Epoxidation of Propene by High-Throughput Screening Method Over Combinatorially Prepared Cu Catalysts Supported on High and Low Surface Area Silica

Derya Duzenli · Erol Seker · Selim Senkan · Isik Onal

Abstract Gas phase epoxidation of propene using molecular oxygen was studied by use of a high-throughput testing technique. A large number of catalysts including promoted and un-promoted Cu were synthesized in a much faster combinatorial fashion using a sol–gel method. Metal catalysts supported on high and low surface area silica were tested and ranked in a high-throughput activity and selectivity testing apparatus at different experimental conditions such as reaction temperature and reactant gas ratio. The amount of Cu loading and the addition of alkali promoters such as K and Li resulted in different tendencies in consumption rate for both silica materials. The maximum PO production rate was obtained as 25.82 μmol/g/cat./min (2.90 % conv. and 20.49 % selectivity) for 3 % Cu–2.25 % K catalyst supported on high surface area silica. There was no noticeable difference in structural and chemical properties of catalysts after modification with K when examined by XRD and TEM; however, the overall activation energy of un-modified catalysts (92 kJ/mol) decreased to 71 kJ/mol for K-modified catalyst. There was negligible difference between the activation energies calculated for PO production (75 vs. 77 kJ/mol).

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

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1 Introduction

Propylene oxide (PO) is an important raw material for the chemical industry. It is produced commercially by the chlorohydrin and hydroperoxide processes. Because of the environmental impacts of the chlorohydrin process, hydroperoxide process technologies are presently being used in the most recently built plants. 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 O_2 or air in the gas phase has been under intense research due to its environmental friendliness and relative simplicity. Among many catalyst formulations, Au and Ag on different support materials are the most widely investigated metals. Since Haruta et al. showed Au on titanium catalyst is very active for certain reactions, many studies 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, propene conversion is very low; e.g. a few percent even with non-porous Ti–SiO_2 [2]. Nevertheless, the addition of H_2 as a co-reactant renders a requirement of extra treatment to separate the product which makes it less desirable for industrial application. However the selectivity to PO decreases drastically without H_2 and propene conversion remains very low [10].

Silver is also one of the most explored catalysts because of its success in ethylene oxide (EO) synthesis reaction even though it has low selectivity (around 5 %) in propene oxidation reaction. The low PO selectivity arising because of allylic hydrogen of propene has been tried to enhance with different support materials and modifiers and even

bimetallic systems such as Au, Cu, Ni etc. catalysts [11–23]. Generally it is reported that larger (max. 800 nm) or proper size of Ag particle (20–40 nm) is necessary for high PO formation [13, 21]. However Lei et al. [22] reported that unpromoted size-selected Ag_3 clusters and $\sim$3.5 nm Ag nanoparticles on alumina supports gave much higher PO formation rate with negligible amount of CO_2 than reported for any Ag catalysts. In addition they showed that oxidized silver trimers are more active and selective for oxidation than extended silver surface with density functional calculation.

Another method applied to improve PO production rate is the surface-initiate gas phase reaction of propene by radical chain mechanisms at low temperature. Mimura et al. studied titanium oxide clusters supported on silica for radical production and obtained 22 % propene conversion and 21 % PO selectivity in the post catalytic bed volume at 568 K and 3.5 atm. They continued their study with screening different metals and support materials in post catalytic bed volume reactor and reached 43.6 % PO selectivity at 17.6 % propene conversion over Mo/SiO_2 catalysts under again a relatively higher pressure of 5 atm [24, 25]. After these studies, DFT calculation performed by Kizilkaya et al. [26] showed that the activation barrier for PO production is lower than that for acrolein formation and combustion reaction for gas-phase radical chain reactions.

Hexagonal mesoporous silicas (HMS) containing transition metals such as Ti- and Al- synthesized with sol–gel method showed 47.8 % of propene conversion and 30.6 % of selectivity of PO. However deactivation of the catalysts during the reaction is very high and it does not disappear completely by the addition of H_2 [27].

The effectiveness of Cu containing catalyst was investigated after determining of Cu is more selective than Ag catalysts for alkene epoxidation [28–37]. Many studies have been performed to understand the reason behind the higher activation of Cu metal and further enhancement of the catalytic activity by use of different support materials and promoters. Torres et al. explained the superior properties of Cu in PO selectivity due to lower basicity of oxygen adsorbed over Cu. The same property is observed in comparison of Cu single system with Ru-Cu bimetallic system by DFT calculation. Kizilkaya et al. [36] stated that the higher basicity of the atomic oxygen adsorbed on Ru-Cu favors the subtraction of allylic hydrogen of propene instead of formation of PO intermediate. The active oxidation state of Cu in epoxidation reaction is investigated by many groups but there is still a lack of complete agreement. Vaughan et al. stated that the active form of copper is Cu^0 species in highly dispersed atomic like form while Zhu et al. stated that of Cu^I is active form [30, 33]. In addition to this, Su et al. concluded that both form of Cu (Cu^0 and Cu^I) especially Cu^0 form in the small oxide cluster are necessary for propene epoxidation. It was reported that the best modifier for Cu is halogen-free K at different reaction conditions [32].

