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SnO_2−CuO−NaCl/SiO_2 Catalysts for Propylene Epoxidation

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ABSTRACT: The discovery of heterogeneous catalysts capable of direct gas-phase production of propylene oxide (PO) from propylene and molecular oxygen remains a challenge in industrial catalysis. The SnO_2−CuO−NaCl/SiO_2 system has been shown to produce PO at 55−60% selectivity with propylene conversion of 1% at 250 °C and 1 bar. A product shift toward CO_2, found to occur during continuous operation, was counteracted by cofeeding 10−50 ppm 1-chloropropane, maintaining peak PO selectivities for 12 h. Temperature-programmed-reduction (TPR) studies indicated that Na increases copper dispersion. Additional catalyst characterization studies performed by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) showed the presence of distinct phases of CuO, SnO_2, and NaCl.

■ INTRODUCTION

Propylene oxide (PO) is a reactive chemical intermediate used in the production of commercial products such as propylene glycol, polyurethane foams, insecticides, antifreeze, and cosmetics.[1,2] Propylene oxide production consumes over 10% of generated propylene, as over 8 million tons of PO are synthesized every year.[1,3] The vast majority of PO is produced by either the hydroperoxide process, which generates coproducts in greater amounts than PO, or the environmentally unfriendly chlorohydrin process.[1,3] Recently, Dow Chemical and BASF jointly built a PO plant, utilizing H_2O_2 from an on-site hydrogen peroxide generating facility.[1] Although this eliminated the need to purchase hydrogen peroxide, a direct propylene oxidation path using molecular oxygen is desirable for the efficient production of PO.

Silver-based catalysts are used for direct *ethylene* epoxidation. However, its use in *propylene* epoxidation results in deep oxidation products due to the reactivity of allylic hydrogens.[1,3,4] While Au-based catalysts have shown excellent selectivity toward PO, deactivation of the catalyst occurs rapidly, and H_2 required in the cofeed exhibits low utilization efficiencies (typically ~20%).[5−7] Therefore, the following direct epoxidation route from propylene and O_2 at relatively low temperatures and atmospheric pressure remains the ideal method for PO production:

$$C_3H_6 + 1/2O_2 \rightarrow C_3H_6O$$

The reaction of propylene and molecular oxygen over a solid catalyst can also result in combustion to CO_2, as well as formation of other partial oxidation products such as acrolein (AC), acetone (AT), propanal (PaL), and acetaldehyde (AD). Catalysts that minimize the formation of these byproducts are highly desirable. Previous transition metal screens have identified supported Cu as a selective catalyst toward PO formation,[8] leading to such binary metal catalysts as Cu-on-Mn/SiO_2, RuO_2−CuO_x/SiO_2, RuO_2−CuO_x−NaCl/SiO_2, and VO_x−CuO_x.[9−11] Here we report the SnO_2−CuO−NaCl/SiO_2 system for the direct epoxidation of propylene. This catalyst exhibits PO selectivities of 55−60% with 1−3% propylene conversion at 250 °C and 1 bar. Although the PO selectivities are on par with previous studies, propylene conversions are lower.[9−11]

■ EXPERIMENTAL SECTION

The supported catalysts were prepared by the coimpregnation method using a high surface area fumed silica support (SiO_2, Aerosil, surface area 350−410 m^2/g) and metal salt solutions of tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$, Alfa-Aesar, ACS, 98.0−103.0%) dissolved in 1.0 M HCl, aqueous copper(II) nitrate hemipentahydrate [$Cu(NO_3)_2 \cdot 2.5H_2O$, Alfa-Aesar, ACS, 98.0−102.0%], and aqueous sodium nitrate ($NaNO_3$, Alfa-Aesar, ACS, 99.0%). These metal salt solutions were combined with the silica support and dissolved in 1 mL of 1.0 M HCl solution. The mixture was then continuously stirred while heating at 165 °C until dry, after which the resulting powder was ground and calcined in air at 480 °C for 6 h. Calcination produced the desired metal oxides as well as small amounts of chlorides.

