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The Effects of Cofeeding Chlorinated Hydrocarbons in the Direct Epoxidation of Propylene by Molecular Oxygen

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Propylene oxide (PO) is a valuable intermediate used in the production of a large variety of valuable consumer products, such as polyurethane foams, polymers, propylene glycol, cosmetics, food emulsifiers and as fumigants and insecticides.[1, 2] Over 8 million tons of PO are produced annually from propylene.[1] The technology, economics, and environmental impacts of current as well as alternate propylene epoxidation processes have recently been reviewed.[1, 2]

Recently, we reported the discovery of a new class of silica-supported RuO_2–CuO_x–NaCl catalysts for the direct epoxidation of propylene by using molecular oxygen under atmospheric pressure.[3] This trimetallic catalyst, at its optimal composition of Ru/Cu/Na = 4:2:1(metal weight ratio, or about 3:4:4 atom ratio) at 12.5 wt% total metal loading, exhibited PO selectivities in the range 40–50% at propylene conversions of 10–20% at 240–270 °C and 1 atm (1 atm = 1.0133×10^5 Pa), and it maintained this activity for up to 4–8 h. However, we subsequently observed a slow, but steady decrease in PO selectivity in experiments over longer time periods. This degradation in performance is not acceptable from a practical standpoint if the RuO_2–CuO_x–NaCl/SiO_2 system is to be exploited commercially.

Here, we report that the introduction of chlorinated hydrocarbon (CHC) additives to the C_3H_6/O_2 feed in the range 1–100 parts per million (ppm by volume) ameliorates the performance degradation problem and enables the steady production of PO, albeit at a decrease in propylene conversion. The beneficial effect of chlorinated hydrocarbons on propylene epoxidation in the RuO_2–CuO_x–NaCl/SiO_2 system appears to be different than the promotional effects observed in Ag catalyzed ethylene oxide (EO) production,[4, 5] although some similarities also exist. The promotion of EO by chlorine on silver has been studied in considerable detail in the past and has been attributed to a combination of geometric/ensemble and electronic effects.[4–7] For example, surface adsorbed Cl atoms (Cl_s) have been suggested to decrease the number of sites for oxygen adsorption, thereby decreasing catalyst activity. Additionally, by site blocking, Cl_s has been proposed to reduce the number of neighboring active sites needed for the dissociative adsorption of O_2. This leads to increased molecular O_2 adsorption (i.e., O_s–O) as opposed to O_s (surface oxygen), thus increasing EO selectivity at the expense of a decrease in activity. In the electronic models, an increase in EO selectivity by chlorine has been attributed to its higher electronegativity.[5, 6] This has been suggested to result in the weakening of the Ag–O bond, which leads to increased EO selectivity.[5] However, the same mechanism also results in an increased activation energy for the dissociative chemisorption of O_2, thereby decreasing the overall activity.[5] In another proposal, EO promotion by chlorine has been attributed to the formation of both surface and subsurface Cl that collectively alter the energetics of the oxymetallacycle (OMC) mechanism towards EO synthesis.[4] Recent computational studies[7] on Ag_2O (001) also point to surface adsorption of Cl to vacant sites next to O_s (thereby favoring O_2 adsorption as O_s–O) as the primary reason for EO promotion. These investigators also predicted a direct EO synthesis route from Ag_2O when oxygen vacancies are not present. This pathway was shown to switch to the less selective OMC mechanism when oxygen vacancies are introduced at low oxygen coverages, which promote dissociative O_2 chemisorption. As evident from the above summary, in spite of decades of research, a consensus has not yet been reached regarding the mechanism(s) of chlorine promotion of EO over silver catalysts.

Considering the more complex physical and chemical nature of the RuO_2–CuO_x–NaCl/SiO_2 system and the presence of alyllic hydrogen atoms in propylene, the development of molecular level insights to account for the beneficial effects of chlorine on propylene epoxidation remains a formidable intellectual challenge. We hope that the experimental results provided in this communication will promote thinking and inspire others to undertake both computational and experimental surface science studies directed towards clarifying the mechanism(s) of propylene epoxidation and the effects of chlorine on PO synthesis.