In spite of world-wide efforts, the lack of a breakthrough in propene epoxidation catalysis 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 [38–42] made pioneering contributions to this field through the development of novel high-throughput catalyst preparation and screening tools. In particular, they developed array channel micro-reactors to rapidly screen a large number of catalytic materials in parallel [38, 39]. Recently, they reported the discovery of a new SiO_2-supported trimetallic RuO_2–CuO_X–NaCl catalysts gave the high PO yield (40–50 % PO selectivity at 10–20 % conversion) for the direct epoxidation of propylene by molecular oxygen under atmospheric pressure [42].

Preparation and screening of a wide variety of catalysts using high-throughput methods allow investigating many parameters such as metal amount, promoter/metal ratio, metal-support interaction, reaction temperature, reactant gas ratio etc. in a short time. In order to be able to synthesize catalysts in a much faster combinatorial fashion, a commercial synthesis apparatus was adapted in our laboratory to prepare catalysts using a sol–gel method. In this respect, a large number of modified Cu catalysts supported on low (SiO_2) and high (m–SiO_2) surface area mesoporous silica were prepared to investigate the effect of metal loading and promoter effects on the propene conversion and PO selectivity at different reaction conditions. High-throughput catalytic screening tests were performed using computer controlled array channel microreactor system.

2 Experimental

2.1 Catalyst Preparation

Cu supported on silica was prepared by a combinatorial approach using a single step sol–gel method. The synthesis apparatus used for this purpose contains 24 cells where catalysts can be simultaneously synthesized. The synthesis reactor block has a capability for reflux by circulating cold water. Magnetic stirring is also provided for each cell where a catalyst is synthesized. Reflux capability is an advantage during synthesis of the catalysts, such as low surface area silica that requires high temperature conditions. Besides, inert gas could be used if required during catalyst synthesis.

Silica (SiO_2) supported catalysts were prepared using the following precursors; tetraethyl orthosilicate (TEOS) as a silica source, ethanol (EtOH) as a solvent, deionized water, 1 M of HNO_3, 0.5 M of NH_4OH and metal nitrate salts as metal sources [such as $Cu(NO_3)_2$, KNO_3, $Y(NO_3)_3$, $Ce(NO_3)_3$ and $LiNO_3$]. All the chemicals used in synthesis were provided from Sigma-Aldrich and Fluka. The basis of preparing metal containing silica was taken as 1 g of SiO_2 and amount of precursors were determined on this basis. The molar ratio of TEOS:EtOH:HNO_3:H_2O:NH_4OH were 1:20:1:13:0.5 for silica and metal loadings were changed from 0.5 to 10 wt%. The metal loading represents the ratio of Cu metal or alkaline metal to the total amount (SiO_2 + metal). The necessary amount of metal nitrate salts was calculated from this metal ratio. During preparation, as a first step TEOS, the corresponding amount of EtOH, 1 M of HNO_3, and water were mixed by stirring at room temperature and then heated to 80 °C. After obtaining a clear solution of TEOS:EtOH:HNO_3:H_2O, the required amount of metal precursor was added into this solution under vigorous stirring and reflux conditions. Finally, NH_4OH was added into the clear solution and stirred until gelling. The obtained gel was aged at room temperature then dried at 120 °C and calcined at 550 °C in air for 5 h.

High-surface area silica (m–SiO_2) was prepared according to the method given in the Ref. [27]. The corresponding amount of dodecylamine (DDA) as a template, deionized water, metal nitrate and the concentrated HNO_3 were mixed in a tube and stirred for 1 h. Then, the mixture of TEOS and EtOH was added to this solution and stirred for 4 h at ambient temperature. Finally, the resulting mixture was aged for 20 h at room temperature. The obtained solid product was filtered, dried and calcined at 650 °C for 3 h to remove the template.

2.2 Activity Tests

Catalyst evaluations were performed using computer controlled array channel microreactor system described previously in Ref. [38]. In the system, up to 80 catalysts could be screened in parallel. However in our study, 20 catalyst candidates were tested in one screening experiment and one data point was obtained ∼3 min for one catalyst. In the array microreactor, 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 [41]. All experiments were performed using 5 mg of catalyst under atmospheric pressure and at a gas hourly space velocity (GHSV) of 20,000 h^{-1}, representing a differential reactor condition. Initial screening experiment was performed at 0.5 of C_3H_6/O_2 molar ratio and at 225, 275, 300 and 350 °C reaction temperatures.

After first screening, activity tests were repeated for different C_3H_6/O_2 molar gas ratios at the same reaction temperature (0.1–1.5). Reactor effluent streams were analyzed by withdrawing the products immediately over the catalyst pellet using a heated capillary sampling probe followed by online gas chromatography [Varian CP-4900 Micro GC with thermal conductivity detector, Porapak Q (10 m) and Molecular sieve 13× (10 m) columns]. The selectivity of PO is defined as the percent of amount of carbon in PO in all the reaction products. The selectivity of the other C_3 products, such as propionaldehyde plus acrolein (PaL + AC), acetone (AT) and acetaldehyde (AD) were calculated in the same way. The formation rate of reaction products was found by multiplying overall consumption rate with selectivity to each product.