Catalyst screenings were carried out using a previously described microarray reactor system.[15,16] Reactive gas flows are passed over 5 mg of compacted catalyst with a GHSV value of 20 000 h^{-1} in the temperature range 200−300 °C at 1 bar. The feed gas consisted of propylene (1 vol %; Matheson, 99%) and oxygen (0−15 vol %; Matheson, 99.9%), with the balance being helium (Matheson, 99.99%). Sampling of reactor effluent was conducted by a 200 μm i.d. fused silica capillary that was positioned within the reactor channel, and the gas was analyzed by a micro gas chromatograph (GC, Varian, CP-4900) utilizing a thermal conductivity detector (TCD, 10 m, PoraPlot U) and molecular sieve 5A (10 m) columns. Product selectivities and propylene conversions were calculated on a carbon balance basis. GC calibrations for gaseous species (propylene, O_2, CO_2) were conducted using mass flow controllers (MKS) with He carrier gas, and calibrations for liquid species (PO, AC, AT, AD) were performed by vaporizing the injected liquids of these species in a heated, evacuated 2250 cm^3 stainless steel tank (He

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as carrier gas). All calibrations yielded linear five-point curves with $R^2 \geq 0.995$, using peak area as the basis for GC calculations. Reproducibility of all experiments was well within ±10%.

X-ray diffraction (XRD) characterization of the catalytic materials was carried out by a PANalytical X'Pert Pro that utilized Cu Kα emission and operated at 40 mA and 45 kV to determine crystalline phases (a 2θ step size of 0.0330° was used). Transmission electron microscopy (TEM) images were acquired on an FEI Titan 80-300 TEM for high resolution imaging with a field emission gun operating at 300 kV.

Temperature-programmed-reduction (TPR) measurements were conducted by loading 250 mg of the catalyst in a quartz tube (0.8 cm i.d., 45 cm long) which was placed in a programmable oven and heated from 25 to 600 °C at 10 °C/min. H_2 gas (Air Liquide, 99.999%) diluted by helium was passed through the tube at 20 cm^3/min, and a 50 μm i.d. fused silica capillary positioned within the tube continuously sampled the effluent gas, allowing effluent H_2 partial pressures to be measured in real time by a quadrupole mass spectrometer (QMS, SRS RGA-200, Sunnyvale, CA).

■ RESULTS AND DISCUSSION

Selectivity and conversion results for single metallic and bimetallic systems involving Cu, Sn, and Na are presented in Table 1 alongside the performance of the Cu−Sn−Na catalysts for a typical testing condition of T = 250 °C, feed-gas molar composition $C_3H_6/O_2/He$ = 1:5:94, and gas-hourly space velocity (GHSV) = 20 000 h^{-1}. As is evident from Table 1, although CuO/SiO_2 produced some PO, acrolein was the primary C_3 product. On the other hand, SnO_2/SiO_2 catalysts formed no partial oxidation products. The addition of sodium to CuO/SiO_2 decreased acrolein production in favor of PO, while sodium addition to SnO_2/SiO_2 led to the production of some PO and acrolein.

Table 1. Percent Selectivity toward Major Products and Percent Propylene Conversion for Various Combinations of the Metals in the Sn−Cu−Na/SiO_2 Catalyst[a]

	% PO selectivity			
sample	PO	AC	CO_2	% C_3H_6 conv
Cu	5	46	41	0.34
Cu + Na	28	17	43	0.38
Sn	0	0	100	0.09
Sn + Na	6	11	83	0.16
Sn + Cu	20	20	53	0.80
Sn + Cu + Na	58	3	39	0.95

[a] Major products are propylene oxide (PO), acrolein (AC), and carbon dioxide (CO_2) (acetone not shown). Metal weight percentages on SiO_2 were 7.8 wt % Cu, 12.5 wt % Sn, and 0.7 wt % Na.

In Figure 1, the PO selectivity and propylene conversion results for the SnO_2−CuO−NaCl/SiO_2 system are shown at a total metal loading of 14 wt %. As noted above, the trimetallic catalysts produced PO as the primary C_3 product together with some acrolein, with the balance being CO_2. As is evident from Figure 1, the trimetallic catalysts exhibited the maximum PO selectivity of about 55% at about 1% propylene conversion. The optimal metal weight ratio was Sn/Cu/Na = 18:11:1, equivalent to an atomic ratio of Sn/Cu/Na = 3.5:4:1. The effects of total metal loading were also examined, and changes in PO selectivities and propylene conversions are presented in Figure 2, where the optimum total metal loading can be seen to be at about 20 wt %.