The direct epoxidation of propylene is described by Equation (1). Yet a variety of byproducts, such as acetone (AT), acrolein (AC), acetaldehyde (AD), and propanal (PaL) could form together with the total oxidation products of CO and CO_2.[3] However, the unique feature of the trimetallic RuO_2–CuO_x–NaCl/SiO_2 catalysts is that PO and CO_2 are the major reaction products.[3]

$$C_3H_6 + {}^1\!/_2\, O_2 \rightarrow C_3H_6O \qquad (1)$$

Before presenting the results, it is important to note again that the silica supported RuO_2–CuO_x–NaCl catalysts lead to the production of PO as the primary C_3 product, with only trace quantities of AC, AT, and AD. Carbon dioxide was the only CO_x product.[3]

Figure 1 shows the results of a typical time-on-stream experiment with our RuO_2–CuO_x–NaCl/SiO_2 catalyst without the addition of a CHC additive under propylene-lean conditions (i.e., 1% C_3H_6, 4% O_2). As seen in Figure 1, the PO selectivity in-

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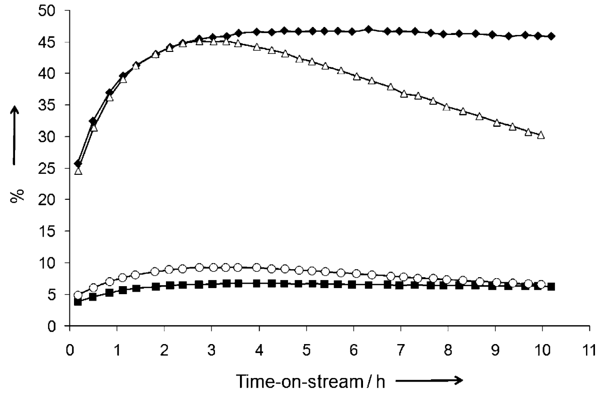

Figure 1. Effects of continuous $EtCl_2$ addition on PO selectivity and propylene conversion. PO selectivity with $EtCl_2$ (◆), propylene conversion with $EtCl_2$ (■), PO selectivity without $EtCl_2$ (△), and propylene conversion without $EtCl_2$ (○).

creased first to a maximum of 45 % at about 2.5 h and gradually decreased thereafter. The initial increase in PO selectivity is a manifestation of the surface restructuring (both physical and chemical) of the trimetallic catalyst, which was observed in all of the experiments with a fresh catalyst. In the first round of CHC experiments, 1,2-dichloroethane ($EtCl_2$) was selected as the additive due to its broad utility in ethylene epoxidation.[2,5] However, other chlorinated hydrocarbons, including chlorinated methane and propanes as indicated in Table 1 also gave similar results. As shown in Figure 1, the introduction of about 100 ppm of $EtCl_2$ to the feed stream had a remarkable effect in preventing a decrease in PO selectivity and in maintaining its level at 45 % for the entire testing period. Interestingly, however, the $EtCl_2$ cofeed had no effect on the initial part (i.e., increasing) of the PO selectivity profile.

In contrast, the introduction of $EtCl_2$ had an adverse effect on propylene conversion. In the absence of chlorine, propylene conversion initially increased reaching a peak of 9 %; at about the same time the PO selectivity reached a maximum. Propylene conversion subsequently and gradually decreased at longer reaction times. In the presence of $EtCl_2$, the propylene peak conversion was only 7 %. However, it remained at the 7 % level for the remaining duration of the experiments. Similar effects were observed under propylene-rich conditions as well as with other chlorinated additives listed in Table 1.

These results indicate that the primary role of the $EtCl_2$ cofeed is to continuously replenish chlorine on the catalyst surface that is normally lost due to volatilization. Since fresh catalysts possess an abundance of chlorine atoms, $EtCl_2$ had no effect in the early period of the experiments (Figure 1). To explore this hypothesis, catalyst samples at long reaction times, in the absence of the $EtCl_2$ cofeed, were removed from the reactor and analyzed for their chlorine contents by using inductively coupled plasma mass spectrometry (ICP-MS). These measurements indicated that the chlorine contents of the RuO_2–CuO_x–NaCl/SiO_2 catalysts exhibited a small, but decreasing trend with an increase in the reaction time, thereby supporting the critical role chlorine plays in maintaining high PO selectivities.

Since the $EtCl_2$ helped maintain the peak PO selectivity, while slightly decreasing propylene conversions, PO yields (i.e., PO selectivity × Propylene conversion) decreased in the presence of chlorinated compounds in the feed. In contrast, the net effect of chlorine on ethylene epoxidation was promotion.[4–7] Increases in EO selectivities are more substantial than decreases in the activity, with the net effect being increased EO yields in the presence of chlorinated hydrocarbons.