2.3 Characterization

After screening various catalysts, some characterization tests were applied to evaluate physical and chemical properties. Powder X-ray diffraction (XRD) analysis was performed using X'pert Pro XRD operated at 40 kV and 45 mA. The surface areas and total pore size of catalysts were calculated using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively from isotherms obtained with Micromeritics Gemini V and Micromeritics ASAP 2010 apparatus. Also, TEM micrographs were obtained using JEOL JEM-2000FX TEM.

3 Results and Discussion

3.1 Characterization Results

Support–metal interaction is one of the parameters that was considered as being effective on the catalytic performance. Therefore various metals and promoters were loaded into the silica materials synthesized with and without template. The morphological effect of these two types of materials was first investigated. The N_2 adsorption–desorption isotherms of undoped SiO_2 and m–SiO_2 materials were given in Fig. 1a, b. Both silicas showed type IV isotherm according to BDDT classification. As seen in Fig. 1a, the broad hysteresis loop belongs to SiO_2 shows desorption branch being much steeper than the adsorption branch; thus indicates the filling and emptying of the mesopores by capillary condensation. The nearly reversible isotherm of m–SiO_2 showed type IVc isotherm which forms due to reversible pore filling and emptying of a narrow range of uniform near-cylindrical pores of critical size. The BET surface area and BJH average pore size were 207 m^2 g and 32 Å for bare SiO_2 and 1185 m^2 g and 26 Å for bare m–SiO_2 respectively.

Fig. 1 N$_2$ adsorption–desorption isotherm of empty **a** SiO$_2$ and **b** m–SiO$_2$ support material
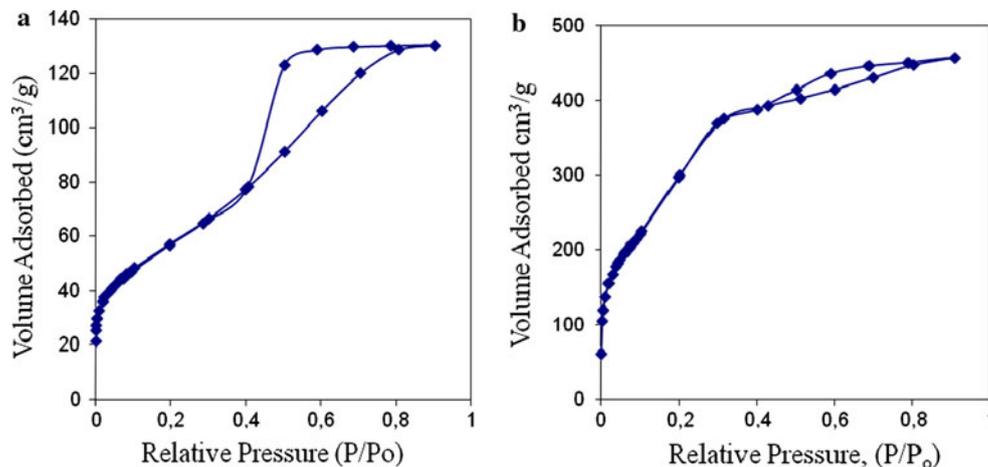
The crystalline phases of the catalysts were determined by XRD technique for selected catalysts. The results showed that both high and low surface area silicas are amorphous and also there is no diffraction peaks corresponding to copper or copper oxides regardless of the loaded Cu amount (these data are not given). No peaks were observed including 9 % metal loading for both support materials. This indicates that copper/copper oxide crystallite size is very small (<5 nm). In fact, these findings were confirmed with TEM measurements as shown in Fig. 2a, b. There was no sufficient contrast between metal/metal oxide particles and silica supports. This may be due to well-dispersed particles and it may not be easily detected by TEM [43]. When the dark area in the TEM image of promoted and un-promoted catalysts were investigated closely there is no fringe belonging to any crystalline phase. In conclusion the particle size of loaded Cu is too small to be detected with XRD and TEM. The addition of K did not change this result.

3.2 Activation Test Results

The first catalytic screening test was performed on low surface area silica (SiO$_2$) supported Cu catalysts with and without promoters at 225, 275, 300 and 350 °C reaction temperatures and 0.5 of C$_3$H$_6$/O$_2$ molar ratio. For catalysts without promoters, the effect of different reaction temperature on the propene consumption and PO production rates were shown in Fig. 3a, b. As seen in Fig. 3, both consumption and production rates increased with reaction temperature. Although there was a small decrease in PO selectivity above 300 °C, propene conversions continued to increase with temperature (Fig. 3b). Hence PO production rates stayed high at 350 °C. The highest PO production rate was obtained as 3.51 μmol/g/cat./min for 2 % Cu containing silica at 350 °C due to high propene conversion rate (68.76 μmol/g/cat./min) at this content. Overall consumption rate and PO production rate decreased with Cu metal loadings higher than 2 %.
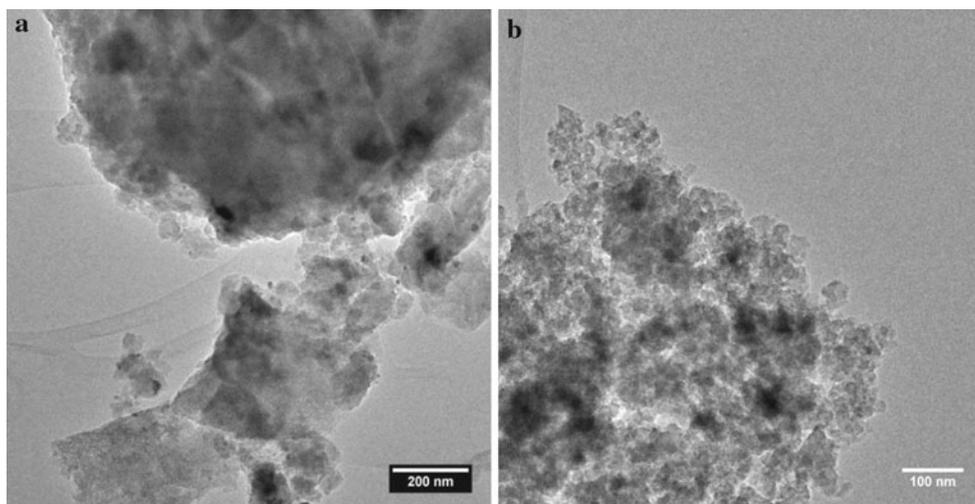
Fig. 2 TEM image of **a** 1 % Cu–SiO$_2$ and **b** 3 % Cu–m–SiO$_2$ catalysts

