

Oxidative dehydrogenation of ethane combined with CO₂ splitting via chemical looping technique utilising redox of In₂O₃

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Significance and Relevance

We developed a novel oxygen carrier Ni_{1-x}Cu_x-In₂O₃, which showed high reaction rates with high oxygen capacity in a chemical looping system, combining ethane oxidative dehydrogenation and CO₂ splitting at a low temperature of 873 K. This oxygen carrier releases and backfills oxygen through non-topotactic redox of In₂O₃ and the transformation of Ni-Cu and Ni-Cu-In alloy, and this unique mechanism achieves outstanding performance. This achievement contributes to efficient ethylene production and CO₂ utilisation and proposes a new strategy for chemical looping processes in general.

Preferred and 2nd choice for the topic: "Green chemistry and biomass transformation, renewable resources conversion", "CO₂ utilization and recycling"

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Currently, ethylene production is responsible for 0.8% of global CO₂ emissions due to its huge demand and the high reaction temperature required (> 1123 K)¹. Catalytic oxidative dehydrogenation of ethane is one promising alternative process because it proceeds at low temperatures, but the mixing of ethane and oxidants is causing difficulties in industrialisation. Applying chemical looping technology for oxidative dehydrogenation (CL-ODH) greatly increases its feasibility². Employing materials with oxygen storage and release ability (oxygen carrier: OC) achieves oxidative dehydrogenation through two separate sub-steps: selective oxidation of ethane with lattice oxygen release from the OC, followed by lattice oxygen backfilling with oxidant. This system, which operates without gas mixing, addresses the challenges of gas separation, side reactions, and safety concerns associated with conventional oxidative dehydrogenation while also enabling higher equilibrium yields compared to direct dehydrogenation. Furthermore, simultaneous conversion to CO can be achieved if CO₂ can be used for OC regeneration.

In this study, we found that In₂O₃ modified with Ni-Cu alloy exhibited excellent performance in ethylene production and CO₂ splitting at a low temperature of 873 K. This presentation will discuss the unique reaction mechanism enabling this coupling of difficult reactions, as well as the roles of In, Ni, and Cu elements in the process.

Materials and Methods

All OCs were prepared by a complex polymerisation method. Activity evaluation was conducted in a fixed bed flow reactor at 873 K. In this test, 500 mg of OC was used, with an alternating supply of 50% C₂H₆ and 50% CO₂ (each at a total flow rate of 60 mL/min). In the performance comparison, the results are based on the analysis of the gas collected in a gas bag during the first 5 min of the 2nd cycle.

Results and Discussion

Based on structural analysis by XRD and STEM-EDX, it was found that Ni_{1-x}Cu_x-In₂O₃ starts with a structure in which In₂O₃ is modified with a Ni-Cu binary alloy, and then

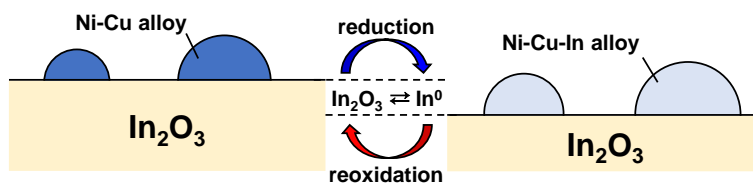


Figure 1 schematic image of redox of Ni_{1-x}Cu_x-In₂O₃.

forms a Ni-Cu-In ternary alloy by incorporating In^0 , which is formed by the reduction of In_2O_3 by C_2H_6 . In the regeneration process with CO_2 , In^0 was oxidised and returned to a structure composed of Ni-Cu binary alloy and In_2O_3 . The schematic image is shown in Figure 1.

C_2H_4 formation was evaluated at 873 K. Modification with Ni and/or Cu significantly enhanced activity compared to bare- In_2O_3 . Among these, Ni-Cu alloy modification exhibited superior performance relative to either Ni or Cu alone. In particular, modification with Cu-rich alloys, such as $\text{Ni}_{0.1}\text{Cu}_{0.9}$, achieved both high activity and selectivity, with a trend toward decreased selectivity as the Ni content increased. $\text{Ni}_{0.1}\text{Cu}_{0.9}\text{-In}_2\text{O}_3$, which exhibited the best performance, was found to release and regenerate more than 4wt% of lattice oxygen, as determined by thermogravimetric analysis. The regeneration process involving CO_2 splitting was faster in Cu-rich OCs, and in $\text{Ni}_{0.1}\text{Cu}_{0.9}\text{-In}_2\text{O}_3$, it was completed in a similar time to the C_2H_6 oxidation process.

