Improving selectivity in ethylene oxide production by nano-structuring catalysts in chemical looping epoxidation

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Highlights
- Strontium ferrite modified with Ag and Na_2CO_3 provides oxygen for chemical looping epoxidation.
- A shell of Na_2CO_3 located between Ag particles and $SrFeO_3$ improves selectivity towards ethylene oxide.
- Covering Ag particles with Na2CO3 results in negligible conversion of C_2H_4.

1. Introduction

Chemical looping selective oxidation offers a promising alternative to conventional oxidation catalysis. In a chemical looping reaction, a hydrocarbon stream is fed over a reactive metal oxide (termed an oxygen carrier, OC), which donates lattice oxygen, driving the synthesis of oxygenated gaseous products. The feed is then switched to air to regenerate the OC and close the chemical loop, giving the safety advantage of inherent separation between the hydrocarbon and $O_{2(g)}$. Production of ethylene oxide (EO) in a chemical looping mode offers comparable performance to incumbent industrial processes, using an Ag catalyst on a $SrFeO_3$ perovskite OC [1].

Recently, a strontium ferrite-based oxygen carrier modified with an external shell of Na_2CO_3 was shown to improve selectivity in oxidative dehydrogenation of ethane [2]. The carbonate shell prevented non-selective oxidation to CO_2, while allowing oxygen to be released to react selectively over a $MoVTeNbO_x$ catalyst to form C_2H_4. Here, we apply the principle of preventing non-selective oxidation at the surface of the OC to chemical looping epoxidation, modifying $SrFeO_3$ with both Ag and Na_2CO_3, allowing for improved selectivity towards EO.

2. Methods

Strontium ferrite ($SrFeO_{3-\delta}$) was produced by solid state synthesis from stoichiometric amounts of $SrCO_3$ (Sigma Aldrich, >98%) and Fe_2O_3 (Honeywell Fluka, >99%), followed by calcination at 1000°C in 4 steps of 3 h, then sieved to 45-180 μm. To produce sodium carbonate shells around the particles of $SrFeO_3$, sodium nitrate solution (Aldrich, >99%) was added dropwise to $SrFeO_{3-\delta}$, then dried for 12 h at 130 C, and calcined at 700°C in air for 5 h. Since $NaNO_3$ melts at 308°C and decomposes at >500°C, the calcination resulted in $NaNO_3$ first wetting the surface of $SrFeO_{3-\delta}$ particles; then decomposing and reacting with atmospheric CO_2 to form a ~50 nm shell of Na_2CO_3 [2]. Samples with target loading of 10wt% Na_2CO_3 were designated $Na_2CO_3/SrFeO_{3-\delta}$. Another set of samples of $SrFeO_3$ were first impregnated with $AgNO_3$ solution, followed by drying and calcination for 5 h at 650°C, for target loading 10wt% Ag (designated $Ag/SrFeO_{3-\delta}$). Samples of $Ag/SrFeO_{3-\delta}$ and $Na_2CO_3/SrFeO_{3-\delta}$ were then further impregnated with Na_2CO_3 and Ag, respectively, producing $Na_2CO_3(Ag/SrFeO_{3-\delta})$ and $Ag(Na_2CO_3/SrFeO_{3-\delta})$; all prepared materials are summarised in Fig. 1. The presence of Na_2CO_3 was confirmed by Raman spectroscopy, and samples were additionally characterised by powder X-ray diffraction, thermogravimetric analysis, and scanning electron microscopy.

Chemical looping epoxidation was performed in a stainless-steel tubular reactor heated to 270°C, with 1.8 g of active material placed below an inert layer of 4.0 g SiC (Alfa Aesar, 46 grit) and secured with quartz wool. Gas was fed from the top of the reactor at 180 mL min^{-1} for a global hourly space velocity of 9600 h^{-1}. One chemical looping cycle comprised 1.5 min reduction in C_2H_4 (5.0vol%, balance N_2), 2 min purge in N_2, 15 min re-oxidation in air (all gases BOC), and the final 2 min purge with N_2.

