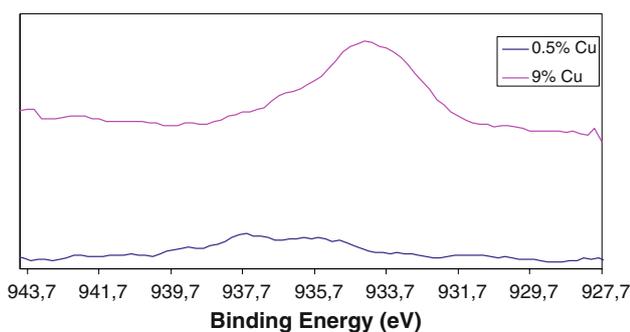


Fig. 4 XPS spectrum of 0.5 and 9%Cu/SiO₂

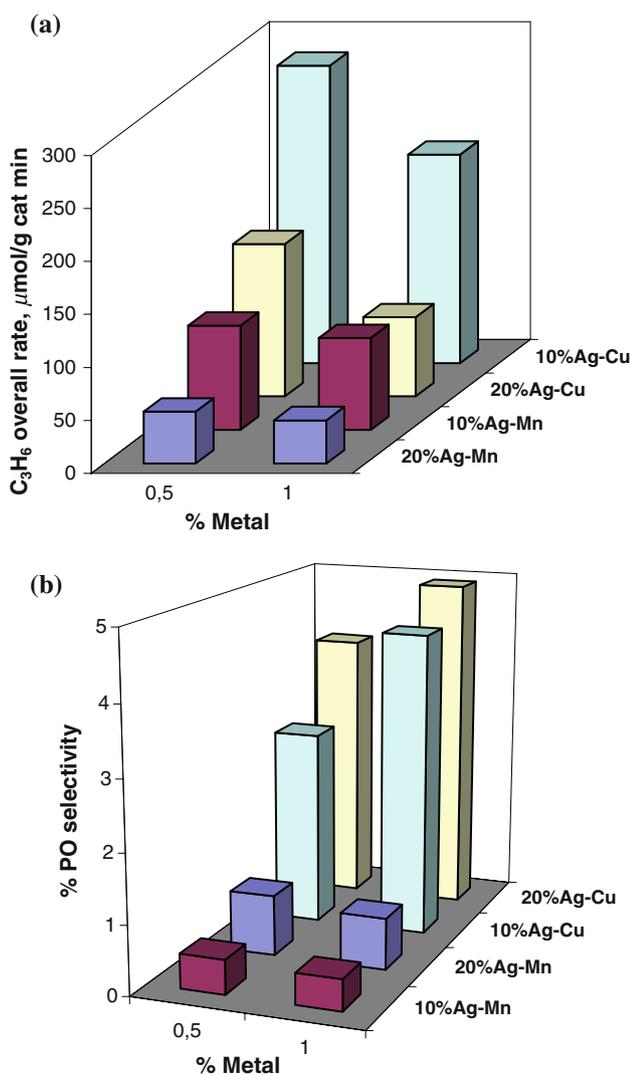


Fig. 5 Activity and selectivity of Ag&Cu and Ag&Mn/SiO₂ catalysts

PO selectivity at 0.2% C₃H₆ conversion). TiO₂ catalyst provided the highest C₃H₆ conversion (8.4%) despite the lower PO selectivity (0.1%). When the results are investigated in terms of the other C₃ products, selectivity to PaL + AC are 45–60% and AT 2–20% at low metal

loadings for all supports except α- and γ-Al₂O₃. The products obtained for Mn supported on γ- and α-Al₂O₃ are almost completely CO₂ (indicating complete combustion rather than partial oxidation so the results are not shown).

3.4 Activity Test Results of Supported Bimetallic Catalysts

A total of 10 and 20 wt% Ag supported on SiO₂ catalysts were promoted with low amounts (0.5 and 1 wt%) of Cu and Mn to improve the PO yield. The propylene consumption rate and PO selectivity were given in Fig. 5a and b. In the absence of Cu and Mn, the propylene consumption rate and PO selectivity were 176 μmol/g cat-min and 0.6% for 10% Ag/SiO₂ and 170 μmol/g-cat min and 0.5% for 20%Ag/SiO₂ respectively. It is of interest that, after addition of Cu at 0.5 and 1 wt% levels, both propylene consumption rate and PO selectivity increased significantly for 10%Ag/SiO₂ catalyst. When 0.5%Cu was added to the 10%Ag, C₃H₆ consumption rate and PO selectivity increased to 281 μmol/g cat-min and 2.9%. Further addition of Cu (1%) increased consumption rate to 197 μmol/g cat-min and PO selectivity to 4.5%. The consumption rate of propylene over 20%Ag catalysts promoted with 0.5 and