a

b
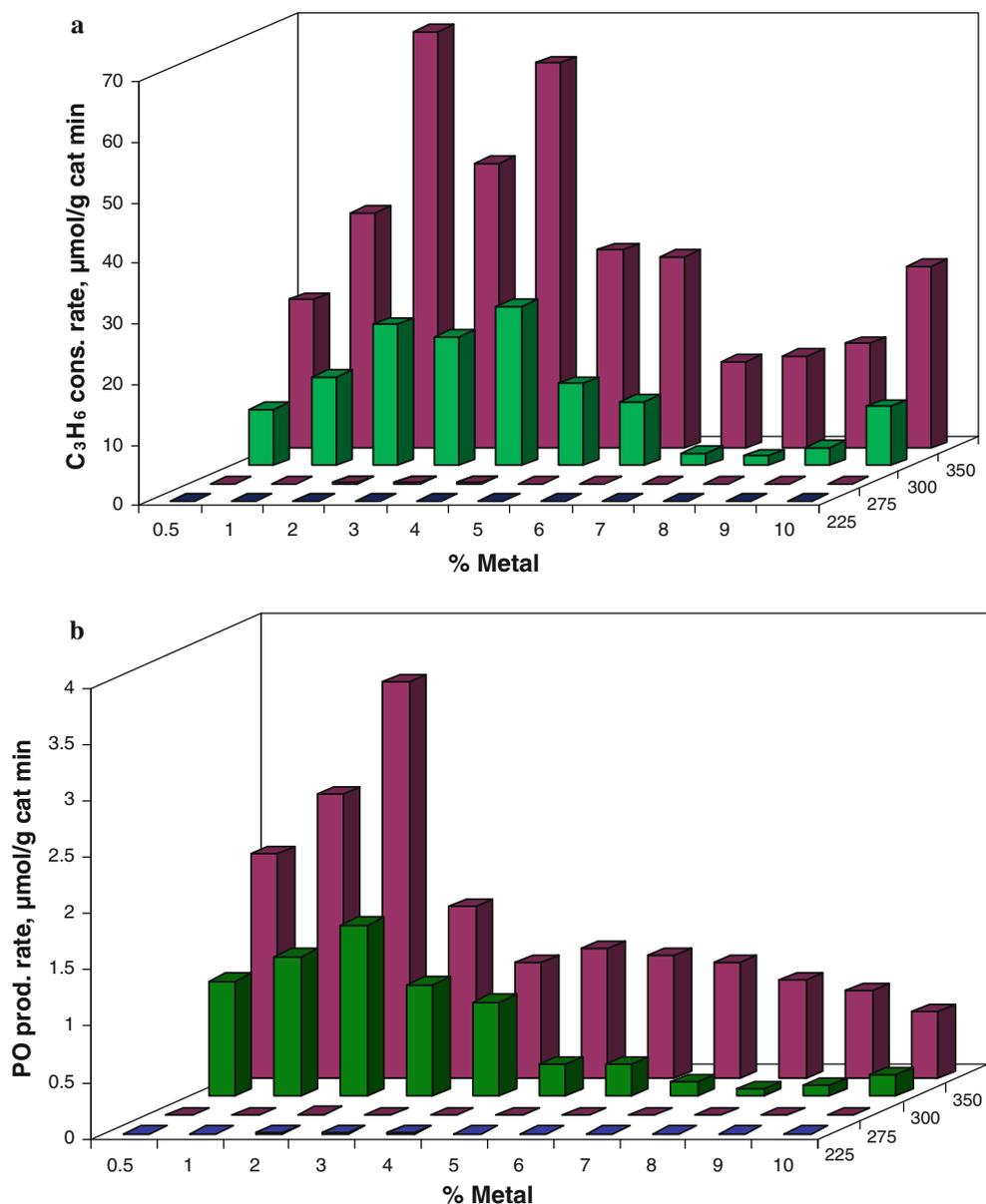
Fig. 3 a Overall consumption and **b** PO production rate of un-promoted Cu/SiO$_2$ catalysts as a function of metal loading at different reaction temperatures