Figure 1. Schematic showing summary of samples prepared by sequential impregnation with Ag and Na_2CO_3

Catalytic performance was determined by assessing the mean conversion of C_2H_4, $\overline{X}$, mean selectivity towards EO, $\overline{S}$, and mean yield of EO, $\overline{Y}$, defined in Eq. 1.

$$\overline{X} = \frac{\int_{t_{start}}^{t_{end}}(y_{EO}+0.5\,y_{CO_2}+0.5y_{CO})\mathrm{d}t}{\int_{t_{start}}^{t_{end}}(y_{C_2H_4}+y_{EO}+0.5\,y_{CO_2}+0.5y_{CO})\mathrm{d}t}; \quad \overline{S} = \frac{\int_{t_{start}}^{t_{end}}(y_{EO})\mathrm{d}t}{\int_{t_{start}}^{t_{end}}(y_{EO}+0.5\,y_{CO_2}+0.5y_{CO})\mathrm{d}t}; \quad \overline{Y} = \overline{X}\cdot\overline{S} \qquad \textbf{[Eq.1]}$$

where y_i is the mole fraction of component i, t_{start} is the first time in each cycle at which y_{EO} exceeded 50 ppm, and t_{end} is the time in each cycle corresponding to the maximum in y_{EO}.

3. Results and discussion

From experiments in the packed bed, shown in Fig. 2, $Ag/SrFeO_{3-\delta}$ shows stable selectivity towards EO of 23% with 19% conversion of C_2H_4, whereas for $Ag(Na_2CO_3/SrFeO_{3-\delta})$ with an internal carbonate shell, selectivity of 35.3% at 11.3% conversion were achieved after 5 cycles. In the absence of the Ag catalyst, $Na_2CO_3/SrFeO_{3-\delta}$ was practically unreactive. Similarly, $Na_2CO_3(Ag/SrFeO_{3-\delta})$, with an external carbonate shell covering the particles of Ag, showed virtually no formation of EO or CO_2. Contrastingly, the minimal conversion over $Na_2CO_3/(Ag/SrFeO_{3-\delta})$ suggests that contact between Ag and the gas phase is needed to produce oxygenated products (EO and CO_2) [3], or, that C_2H_4 does not adsorb onto Na_2CO_3.
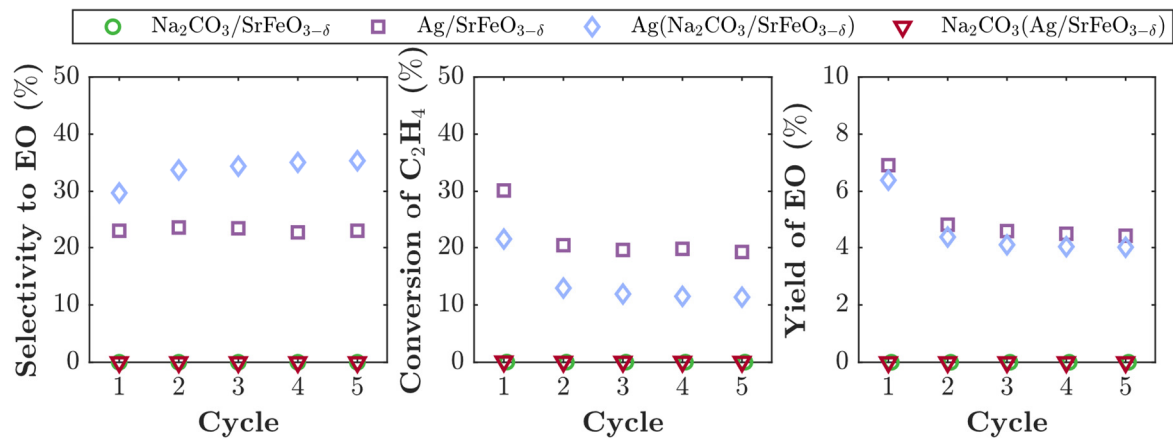

Figure 2. Comparison of conversion, selectivity, and yield of EO during chemical looping epoxidation over 5 cycles.

4. Conclusions

Modification of $Ag/SrFeO_3$ for chemical looping epoxidation by adding an internal Na_2CO_3 shell is an effective strategy for improving selectivity towards EO, while preventing non-selective reactions. Thus, nano-structured materials can help improve the competitiveness of chemical looping methods.

References

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