Highly Diluted Copper in a Silica Matrix as Active Catalyst for Propylene Oxidation to Acrolein

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Abstract The use of copper phthalocyanine as the copper precursor extremely diluted in a silica matrix (below 0.1%) was found to result in a very active catalyst in the selective oxidation of propene by oxygen to produce acrolein with selectivities above 50% and yields of $\sim 10\%$.

1 Introduction

The long known direct oxidation of propene either to acrolein or acrylic acid using molecular oxygen as oxidant has recently attracted renewed interest both in academia and industry, because of fundamental reasons concerning hydrocarbon activation and oxygen insertion, in spite of the fact that already a large variety of catalysts had been investigated for this reaction. The benchmark nowadays is of course the industrially used bismuth molybdate system [1], but earlier, a number of copper based catalysts had been reported as well.

For instance, in the late forties Hearne and Adams were the first to discover that cuprous oxide is a selective catalyst for the oxidation of unsaturated hydrocarbons. These studies led to an industrial process in which a Cu_2O/SiC material with high copper loadings (1:2 molar ratio Cu/SiO_2) was used as catalyst. In this process, I_2 was employed as promoter and water was used to improve the acrolein selectivity, getting 10–12% conversion and 60–80% selectivity [2, 3]. In very early work from Woodcock,

copper was impregnated onto a support composed of a mixture of Fe_2O_3 and Al_2O_3 [4, 5]. During reaction, a stream of selenium was passed through the catalyst bed, by which reaching 18% propylene conversion and 62% selectivity to acrolein.

In previous studies, copper catalysts were also obtained by ion exchange of copper nitrate with zeolite X and Y [6, 7]. However, the resultant material showed lower yield to acrolein in comparison with the above mentioned processes (5% yield at conversion of propylene equal to 70%). Alternatively, copper based materials were obtained via wet impregnation (to result in relatively high copper amount) of SiO_2. With these materials acrolein was detected as main reaction product, the best reported result being 9% conversion and 35% selectivity to acrolein [8]. In 2006, Wang and co-workers [9] used a halogen-free modified CuO_x/SBA-15 with a high oxygen excess for the epoxidation of propylene. This material showed better activity for the epoxidation reaction, but similar results concerning the acrolein production in comparison with more conventional materials.

The influence of copper oxidation state and copper oxide(s) structure on catalytic activity and selectivity is still under debate. In fact, both aspects are highly dependent on reaction conditions (i.e. gas composition and reaction temperature). In particular it should be noted that while propylene is a reducing agent, molecular oxygen is an oxidizing agent. Thus, depending on the gas phase composition, different oxidation states and substrate surface compositions may be present during reaction. Additionally, reaction temperature may influence the above mentioned parameters making the situation more complicated. For instance, Wise and colleagues [10] proposed that the selectivity to acrolein reaches a maximum at a catalyst composition close to the stoichiometric cuprous (I) oxide,

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while the presence of CuO lead to complete oxidation products. However, a well established reaction mechanism and a complete agreement concerning the above mentioned issues are still lacking.

In a high throughput program focused on propene oxidation we have recently identified a surprisingly active copper catalyst on SBA-15 with an extremely low copper loading and correspondingly a very high per site activity for propene oxidation to acrolein. Although the system does not reach the performance of the commercial bismuth molybdate composition, it nevertheless has remarkable and promising properties, which will be reported in the following.

2 Experimental

The support of choice was SBA-15 which was prepared according to literature [11]. Copper phthalocyanine (Alcian blue pyridine variant, $C_{56}H_{40}Cl_4CuN_{12}$, Sigma-Aldrich) was dissolved in water and loaded onto the support by incipient wetness impregnation. The samples were subsequently dried at 50 °C overnight, and calcined at 450 °C for 3 h. Furthermore, the amount of copper precursor impregnated was varied in order to obtain different metal loadings (Cu/SBA-15; 0.06, 0.3, 0.9, 1.2 wt% of Cu as adjusted by the loading.