Since we observed low PO yields (maximum at 0.08 % for 2 % Cu–SiO$_2$ catalyst), Cu/SiO$_2$ catalysts were promoted with metals, such as K, Li, Ce and Y. Promoter/metal ratio ranged between 0.1 and 1.0 % for all catalysts. Although the promoter effect of K and Li over Cu containing catalysts was investigated by several research groups [32], the promoter effect of Ce or Y for Cu based catalysts has not studied. Our activity test results showed that Ce and Y enhanced the overall propene consumption rate sharply while decreasing PO selectivity but increasing selectivity to PaL + AC regardless of the metal amount. However, K and Li enhanced both the overall propene consumption and PO production rates for all Cu content.

Although 2 % Cu catalyst gave the highest production rate, the PO selectivity was maximum (8.08 %) for 0.5 % Cu catalyst. So the promoter effect of K and Li was summarized for 0.5 % Cu catalyst in Fig. 4a, b at 300 and 350 °C reaction temperature respectively. These two reaction temperatures were selected because of the higher selectivity and conversion values. As seen in the Fig. 4a, the addition of 0.05 wt% of K and Li sharply increased overall propene consumption rate and this was significant especially for Li promoter. In fact the consumption rate increased from 24.57 to 82.21 µmol/g/cat./min on Li promoted catalyst whereas to 71.12 µmol/g/cat./min on K promoted catalysts at 350 °C. In contrast to this activity
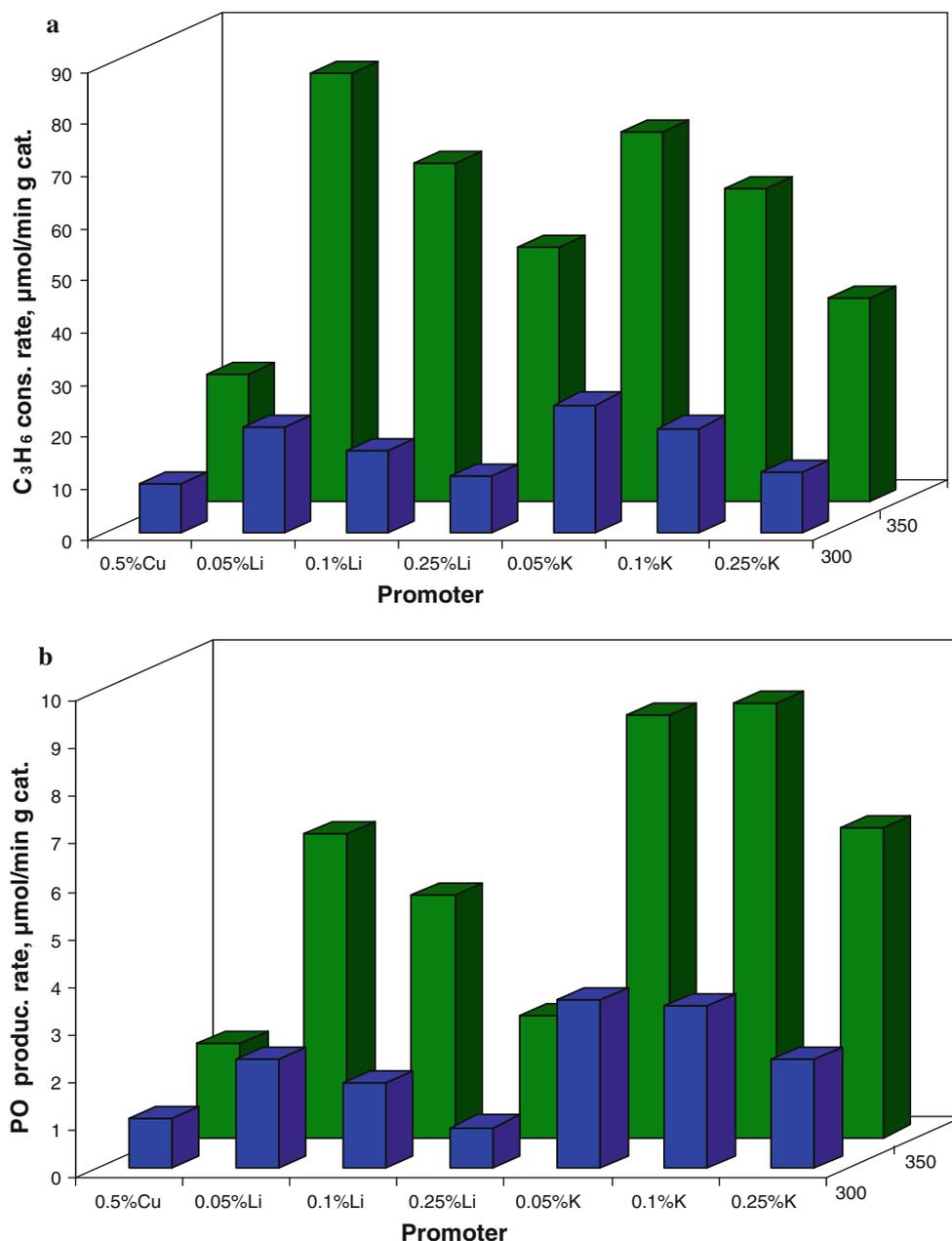
Fig. 4 **a** Overall consumption and **b** PO production rate of K and Li-promoted 0.5 % Cu/SiO$_2$ catalysts at 300–350 °C