Previous studies have shown that CuO nanoparticles are likely be the active sites for PO production, owing to the low Lewis basicity of Cu that allows for the oxametallacycle intermediate formation that has been proposed to be the defining step in PO synthesis.[12] Additions of either Na or Sn to the Cu/SiO_2 system greatly reduced acrolein formation in favor of PO. However, the addition of Sn increased propylene conversions while Na addition left the conversion unaffected. The presence of both Na and Sn significantly suppressed AC formation, and also decreased CO_2 production (a result that was not seen in Na or Sn addition alone). Separate experiments using PO and O_2 as the feed indicated 75−80% PO flow through the SnO_2−CuO−NaCl/SiO_2 catalyst bed at 250 °C, suggesting that the PO yields in the actual experiments are largely controlled by the intrinsic selectivity of the catalyst and not limited by PO combustion.

The effects of reaction temperature on product formation rates were also examined for the optimal trimetallic catalyst. The CO_2 formation rate increases exponentially with increasing temperature, corresponding to an activation energy of about 22 kcal/mol; PO and AC formation rates exhibited much lower activation energies. These results are consistent with previous findings on the effect of reaction temperature on product formation rates.[8] At temperatures below 250 °C, PO selectivity exceeds 70%, while propylene conversion falls below 0.5%.

Both the PO and CO_2 formation rates first increased with increasing O_2/C_3H_6 ratio in the feed and then leveled off characteristic of a Mars−van Krevelen mechanism, where O_2 interacts with the surface and replenishes the lattice oxygen, followed by the reaction of C_3H_6 with the lattice oxygen on the surface.

Time-on-stream testing of the optimum SnO_2−CuO−NaCl/SiO_2 catalyst for a 12-h period displayed a deterioration in PO selectivity after 4 h of reaction, although propylene conversion remained constant at about 1%. An inductively coupled plasma mass spectrometry (ICP-MS) examination of the catalyst indicated a decrease in chloride content after 4 h of reaction due to the volatilization of chlorine compounds. Consequently, it was speculated that if small amounts of a chlorinated hydrocarbon were to be cofed with the reactant gases, the chlorine levels in the catalyst could be maintained, thereby preventing the decrease in PO selectivity. This is similar to the promotion of ethylene epoxidation over silver catalysts with the use of 1,2-dichloroethane additive.[13] Figure 3 shows a 12-h time-on-stream study of identical SnO_2−CuO−NaCl/SiO_2 catalysts with and without the continuous cofeed of 24 ppm 1-chloropropane. It is evident from Figure 3 that the addition of 1-chloropropane sustained the catalyst's ability to produce PO at its peak selectivity, negating the shift to combustion by facilitating the formation of lower basicity surface oxygen species which are more favorable to the PO reaction pathway.[12]

Characterization. XRD spectra of the SnO_2−CuO−NaCl/SiO_2 catalyst as well as of the individual supported metal oxides are shown in Figure 4. It is clear that distinct crystalline CuO, SnO_2, and NaCl phases are present, and their immiscibility is indicated by the absence of mixed metal oxides. NaCl is present only in small amounts due to the restriction of sodium loading. Although larger CuO crystals were observed, it is more likely that the smaller CuO crystals are responsible for the observed PO formation. A TEM image of the supported catalyst shown