Other Cu/SiO_2 catalysts for comparison were prepared by incipient wetness impregnation, using different precursors ($Cu(NO_3)_2$, $Cu(Ac)_2$, CuPc- tert-butyl (Alcian Blue, dye content 97%, $C_{48}H_{48}CuN_8$, Sigma-Aldrich) and supports (amorphous SiO_2, u i.e. Aerosil 380, Degussa), amorphous TiO_2 (purity 99,9 Sigma-Aldrich), Al_2O_3 (puriss. Sigma-Aldrich) and Zeolite Na-Y ($SiO_2/Al_2O_3 = 5.9$, Degussa).

Catalytic tests were carried out in a fixed-bed quartz reactor operating at atmospheric pressure. Different amounts of catalyst were loaded into the middle of the hot zone of the quartz tube reactor for catalytic evaluation. Reaction temperature was measured by a thermocouple placed in the catalytic bed. Another thermocouple, placed externally in the same position of the above mentioned one together with a Eurotherm 2216e temperature controller, was used to set reaction temperature and heating rates. A reaction mixture consisting of ($C_3H_6/O_2/N_2 = 1/5/94$) was passed through the catalyst bed of catalyst particles of 50 μm; total flow rates were varied from 6.25 to 100 mL/min (STP), and catalytic activity was usually evaluated in the 300–500 °C temperature range.

The effluent gas was analyzed by an on line gas chromatograph (Agilent Technologies 6890N) equipped with a Restek RTX-1 # 10187 column, methanizer, and a flame ionization detector. The carbon mass balance based on the carbon atoms of propene entering the reactor was monitored for all experiments and typically closed to $100 \pm 5\%$.

3 Results and Discussion

CuPc-Py/SBA-15 catalysts having different metal loadings were tested under different reaction conditions in the selective oxidation of propylene. The first parameter taken into account was the effect of temperature on conversion and selectivity. With respect to this, it has been found that independently from other parameters the best activity and selectivity could be obtained in the 475–500 °C temperature range. It has to be mentioned that the bare SBA-15 has been also tested as a blank under all reaction conditions employed here, showing always conversions below 2%. Besides acrolein which was under optimized condition the main reaction product, other detected products were CO, CO_2, and acetic aldehyde, as also shown in Fig. 1. Acetic aldehyde starts to be formed at temperatures exceeding 425 °C.

A survey of selected results obtained in the 475–500 °C temperature range under several experimental conditions is given in Table 1. Copper loading and oxygen partial pressure in the gas mixture were identified from the very beginning as key parameters in order to obtain high selectivity to acrolein. The influence of metal loading on the selectivity to acrolein can be easily visualized for catalysts tested under identical conditions (compare entries Nr. 1, 4 and 8 in Table 1). It is evident that acrolein selectivity decreases drastically when the copper loading increases, from ca. 42% (0.06 wt% Cu) to ca. 11% (0.9 wt% Cu). This coincides with an increase in propylene conversion (from 13.5 to 72.4%) and selectivity towards CO and CO_2. The copper catalyst loading at which optimal performance is obtained is very low, if it is compared to either Lambert's work [8] or other Cu-based catalyst reported to date [9]. The influence of oxygen partial pressure on the selectivity to
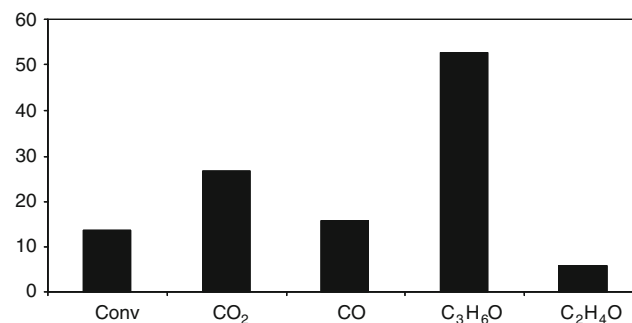