The result of C_2H_6 -TPR measurement showed that modification with Ni and/or Cu significantly improves the reduction of In_2O_3 . Since Cu itself has a poor ability to activate C_2H_6 ; therefore, it is considered that Cu plays a role in facilitating access of the gas phase to the lattice oxygen of In_2O_3 by incorporating In^0 by alloying. There are two peaks in the region below 873 K in the TPR profile (peak 1 and peak 2 in Figure 3). Peak 1 attenuated as the Ni content decreased, and this was consistent with the trend in CO_2 selectivity during C_2H_6 supply. Therefore, peak 1 is considered to correspond to the decomposition of C_2H_6 over Ni ensemble and the combustion of products by the lattice oxygen of In_2O_3 . $\text{Ni}_{0.1}\text{Cu}_{0.9}\text{-In}_2\text{O}_3$ exhibited superior activity and selectivity compared to $\text{Cu-In}_2\text{O}_3$, with the only difference in the TPR profile being the presence of peak 2, indicating that peak 2 contributes to the selective oxidation of C_2H_6 . Detailed examination of the structural changes during the OC reduction process and evaluation of the activation barrier of C-H cleavage at each active site by theoretical calculation were conducted, and it is suggested that peak 2 corresponds to ethane dehydrogenation at Ni sites in the Cu-Ni-In ternary alloy formed during the reaction process and hydrogen combustion.

In conclusion, the modification with Ni-Cu significantly improved the performance of In_2O_3 as an oxygen carrier. In the selective oxidation process of C_2H_6 , In_2O_3 was reduced to In^0 and incorporated into the Ni-Cu alloy to form the ternary alloy. The incorporation of In^0 prevents In_2O_3 surfaces from being covered by In metal and assists in the reaction by releasing lattice oxygen of In_2O_3 . Cu suppressed side reactions by breaking Ni ensemble and promoted the CO_2 splitting step. Ni promoted the activation of C_2H_6 , and in particular, the Ni species in ternary alloy formed during the reaction showed higher activity.

References

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2. Y. Gao, L. Neal, D. Ding, W. Wu, C. Baroi, A. M. Gaffney, and F. Li, *ACS Catal.* **2019**, 9, 8592–8621.

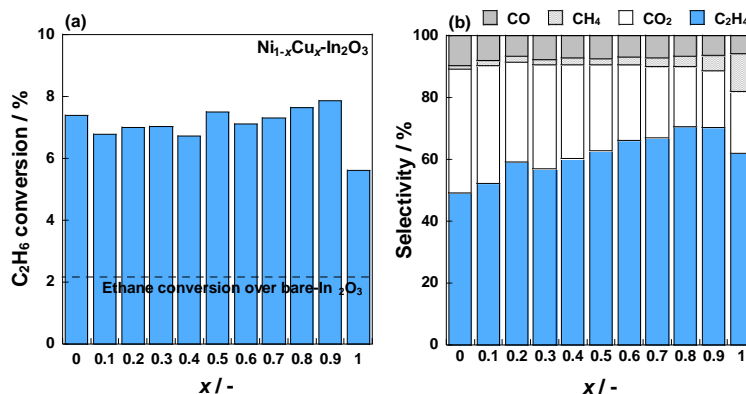


Figure 2 (a) C_2H_6 conversion and (b) products distribution during the ethane oxidation step over $\text{Ni}_{1-x}\text{Cu}_x\text{-In}_2\text{O}_3$.

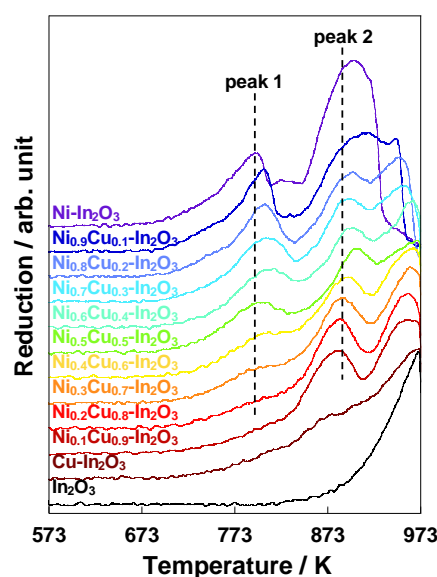


Figure 3 C_2H_6 -TPR profiles of $\text{Ni}_{1-x}\text{Cu}_x\text{-In}_2\text{O}_3$.