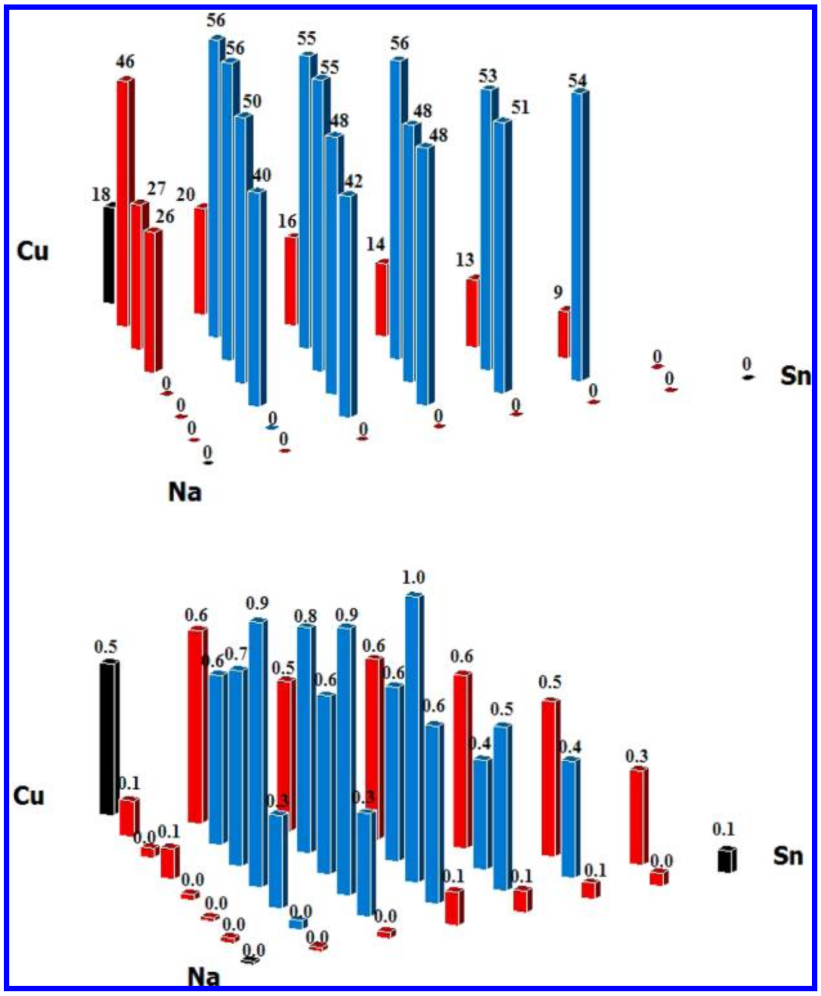

Figure 1. Percent PO selectivities (top) and propylene conversions (bottom) as a function of Sn−Cu−Na concentrations (wt %) on silica support. T = 250 °C; feed-gas composition $C_3H_6/O_2/He$ = 1:5:94; gas-hourly space velocity (GHSV) = 20 000 h^{-1}. Total metal loading kept at 14 wt %. Best PO selectivity seen in trimetallic range of near even Cu and Sn with smaller amounts of Na. Each corner of the diagrams represents the designated pure metal at 14 wt % loading.

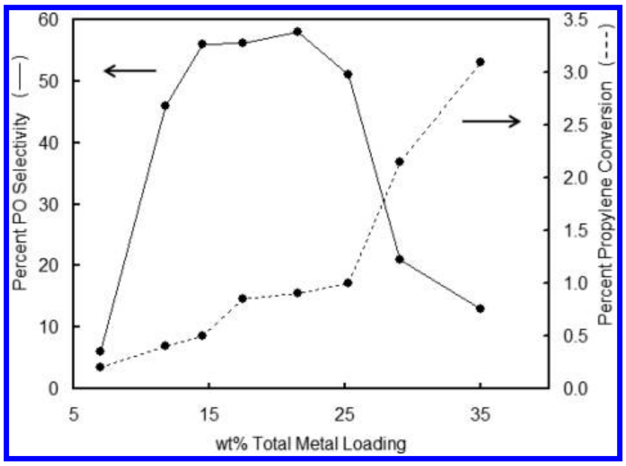

Figure 2. Increasing total metal loading leading to increased PO selectivity up to the optimum of 21 wt %, after which there is a sharp decline. Propylene conversion escalates as the loading is increased. T = 250 °C, GHSV = 20 000 h^{-1}, Sn/Cu/Na = 18:11:1 by weight.