Fig. 1 Conversion and selectivity versus main reaction products at propylene/oxygen ratio 1:1 over 0.06 wt% CuPc-Py/SBA-15 working at 5,000 cm^3 g_{cat}^{-1} h^{-1} and 500 °C

acrolein can be seen from entries Nr. 4, 5, 6 (0.3 wt% Cu) and 11, 12 (0.06 wt% Cu) in Table 1. As one can see, a decrease of oxygen partial pressure (the propylene partial pressure in the gas mixture has always been kept equal to 1×10^{-3} MPa) corresponds to an increase in acrolein selectivity. Furthermore, as observed for the metal loading, also in this case a decrease in acrolein selectivity coincides with an increase in conversion.

Influence of space velocity was also studied. It was generally observed that product composition was a function of the above mentioned parameter for all copper loadings studied. In fact, selectivity increased when lower contact times were employed (entry Nr. 8, 10 and entry Nr. 2,7 for the 0.06 wt% and the 0.3 wt% materials, respectively). The opposite trend was obviously observed for propylene conversion.

Although a thorough investigation of the dependence of the acrolein selectivity on the oxidation state of copper was not the goal of this work, it is interesting to notice that acrolein was still the main reaction product (selectivity up to 42%) at temperatures as high as 475 °C and with a propylene/oxygen ratio equal to 1/5. Under these conditions, copper would most likely be present on the catalyst as Cu (II) (i.e. CuO). This is quite surprising, since in previous studies performed by Lambert and colleagues, Cu (II) was identified as species responsible for full combustion [8]. It would be interesting to determine the oxidation state of the copper during the reaction. However, due to the extremely low copper concentration this is almost impossible with the catalysts studied here.

Influence of calcination temperature on catalytic activity was also taken into account. CuPc-Py/SBA-15 (0.3 wt%) was submitted to calcination treatment at different temperatures (450, 550 and 650 °C). The obtained materials were subsequently tested, showing almost identical activity, indicating that calcination prior to catalytic evaluation is not a key parameter for the preparation of active materials. Lower calcination temperatures have not been taken into account because of the decomposition temperature of the copper phthalocyanine (Fig. 2), as studied by thermogravimetry performed using a Netzsch STA 449C thermal analyzer operated in air flow with a heating rate of 5 °C min^{-1}.

As one can see, complete decomposition of pure copper phthalocyanine is observed at a temperature of ca. 380 °C. Although this temperature might be somewhat different for supported copper phthalocyanine, all materials were calcined at 450 °C prior to catalytic evaluation.

Finally, the CuPc-Py/SBA-15 was characterized by TEM before and after reaction and no bulk copper phase
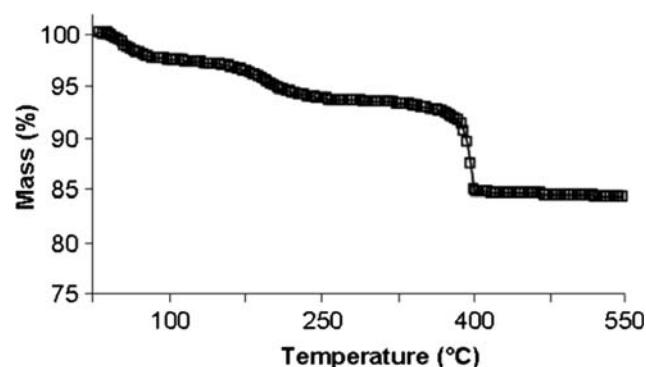