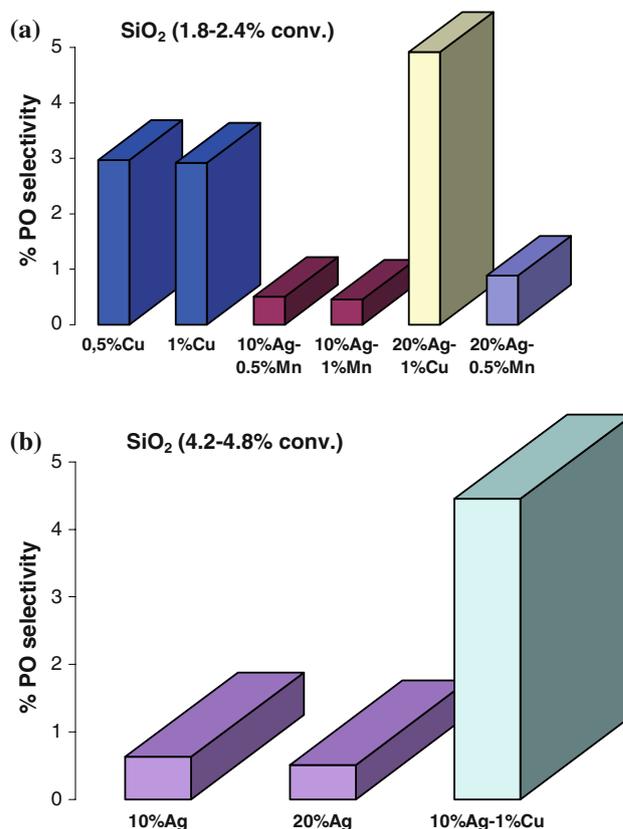


Fig. 6 PO selectivity of Ag&Cu and Ag&Mn/SiO₂ catalysts at the same conversion values (a) 1.8–2.4% and (b) 4.2–4.8% conversion

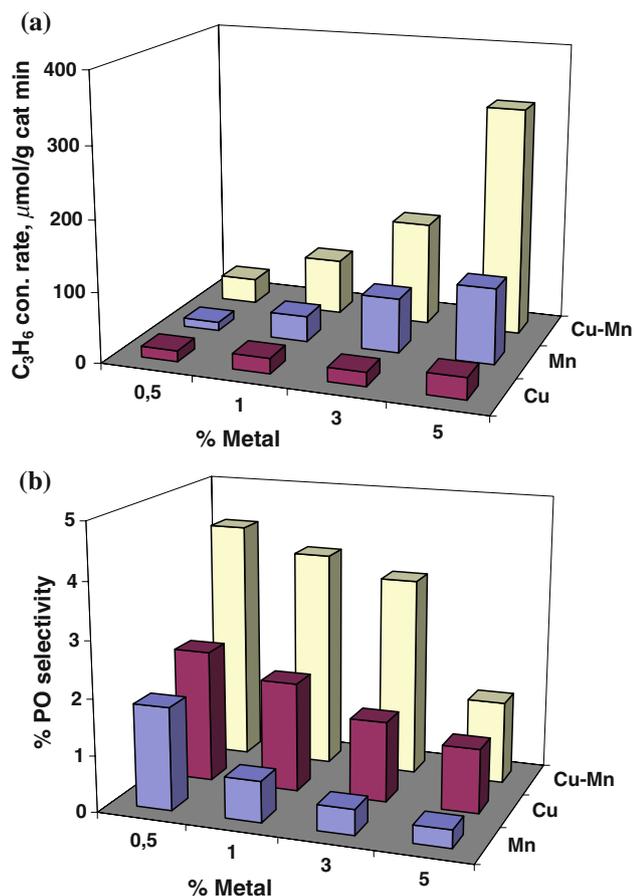


Fig. 7 Activity and selectivity of Cu, Mn and Cu–Mn/ α -Al₂O₃

1 wt%Cu decreased from 176 to 144 and 75 μ mol/g cat-min respectively but it led to an improvement toward the PO selectivity by a factor of 7–10 as compared to an unpromoted Ag catalyst (0.5%) and by a factor of \sim 2 as compared to single Cu catalyst at almost the same conversion levels. 10%Ag/SiO₂ catalysts promoted with 0.5 and 1wt% Mn did not show better PO production rate despite a decrease in C₃H₆ conversion. Although slightly better PO selectivity were observed over the 0.5%Mn-20%Ag/SiO₂ and 1%Mn-20%Ag/SiO₂ catalysts, these catalysts showed remarkably low propylene conversion (\sim 45 μ mol/g cat-min). A synergistic effect of Ag–Cu catalysts is clearly illustrated on isoconversion–selectivity graphs as seen in Fig. 6a and b. When propylene conversions were between 1.8–2.4% (Fig. 6a) and 4.2–4.8% (Fig. 6b), the highest selectivity toward PO was obtained for 20%Ag-1%Cu as 4.9% and for 10%Ag-1%Cu as 4.4%.