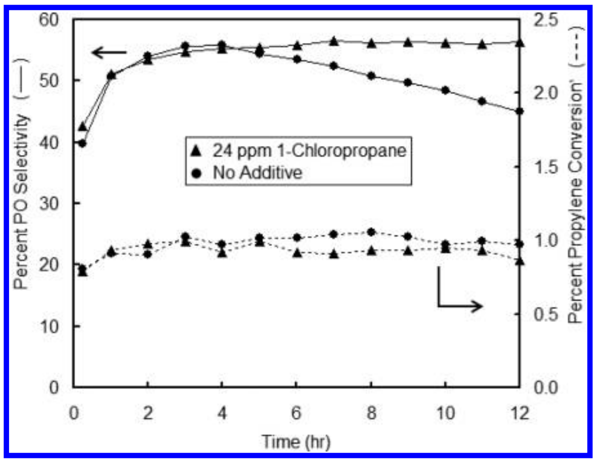

Figure 3. Time-on-stream behavior of optimized SnO_2−CuO−NaCl/SiO_2 catalyst with and without 24 ppm 1-cloropropane cofeed. PO selectivity (left axis) is sustained at its maximum for the duration of the study with 1-chloropropane addition; propylene conversion is unaffected by addition of the chlorinated hydrocarbon. T = 250 °C, GHSV = 20 000 h^{-1}.

in Figure 5 indicates that different crystalline phases are 5−10 nm in size and highly dispersed.

Copper Dispersion Measurements. Measurements of copper dispersion on silica were carried out according to the

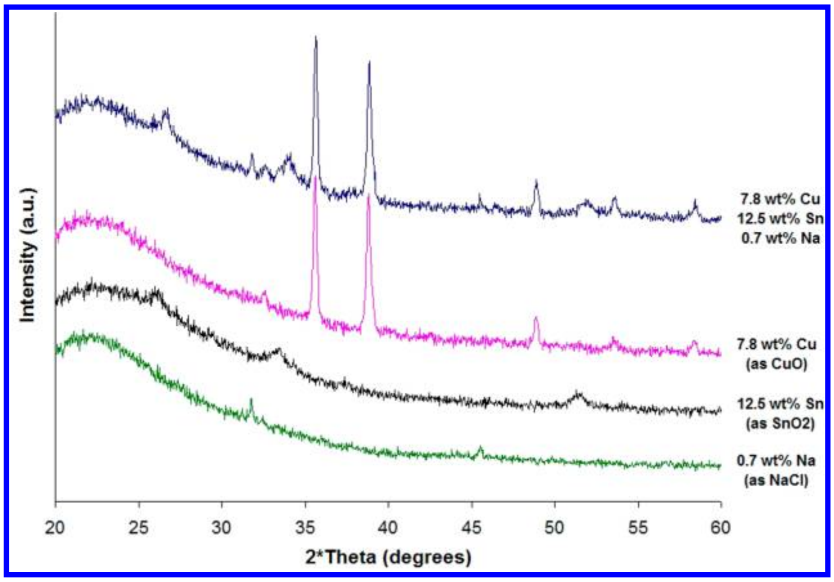

Figure 4. XRD spectra of supported individual metals and combined multicomponent catalyst. all catalysts were impregnated on SiO_2. Clear crystalline phases of CuO, SnO_2, and NaCl are present, and no mixed metal oxides are evident.