Fig. 2 TG measurement for decomposition of copper phthalocyanine in SBA-15

Table 1 Propylene conversion and selectivity to acrolein over CuPc/SBA-15 catalysts

| Entry Nr.	Cu loading (wt%)	C_3H_6/O_2 ratio	Space velocity ($cm^3\ g_{cat}^{-1}\ h^{-1}$)	Temp (°C)	Conversion (%)	Selectivity (%)	Yield (%)
1	0.9	1/5	15,000	475	72.4	10.9	7.9
2	0.3	1/5	30,000	475	21.4	30.6	6.5
3	0.3	1/3	30,000	475	7.9	39.4	3.1
4	0.3	1/5	15,000	475	30.5	28.1	7.8
5	0.3	1/3	15,000	475	13.1	48.2	6.3
6	0.3	1/1	15,000	475	6.7	54.8	3.7
7	0.3	1/5	7,500	475	59.0	14.9	10.0
8	0.06	1/5	15,000	475	13.5	41.8	5.6
9	0.06	1/5	7,500	475	19.6	42.1	8.3
10	0.06	1/5	5,000	475	27.3	34.7	9.5
11	0.06	1/3	5,000	500	21.8	41.7	9.1
12	0.06	1/1	5,000	500	14.5	52.8	7.7
13	0.06	1/5	3,750	475	40.1	25.5	10.2
14	0.06	1/5	3,750	400	18.9	42.0	7.9
15	0.06	1/1	2,500	500	22.6	41.7	9.4
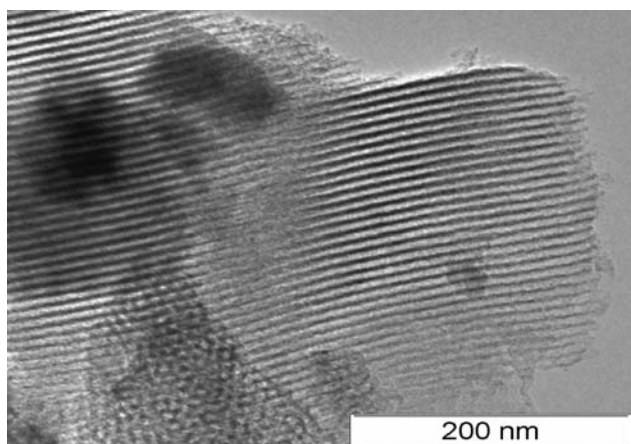
Fig. 3 CuO$_x$/SBA-15 0.3 wt% catalyst after reaction

was observed either in the mesopore channels or on the outer surface. Large particles of copper containing species would be detectable even at the low copper loading. The fact that the copper obviously remains in a highly dispersed state is attributed to the very low copper loading which prevents aggregation of copper species to bigger particles (Fig. 3).

Catalysts based on CuPc-Py/SBA-15 were compared with catalysts prepared with different precursors and supports. Results of this comparison are shown in Table 2.

Best activity and selectivity to acrolein were obtained with copper phthalocyanine pyridine as precursor. Use of conventional amorphous silica instead of the ordered mesoporous SBA-15 did not change the activity and selectivity significantly. However, irrespective of the specific form, silica was identified as the best support for this reaction, since activity and selectivity obtained over other supports were much worse. This is clearly visible by looking at entries 6, 7 and 8 in Table 2.

Furthermore, since previous studies had suggested that potassium has a beneficial effect on this reaction [9], a

CuPc-Py-K/SBA-15 catalyst was prepared by incipient wetness impregnation of an equimolar solution containing copper phthalocyanine and KNO$_3$ in SBA-15. The obtained catalytic results for this material are also compiled in Table 2. Entries 9 and 10 show, that the potassium doped material has lower activity than the standard CuPc-Py based system, although selectivities were rather similar. Potassium thus rather seems to have a detrimental effect in our system.

It is important to remark that the heating rate to reaction temperature in the reaction gas is extremely important for the catalytic activity as well. For all catalysts the heating rate was very slow, equal to 1 °C min^{-1}. When the heating rate was increased to 9 °C min^{-1}, conversion increased from 28.19 to more than 60%, but selectivity decreased from 30 to ca. 15%.