trend, K was more effective promoter for PO production rate because of relatively higher PO selectivity. It increased from 1.99 to 8.87 μmol/g/cat./min on K whereas to 6.39 μmol/g/cat./min on Li promoted catalyst at a K/Cu rate of 0.1 (0.5 % Cu–0.05 % K/SiO$_2$). An addition of 0.1 wt% K (K/Cu = 0.2) had again a positive effect on PO formation and further increase in promoter loading (K/Cu = 0.5) caused a decrease in both consumption and production rates but they were still higher than those of un-promoted catalyst. PO production rate reached 9.13 μmol/g/cat./min (15.21 % selectivity and 1.41 % conversion) for 0.1 % K–0.5 % Cu catalyst.

The same trend was observed for 1–2 % catalysts. An addition of K at a ratio of 0.1 increased the rate from 2.51 μmol/g/cat./min (6.48 % selectivity and 0.89 % conversion) to 9.40 μmol/g/cat./min (11.83 % selectivity and 1.87 % conversion) for 1 % Cu catalyst. For 2 % Cu catalyst, it increased from 3.51 μmol/g/cat./min (5.10 % selectivity and 1.58 % conversion) to 10.99 μmol/g/cat./min (7.90 % selectivity and 3.14 % conversion). Lithium did not enhance catalytic performance as much as K. Among all the catalysts tested, 0.5 % Cu catalyst again gave the highest selectivity to PO (16.69 %) at a K/Cu ratio of 0.5. However K promoted not only PO selectivity but

Table 1 Promoter effect of K on selectivity of reaction products for 0.5 % Cu/SiO$_2$ catalyst at 350 °C

K/Cu	Conv. (%)	Selectivity (%)				
		PO	PaL + AC	AT	CO$_2$	AD
0	0.57	8.08	65.18	3.66	22.14	0.93
0.1	1.60	12.47	57.84	1.87	27.26	0.56
0.2	1.41	15.21	52.53	1.32	30.47	0.47
0.5	0.88	16.69	50.47	1.05	31.35	0.43

also CO$_2$ selectivity while decreasing the production of PaL + AC and AT. Table 1 summarizes the product distributions of 0.5 % Cu/SiO$_2$ catalyst at different promoter ratio and a reaction temperature of 350 °C.

After determining the best catalysts as 0.5 % Cu–0.1 % K catalyst with 9.13 μmol/g/cat./min PO production rate for low surface silica supported catalysts, the catalytic activity tests were performed for high surface area silica (m–SiO$_2$) based catalysts. First, the screening test was performed over un-promoted catalysts. Contrary to the SiO$_2$ supported catalysts, propene consumption rate increased with Cu loading and reached to 653.39 μmol/g/cat./min for 10 % Cu/m–SiO$_2$ catalyst at 350 °C with low PO selectivity (2.49 %). However, for SiO$_2$ supported catalyst, the maximum PO production (3.52 μmol/g/cat./min) and propene consumption rate (68.76 μmol/g/cat./min) were obtained for the catalyst containing 2 % Cu and a further increase in the loading decreased propene consumption and selectivity to PO. It can be concluded that Cu might be more dispersed over high surface area support than low surface area silica. However the average pore size of the m–SiO$_2$ support is less than that of SiO$_2$ support and this size might not be enough to allow the desorption of

oxygenated products. The captured products in the pores are oxygenated further and produce more combustion reaction product.

Since a positive effect of promoters was observed on the low surface area silica based catalysts, the same promoters were also loaded into the high surface area silica supported Cu catalysts. The first screening test showed that all the promoters had the same enhancement effect on PO yield at all Cu loadings, but it was again more on K promoted catalysts. Therefore, we focused our attention on K promoted Cu/m–SiO$_2$ catalysts to find out optimum K/Cu ratio.

When the PO production rate was investigated as a function of K/Cu ratio, the better performance was obtained at 0.5 and 0.75 K/Cu ratio. Figure 5 shows the performance of promoted catalysts at a promotion ratio of 0.5 and different reaction temperatures. As seen in Fig. 5, the PO rate showed a dome shape of activity versus metal loading at each reaction temperatures and this was easily seen at 350 °C. Among all the catalysts, 5–7 % Cu catalysts gave relatively better performance at 0.5 ratio because of high propylene consumption and then PO production dropped for 10 % Cu catalyst. The modification of 10 % Cu catalyst with K caused noticeable decrease in propene conversion without significant improvement in PO selectivity. On the other hand PO production rate of 5 % Cu catalyst increased from 14.39 μmol/g/cat./min (2.45 % selectivity and 13.77 % conversion) to 23.61 μmol/g/cat./min (9.18 % selectivity and 5.92 % conversion) at 350 °C. At this K/Cu ratio, production rate obtained over 3 % Cu catalyst was 19.55 μmol/g/cat./min (18.16 % selectivity and 2.48 % conversion).