The effects of chlorine on propylene epoxidation were also investigated when $EtCl_2$ was added intermittently. In these experiments, 100 ppm of $EtCl_2$ was introduced into the feed *after* PO selectivity started to decrease for a short period of time. As shown in Figure 2, the introduction of $EtCl_2$ at 5.25 h had an immediate beneficial impact on PO selectivity, reversing its decreasing trend, and led to increasing PO selectivity towards its maximum. Immediately after the $EtCl_2$ was turned off, PO selectivity reverted to its decreasing trend again. These results are consistent with a model that involves the continuous loss of chlorine from the catalyst surface in the absence of $EtCl_2$ and the dynamic replacement of these volatilization losses by cofeeding $EtCl_2$.

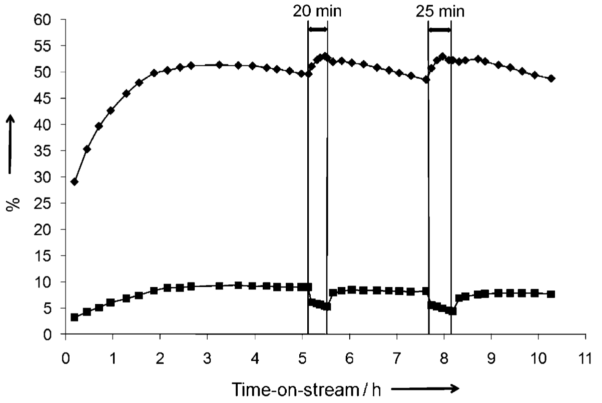

Figure 2. Effects of intermittent $EtCl_2$ addition on PO selectivity and propylene conversion. $EtCl_2$ (100 ppm) is first introduced at 5.25 h for 20 min and also at 7.7 h for 25 min. PO selectivity (◆) and Propylene conversion (■).

As shown in Figure 2, the introduction of $EtCl_2$ also inhibited propylene conversion, concomitant with an increase in PO selectivity. In addition, stopping the $EtCl_2$ feed caused the conversion to revert to its earlier levels. It is important to note that the effects of $EtCl_2$ were reproducible, with another example shown after 5 h in Figure 2. Intermittent cofeeding of other chlorinated hydrocarbons shown in Table 1 also had similar effects, both under oxygen-rich and propylene-rich conditions.

Although propylene epoxidation by RuO_2–CuO_x–NaCl/SiO_2 catalysts[3] is significantly different from ethylene epoxidation by silver catalysts,[4–9] similar ideas could be proposed as a starting point to account for the effects of chlorine reported above. As discussed by Seubsai et al.,[3] the RuO_2–CuO_x–NaCl/SiO_2 catalysts consists of NaCl promoted CuO nanoparticles and RuO_2 nanorod crystals, all of which are supported on larger SiO_2 clusters made from 30–40 nm diameter elementary SiO_2 particles. The adsorbed Cl atoms could interact with CuO, forming species such as $CuCl_2$ and could, therefore, alter the reaction mechanism. Similarly, Ru chlorides can also play a role in the current catalytic system.

The beneficial effects of chlorine on PO selectivity could be due to geometric/ensemble and electronic effects,[4–7,10,11] as well as gas-phase kinetic effects.[8,9] The former effects include site blocking by Cl_s, thereby changing the relative surface concentration of adsorbed oxygen, molecular oxygen (O_s–O) and O_s, as well as the basicity of O_s[12] on the CuO sites. The surface Cl_s can alter the adsorption energies of oxygen, thereby changing the relative surface concentrations of species during the reaction thus altering the reaction mechanism in an analogous manner to ethylene epoxidation.[7] Since Cl atoms could also diffuse below the surface, they may alter the reaction mechanism by modifying the electronic properties of the CuO.[5,6]

Because the CHC cofeed decreased the activity of the RuO_2–CuO_x–NaCl/SiO_2 catalysts, they can also be viewed as catalyst poisons.[6] Chlorine and chlorinated compounds adsorbed on the catalyst surface decrease the overall activity by reducing the number of available sites for oxygen adsorption. Alternately, chlorinated species can alter the reaction mechanism by adsorbing on specific sites. For the case of ethylene epoxidation over silver, Cl has been suggested to preferentially block sites leading to CO_2 formation.[4–7] The situation in propylene epoxidation on RuO_2–CuO_x–NaCl/SiO_2 catalysts could be similar, although the catalytic system clearly is more complex.