Catalyst stability has been studied as well, and the results are shown in Fig. 4. As one can see, C$_3$H$_6$ conversion decreased slightly from 39 to 32% in the first 12 h,
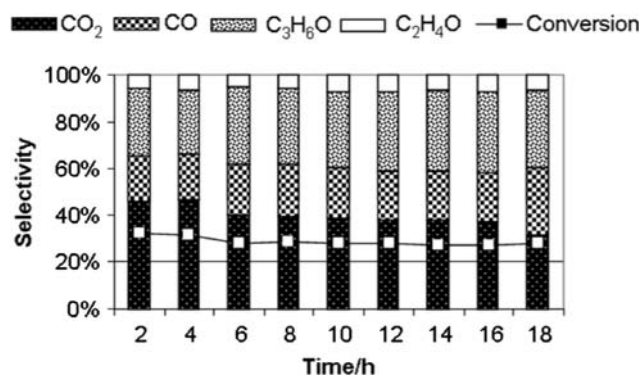

Fig. 4 Changes of catalytic performances with time on stream for the oxidation of propylene over the 0, 06 wt% CuPc-Py/SBA-15 catalyst. Reaction conditions: T = 475 °C; propylene/oxygen ratio 1:5; Space velocity 3,750 cm^3 g$_{cat}^{-1}$ h^{-1}]

Table 2 Propylene conversion and selectivity to acrolein over different catalysts at propylene/oxygen ratio 1:5 at 475 °C

Entry Nr.	Catalyst	Cu loading (wt%)	Space velocity (cm^3 g$_{cat}^{-1}$ h^{-1})	Conversion (%)	Selectivity (%)
1	CuPc-Py/SBA-15	0.3	15,000	28.2	27.8
2	CuPc-terbutyl/SBA-15	0.3	15,000	18.2	29.8
3	CuPc-Py/SiO$_2$	0.3	15,000	29.5	25.3
4	CuPc-Py/Aerosil 90	0.3	15,000	28.8	29.1
5	Cu(NO$_3$)$_2$/SBA-15	0.3	15,000	18.5	29.8
6	CuPc-Py/Al$_2$O$_3$	0.3	15,000	93.4	–
7	Cu(Ac)$_2$/TiO$_2$	0.3	15,000	79.3	–
8	Cu(NO$_3$)$_2$/Y-Na	0.3	15,000	89.4	–
9	CuPc-Py-K/SBA-15	0.06	7,500	5.1	37.0
10	CuPc-Py/SBA-15	0.06	7,500	19.6	42.1

keeping then a stable value. Selectivities, however, did not change appreciably during the entire time of the test.

Currently we could only speculate on the influence of the state of copper on the catalytic performance due to the very low copper levels at which the best performance of the solids is reached. We assume that isolated copper centers in the silica matrix are responsible for the selective oxidation reaction. This is indicated by the fact that the selectivity of the systems increases with decreasing copper content, while the copper normalized activity increases. Moreover, the fact that the phthalocyanine precursor has proved to be the most suitable one may be related to the size of the molecule (diameter about 1.3 nm). This could facilitate the formation of isolated copper species in the silica matrix.

The most dilute systems (0.06% Cu) have a high turnover frequency of 0.55 s^{-1}. The turnover frequency was calculated with the assumption that each copper center in the material contributes to activity equally. This value is in the same order of magnitude as the turnover frequency in bismuth molybdate catalysts, if one takes a surface area normalized rate constant of 0.04 μmol m^{-2} s^{-1} given by van Well et al. [12] and assumes a space requirement of about 1 nm^2 for the active site which can be estimated from the structure of the different bismuth molybdates [13].

Also in this catalyst, site isolation has been identified as a key factor in governing the performance of the catalysts [14]. We are currently exploring up to what limit of dilution the copper-normalized activity still increases and whether this corresponds to further increasing selectivity to acrolein.

4 Conclusion

We have found a new copper on silica catalyst, obtained from a copper phthalocyanine precursor, for the oxidation of propene to acrolein, using highly diluted copper in the silica matrix. These catalysts have high selectivity and yield of acrolein, in spite of very low copper concentrations well below 0.1%. The acrolein selectivity increases with decreasing copper loading, suggesting that isolated copper sites are ideal for good performance. However, the characterization of the state of the active species is very difficult, but work to elucidate more details on this system and to improve the performance by the addition of other elements are in progress in our laboratory.

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