However when the K/Cu ratio was increased to 0.75 ratio, the PO production rate continued to increase for 3 % Cu catalyst while it decreased for other catalysts. When all
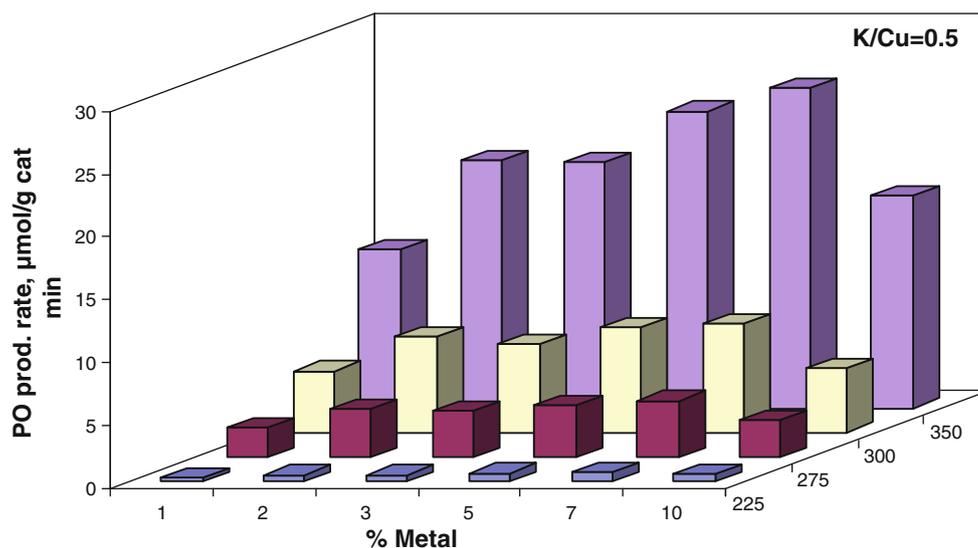
Fig. 5 PO production rate for modified Cu catalysts at a K/Cu ratio of 0.5

Fig. 6 PO production and propene consumption rate for promoted 3 % Cu/m–SiO$_2$ catalyst at 350 °C
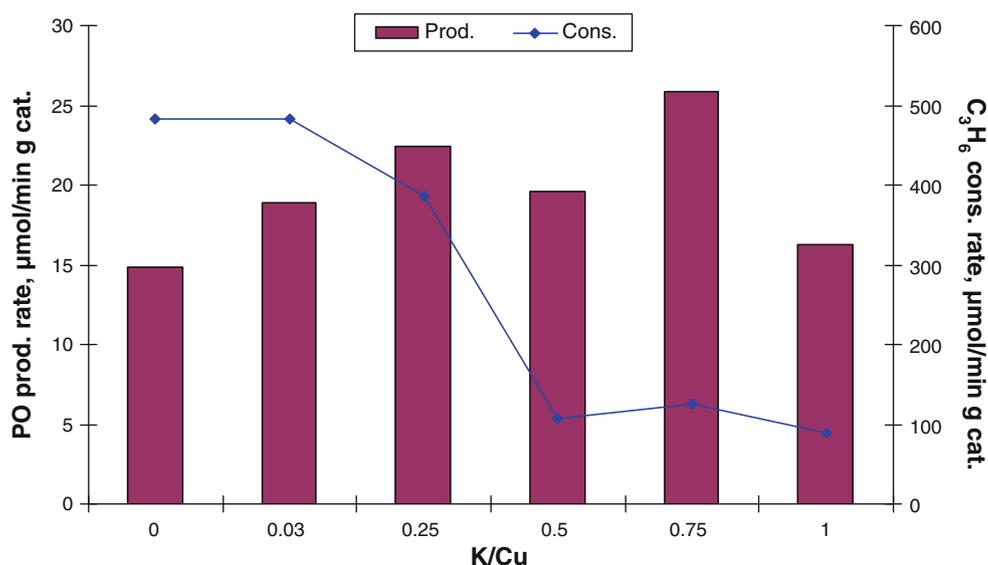
the catalysts modified with K were compared, the maximum PO production rate, 25.82 µmol/g/cat./min (20.49 % selectivity and 2.90 % conversion) was obtained for 3 % Cu–2.25 % K (K/Cu = 0.75) catalyst at 350 °C even with lower consumption rate. So the promoter effect of K at different promotion ratio over overall consumption and PO production rate were summarized for 3 % Cu/m–SiO$_2$ catalyst in Fig. 6 and Table 2.

As seen in Fig. 6, there was a sharp decrease in consumption rate with K/Cu ratio especially >0.25. Above that point the consumption rate stayed approximately constant. Despite this noticeable decrease in propene consumption, PO production rate increased and reached the maximum value (25.82 µmol/g/cat./min) at a Cu/K ratio of 0.75. It also showed high performance at 0.25 ratio because of high conversion (8.89 % conversion and 5.80 % selectivity). However the maximum value at 0.75 is due to high PO selectivity (20.49 % selectivity and 2.90 % conversion). Table 2 showed the product distribution as a function of K/Cu ratio for 3 % Cu/m–SiO$_2$. Un-promoted Cu catalyst generally gave PaL + AC and CO$_2$ as the main oxygenated products. However, the addition of K caused inhibition of

PaL + AC production while increasing the PO selectivity and also small change was observed for other reaction products.