Finally, chlorine and chlorinated compounds may inhibit gas phase reactions by reducing the concentrations of free radicals such as HO_2, O, and OH, thereby reducing the total oxidation of PO and C_3H_6 to CO_2. The inhibition of combustion reactions by chlorinated compounds is well-known.[13] This mechanism could play a role in the gas-phase epoxidation of propylene as suggested by some of the earlier investigators.[10,14]

In conclusion, chlorinated additives serve a useful purpose in maintaining peak PO selectivities over RuO_2-CuO_x-NaCl/SiO_2 catalysts at a slight reduction in activity. Although chlorinated hydrocarbon additives appear to replenish surface chlorine atoms lost due to the volatility of their compounds, we are not in a position to formulate the exact mechanisms of these events. However, with surface science experiments and modeling work (i.e., DFT studies), molecular level insights on the mechanism of propylene epoxidation on RuO_2–CuO_x–NaCl/SiO_2 catalysts could be developed and we should be able to describe how surface chlorine influences this mechanism.

Experimental Section

Catalytic materials were prepared by using impregnation as previously described.[3] Briefly, predetermined weights of amorphous fumed silica powder (SiO_2, Alfa Aesar, surface area 145 $m^2 g^{-1}$) were mixed with aqueous solutions of Ru ($[RuCl_6(NH_4)_2]$, Aldrich), Cu [$Cu(NO_3)_2$, Alfa Aesar, ACS, 98.0%–102.0%], and Na ($NaNO_3$, Alfa Aesar, ACS, 99.0% min). The solution was allowed to impregnate the silica support for 24 h, and the resulting material was then heated at 150 °C until dry and calcined at 500 °C for 12 h in air. We also determined that the Ru, Cu, and Na metal ratio of 4:2:1 (weight ratio, or about 3:4:4 atom ratio) at 12.5 wt% total metal loading maximized the propylene oxide (PO) selectivity. This optimum catalyst formulation was used in the experiments reported here.

In Table 1, the list of chlorinated hydrocarbons (CHC) considered and their concentrations in the feed are presented. Gaseous CHC were directly metered and fed by using a high accuracy rotameter and subsequently mixed with the feed gases by using a static mixing tube. For the case of liquid CHC, a special evaporation system was built and used. In this system, a predetermined volume of liquid CHC (e.g., 1–10 μL) was injected into a preheated 2.25 L stainless steel tank that was also pre-evacuated by using a mechanical vacuum pump. After liquid injection, the tank was *slowly filled* with helium to ensure the evaporation and complete mixing of the CHC. The entire filling process took about 5–7 min. The final pressure in the tank was kept at about 5 atm ($1 \text{ atm} = 1.0133 \times 10^5$ Pa), which was adequate to perform continuous experiments for about 60–120 min, depending on the concentration of CHC fed into the reactor bank. In long time-on-stream experiments, the CHC gas mixtures were quickly replenished. If more precise experiments were needed, two tanks in parallel could be used by switching the flows back and forth between filling cycles.

The experiments were performed by using our unique computer controlled array channel microreactor system described previously.[14] In array microreactors, reaction gases flowed over the flat surfaces of compacted powders (5 mg) of catalytic materials that were placed into wells along each reactor channel. This flow regime resulted in the establishment of identical contact times in each channel, thereby enabling the direct comparison of the catalytic materials in a rapid fashion. The system allowed the parallel screening of up to 80 catalytic materials. However, the actual

Table 1. The chlorinated hydrocarbon additives used and the experimental conditions.[a]

Additive	State	Boiling point [°C]	Density [mg μL^{-1}]	Temperature[b] [°C]	Set-up	Concentration[c] [ppmv]	
						C_3H_6-Lean	C_3H_6-Rich
chloromethane	pressurized liquid	–	–	–	rotameter	25	25
chloroethane	pressurized liquid	–	–	–	rotameter	25	25
1,2-dichloroethane	2000 ppm in He	–	–	–	rotameter	100	150
1-chloropropane	liquid	47	0.892	100	evap. sys.	12	24
1,2-chloropropane	liquid	95	1.157	120	evap. sys.	4.6	–
1,3-chloropropane	liquid	120	1.190	140	evap. sys.	2.5	–
1,2,3-trichloropropane	liquid	158	1.385	170	evap. sys.	4.7	–
allylchloride	liquid	46	0.939	100	evap. sys.	5.2	–