Cu and Mn supported on m-SiO₂, α -Al₂O₃ and TiO₂ were also studied. α -Al₂O₃ and TiO₂ supported Cu–Mn showed better catalytic performance than their corresponding single metal catalysts. The synergy between Cu and Mn on these support materials improves PO yields by several folds. For α -Al₂O₃ supported bimetallic and

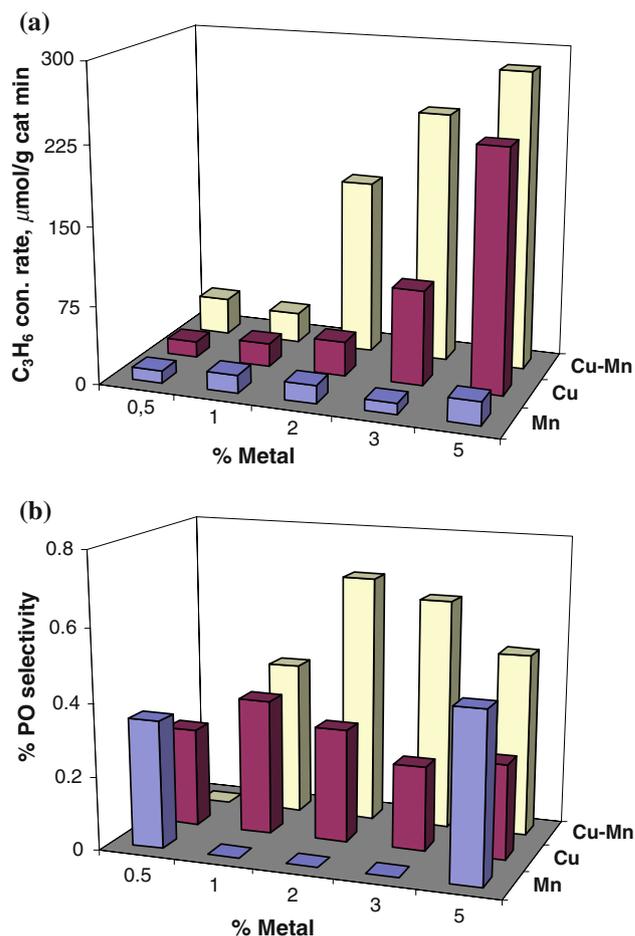


Fig. 8 Activity and selectivity of Cu, Mn and Cu–Mn/TiO₂ catalysts

unimetallic catalysts, Cu–Mn combination gave a better PO selectivity and a propylene consumption rate than their unimetallic counterparts (Fig. 7a and b). At similar low and high conversion levels, PO selectivity is approximately 5 times higher as compared to single metal catalysts. TiO₂ supported catalyst group again showed a better activity and a PO selectivity for the bimetallic systems (Fig. 8a and b). Generally, at 0.7–0.9% and 3.1–5.8% iso-conversion values the bimetallic systems gave slightly better catalytic performance than unimetallic systems. However, at high conversions, PO production rate of Cu/TiO₂ catalyst was higher than the bimetallic system. Cu–Mn/m-SiO₂ catalysts did not enhance the catalytic activity and the PO selectivity as compared with Cu/m-SiO₂ catalyst. This observation is contrary to what is observed for Cu–Mn/ α -Al₂O₃ and Cu–Mn/TiO₂ catalysts systems.

4 Conclusions

High-throughput sol–gel catalyst synthesis and also high-throughput screening methods were used to investigate the

effects of metal loading, support-metal and metal–metal interactions for the direct synthesis of PO from propylene and oxygen. Our results show that the most appropriate support material is silica synthesized with the DDA template and Cu is the most promising metal for direct epoxidation of propylene to PO at low Cu loadings. Ionic species of Cu^{2+} and large metallic Ag particles seem to be responsible for PO gas phase synthesis. The results also show that multimetallic systems can exhibit synergistic effects, improving the PO yield by several folds especially for Ag promoted with Cu on SiO_2 synthesized without template and Cu and Mn bimetallic system supported on $\alpha\text{-Al}_2\text{O}_3$. These new leads reported in this manuscript must be studied in more detail in order to optimize both the catalyst preparation process and the reactor operating conditions (e.g. residence time, temperature, inlet gas stoichiometry etc.) to fully explore the potential of Cu on silica, Ag–Cu and Cu–Mn bimetallic systems in direct PO synthesis. These results illustrate the importance of exploring multimetallic systems and the useful role that high-throughput methods may play in catalyst research and development.

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