After 3 % Cu–2.25 % K/m–SiO$_2$ catalyst was determined as the best catalyst, the reproducibility in terms of the activity of this catalyst was tested several times to determine reliability. The reproducibility of this catalyst for PO production rate is within 3 %. If the catalyst was kept in air-proof environment, its PO production rate did not change. If it was exposed to air, its catalytic performance decreased.

In addition to testing at different reaction temperatures, C$_3$H$_6$/O$_2$ molar ratio was also changed from 0.1 to 1.5 to determine an appropriate reactant gas ratio leading to a high PO production rate at the beginning of the study. These results showed the optimum ratio to be 0.5 for silica supported Cu catalysts at all temperatures.

Arrhenius plots given in Fig. 7 shows the effect of addition of K on the temperature dependence of propene consumption and PO production. The activation energy of un-promoted 3 % Cu catalyst (92 kJ/mol) is higher than 2.25 wt% K-promoted catalyst (71 kJ/mol). However, the activation energies for PO production of two catalysts were approximately the same ($\sim$75 kJ/mol). The obtained activation energies for the overall consumption rate of modified and un-modified catalysts are comparable to those obtained for CuO$_x$/SBA-15 catalyst by Wang et al. [32].

4 Conclusions

High-throughput sol–gel catalyst synthesis and also high-throughput screening methods were used to investigate the effects of metal loading, support type and promoter for the direct synthesis of PO from propene and oxygen at

Table 2 Promoter effect of K on selectivity of reaction products for 3 % Cu/m–SiO$_2$ catalyst at 350 °C

K/Cu	Conv. (%)	Selectivity (%)				
		PO	PaL + AC	AT	CO$_2$	AD
0	11.12	3.1	55.7	1.0	39.9	0.4
0.03	11.34	3.9	52.7	0.9	42.1	0.3
0.25	8.89	5.8	53.6	0.7	39.5	0.4
0.5	2.48	18.2	42.2	0.5	38.9	0.3
0.75	2.90	20.5	40.8	0.6	37.7	0.3
1.0	2.10	18.2	43.2	0.5	37.8	0.3
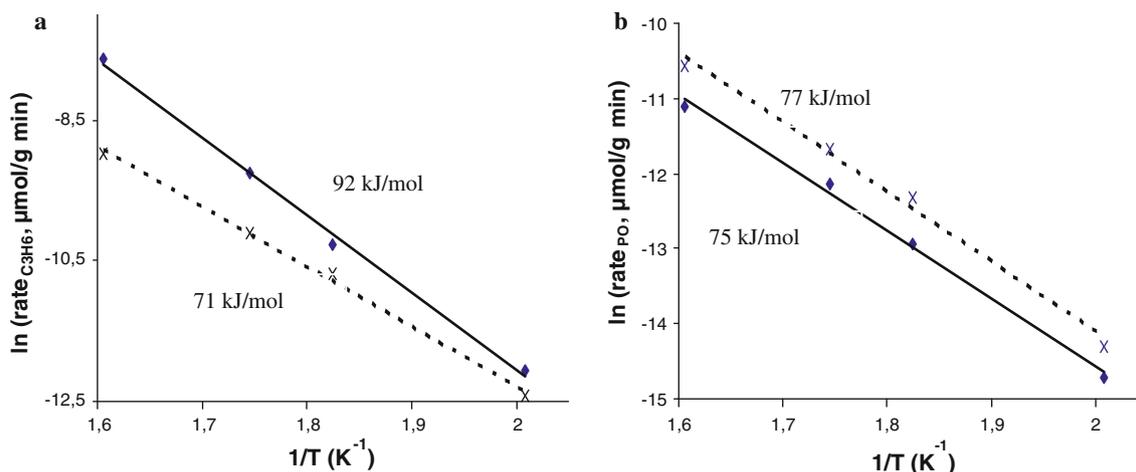
Fig. 7 Arrhenius plots for the oxidation of propene (**a**) and PO production (**b**) over 3 % Cu/m–SiO$_2$ (*straight line*) and 3 % Cu–2.25 % K/m–SiO$_2$ (*dashed line*) catalysts

atmospheric pressure. Our results showed that both types of mesoporous silicas with different pore sizes showed different activity and selectivity behavior as a function of metal loading. High Cu loadings resulted in high C$_3$H$_6$ conversions over m–SiO$_2$ while overall conversion rate decreased above 2 % loading over SiO$_2$ catalysts. This could be explained by the higher agglomeration of Cu on SiO$_2$ as opposed to that on m–SiO$_2$. Large Cu metal particles decreased the catalytic performance. Because of high conversion and selectivity, the highest PO production rate was obtained over m–SiO$_2$ catalysts. The addition of a promoter such as K enhanced production rates by increasing the PO selectivity. There was no noticeable change in XRD diffraction patterns and TEM images due to addition of K. However K addition resulted in lowering activation energy for overall consumption rate (from 92 to 71 kJ/mol). The activation energies for PO production are the same for both promoted and un-promoted catalysts (77 vs. 75 kJ/mol). This indicates that K neutralizes the acid sites of silica.

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