[a] Testing condition: 250 °C, using 5.0 mg of fresh catalyst, GHSV = 20 000 h^{-1}; C_3H_6 lean: 1% of C_3H_6, 4% of O_2, and He as balance; C_3H_6 rich: 2.5% of C_3H_6, 1% of O_2, and He as balance. [b] Temperature of the 2.25 L tank. [c] Additive concentration in the feed.

number typically tested would be less because of duplicates and blank sites used for improved quantifications. All of the experiments were carried out at 250 °C, under 1 atm of pressure and at a gas hourly space velocity (GHSV) of 20 000 h^{-1}. The feed gas consisted of 1–2.5 vol% propylene (C_3H_6, Matheson, 99% purity) and 1–4 vol% O_2 (Matheson, 99.9%), and the balance He (Matheson, 99.99%).

Gas sampling was accomplished by withdrawing reactor exit gases by using a passivated 200 micron ID capillary sampling probe that was positioned within the reactor channel, followed by on-line gas analysis by using a Micro-Gas Chromatograph (Varian, CP-4900) equipped with a thermal conductivity detector (TCD) and Porapak U (10 m) and Molecular sieve 13X (10 m) columns. The propylene conversions, product selectivities, and yields (calculated as selectivity of a product × propylene conversion) of the products were calculated on the basis of product analysis and checked by using carbon, hydrogen, and oxygen balances. GC calibrations for propylene, oxygen, and CO_2 were performed by using mass flow controllers (MKS) and He as a carrier gas. Calibrations for PO, acrolein (AC), acetone (AT), and acetaldehyde (AD) were performed by vaporizing known quantities of the liquid in the same heated, evacuated 2.25 L stainless steel tank system described earlier. All of the calibrations yielded linear 5 point curves with R^2 values of at least 0.995, by using peak area as the basis for GC calculations. Reproducibility of the experiments was well within ±10%.

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[1] F. Cavani, J. H. Teles, *ChemSusChem* **2009**, *2*, 508–534.
[2] T. A. Nijhuis, S. Musch, M. Makkee, J. A. Moulijn, *Appl. Catal. A* **2000**, *196*, 217.
[3] A. Seubsai, M. Kahn, S. Senkan, *ChemCatChem* **2011**, *3*, 174–179.
[4] D. Torres, F. Illas, R. M. Lambert, *J. Catal.* **2008**, *260*, 380–383.
[5] K. C. Waugh, M. Hague in *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis* (Ed.: S. T. Oyama), Elsevier, Amsterdam, NL **2008**, Chap. 7, pp. 85–110.
[6] J. T. Jankowiak, M. Barteau, *J. Catal.* **2005**, *236*, 379–386.
[7] M. O. Özbek, I. Onal, R. A. van Santen, *ChemCatChem* **2011**, *3*, 150–153.
[8] H. Orezsek, R. P. Schulz, U. Dingerdissen, W. F. Maier, *Chem. Eng. Technol.* **1999**, *22*, 691–700.
[9] Z. X. Song, N. Mimura, J. J. Bravo-Suarez, T. Akita, S. Tsubota, S. T. Oyama, *Appl. Catal. A* **2007**, *316*, 142.
[10] O. P. H. Vaughan, G. Kyriakou, N. Macleod, M. Tikhov, R. M. Lambert, *J. Catal.* **2005**, *236*, 401.
[11] W. Zhu, Q. Zhang, Y. Wang, *J. Phys. Chem. C* **2008**, *112*, 7731–7734.
[12] D. Torres, N. Lopez, F. Illas, R. M. Lambert, *Angew. Chem.* **2007**, *119*, 2101–2104; *Angew. Chem. Int. Ed.* **2007**, *46*, 2055–2058.
[13] "Survey of Rate Constants in the C/H/Cl/O System": S. Senkan in *Gas-Phase Combustion Chemistry* (Ed.: W. C. Gardiner, Jr.), Springer, NY **2000**, 389–487.
[14] a) S. Senkan, K. Krantz, S. Ozturk, V. Zengin, I. Onal, *Angew. Chem.* **1999**, *111*, 867–871; *Angew. Chem. Int. Ed.* **1999**, *38*, 791–795; b) S. M. Senkan, S. Ozturk, *Angew. Chem.* **1999**, *111*, 2965–2971; *Angew. Chem. Int. Ed.* **1999**, *38*, 2794–2799.

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