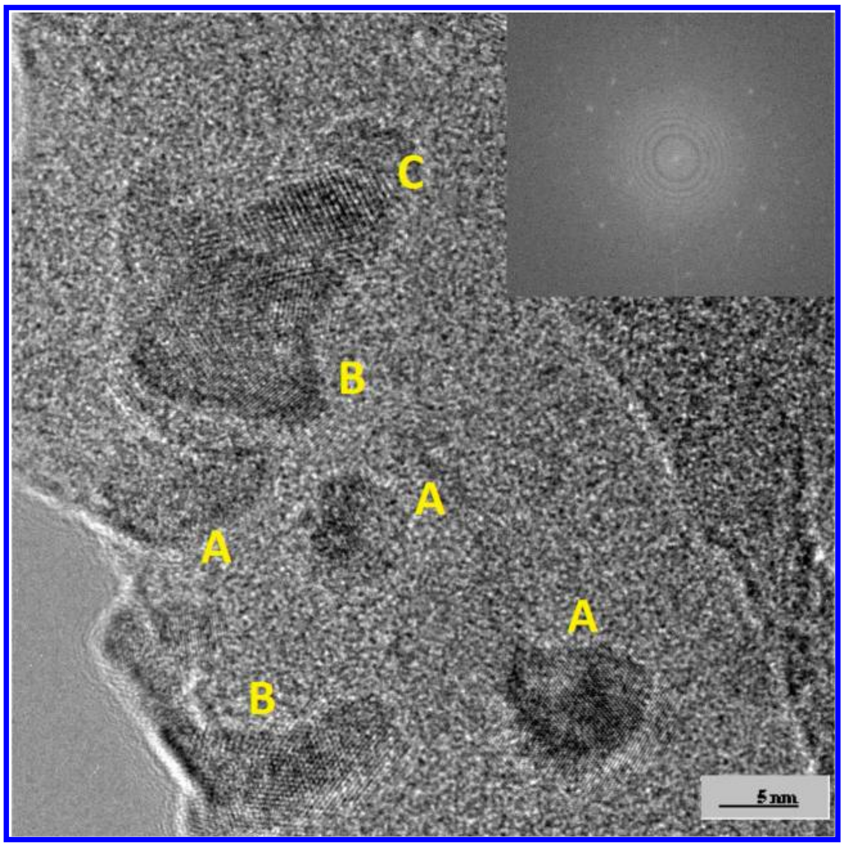

Figure 5. TEM image of SnO_2−CuO−NaCl catalyst with corresponding fast Fourier transform (FFT) diffraction pattern. Clusters of CuO (A), SnO_2(B), and NaCl (C) were identified using the FFT with known interplanar distances.

method described in detail by Sato et al. involving H_2-TPR.[14] The dispersion (D) of copper is defined as the fraction of copper atoms that are positioned on the surface of particles relative to the total amount of copper in the catalyst. Larger dispersion values therefore represent smaller average particle sizes, as the surface-to-volume ratio is increased. The method involves three steps: (1) H_2-TPR (5 vol % H_2 in He) of the fresh catalyst from 25 to 600 °C at 10 °C/min, after which the catalyst is cooled back to 25 °C, (2) exposure to N_2O at 25 °C for 15 min, and (3) a second H_2-TPR of the catalyst from 25 to 600 °C at 10 °C/min. N_2O flow at 25 °C has been shown to only oxidize surface Cu^0 to Cu^+ due to the trivial oxidation rate of bulk Cu^0 at this temperature.[14] Since H_2 consumption in the initial TPR results from CuO reduction to Cu^0 (denoted A_1), and H_2 consumption in the second TPR results from Cu_2O

reduction to Cu^0 (denoted A_2), dispersion can then be determined from the ratio $D = 2A_2/A_1$.

Dispersion measurements for various Cu loadings, as well as sodium and chlorine addition, are shown in Table 2. As seen in Table 2, when copper loading is increased, the dispersion decreased due to the formation of larger particles. Addition of 0.7 wt % Na had a beneficial effect, causing the copper dispersion to increase to 0.22; added sodium cations apparently hindered the agglomeration of copper particles. On the other hand, the presence of chlorides (from HCl experiments) did not affect the copper dispersion, indicating that positive influence of chlorine on PO formation is more of an electronic effect than a physical one involving the particle size. Dispersion measurements of bimetallic SnO_2-CuO/SiO_2 were not possible because interdiffusion during the initial reduction of the sample resulted in the formation of Sn^0-Cu^0 alloys (i.e., bronze), which was confirmed by XRD.

Table 2. Dispersion (*D*) Values for Samples Impregnated in SiO_2

sample	*D*
3.9 wt % Cu	0.19
7.8 wt % Cu	0.14
15.6 wt % Cu	0.11
7.8 wt % Cu + HCl	0.14
7.8 wt % Cu + 0.7 wt % Na	0.22

■ CONCLUSIONS

The $SnO_2-CuO-NaCl/SiO_2$ system results in propylene epoxidation selectivities in the range 55−60% at propylene conversions of about 1−3% at 250 °C. The XRD and TEM measurements indicate the presence of distinct metal oxide nanoparticles (crystals) necessary for the observed epoxidation catalysis. The presence of Na and Cl in the catalyst had two separate but beneficial effects. First, Na cations were shown to improve copper dispersion, thereby creating smaller CuO nanoparticles. The effects of chlorine appear to be electronic by promoting the formation of low basicity O atoms on the catalyst surface. However, volatility losses of chlorine led to PO selectivity degradation in long reaction times. Cofeeding trace amounts of chlorinated hydrocarbons (10−50 ppm) ameliorated this problem and enabled the continuation of peak PO selectivities over 12 h.

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Notes

The authors declare no competing financial interest.

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