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Deciphering the impact of Nickel–doped modulation of AgO catalysis in aerobic ethylene epoxidation

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Ethylene oxide (EO) is an important chemical intermediate for manufacturing plastics, solvents, and detergents in major, thus with a continuous market growth in recent decades. However, traditional aerobic ethylene epoxidation over AgO/α-Al_2O_3 catalyst is hard to simultaneously achieve high selectivity and per-pass conversion, ascribing to competitive EO deep oxidation into carbon dioxide and water.[1] Consequently, to decrease the formation of side products, the per-pass ethylene conversion is generally carried out at 10 to 15% while EO selectivity remains around 90% in industry, leading to high energy consumption and carbon dioxide emission. Therefore, it is of great meaning to improve EO selectivity at high conversion through catalyst design innovation.

The catalysis origin of AgO/α-Al_2O_3 catalyst attributes to high oxygen adsorption volume, yet meanwhile intensifies both the primary ethylene combustion and secondary EO combustion, respectively, thus with a quite low EO selectivity of 50 to 60% at conversion below 10%. To mitigate these combustions, chlorine (Cl) is indispensably employed in industrial EO production, exhibiting selectivity increased by around 25% over pure AgO catalyst (around 55%). On the basis of Cl promoter, the introduction of other promoters, such as alkali metals (e.g., Cs and Li) and oxyanions of transition metals (e.g., Mo and Re), can further slightly increase EO selectivity of 1 to 5%, yet deciphering the intricate functions of various promoters remains a challenge. Nevertheless, this combination strategy still cannot eliminate the corrosive

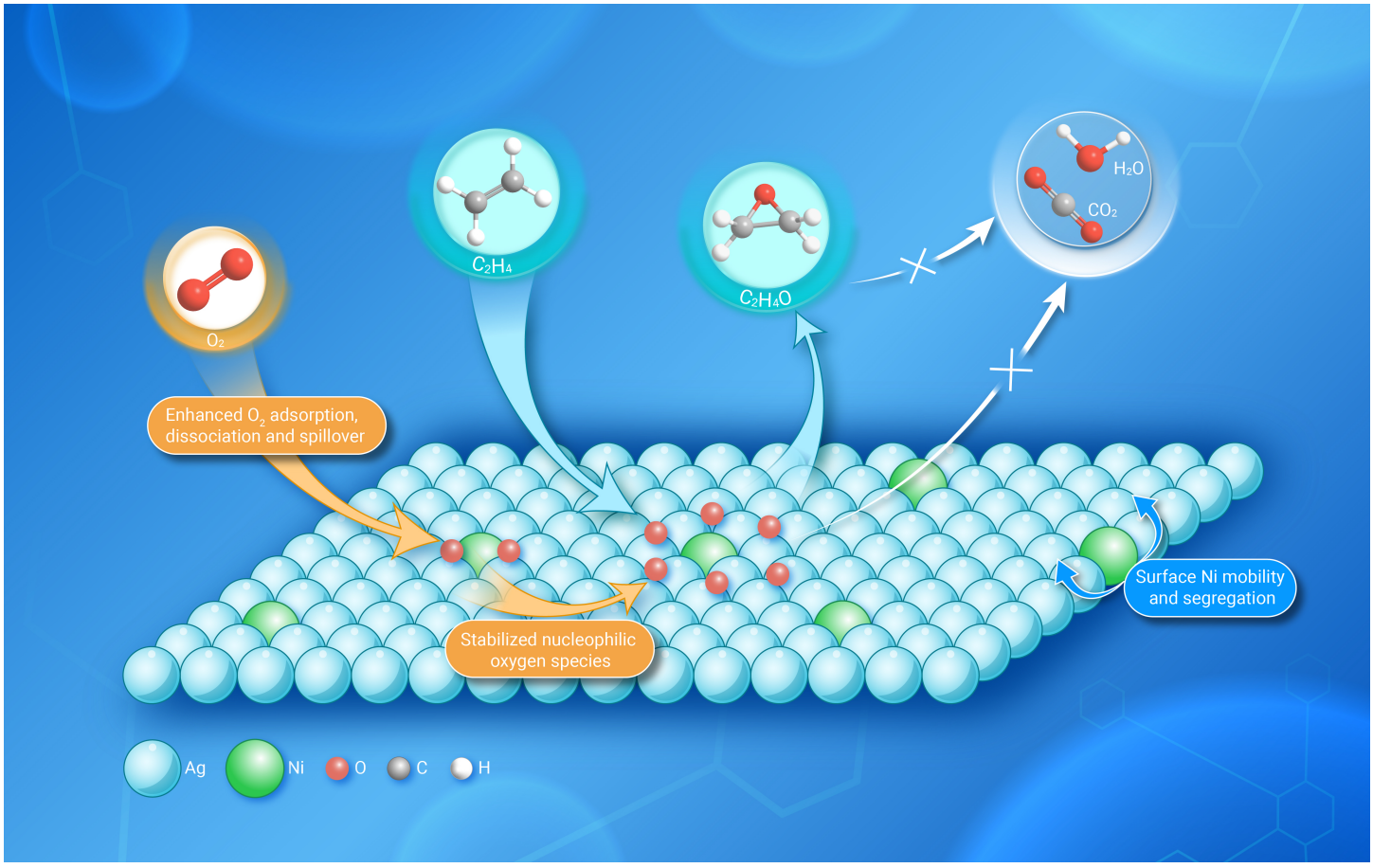

Figure 1. Scheme of NiAg catalyzed ethylene epoxidation process.

properties and environmental hazards associated with Cl promoter.[2]

Recently, a groundbreaking study by Jalil et al., published in the journal Science, has demonstrated that incorporating dilute nickel (Ni) as an independent dopant into AgO catalysts can function similarly to the Cl promoter, resulting in an approximately remarkable 25% increase in EO selectivity, which challenges the long-entrenched reliance on Cl in ethylene epoxidation catalysis.[3] The discovery of new promoters is theory-guided using single-atom alloy (SAA) concept by density function theory (DFT) method. Ni as a single-atom dopant disrupts the scaling relationship between the O_2 dissociation barrier ($E_{a,diss}$) and the adsorption energy of dissociated O atoms ($E_{ads,2O}$) for each single-atom dopants in Ag(111). It facilitates a near-barrierless dissociation of O_2 (< 0.05 eV) while concurrently maintaining a moderate binding energy (−2.2 eV).[4] As a result, temperature-programmed desorption of adsorbed oxygen (O_2-TPD) confirms that the Ni alloyed Ag(111) surface enables facial uptake and spillover of oxygen at low 10^{-6} Torr pressure of O_2, which cannot occur on the pure Ag(111) surface. Furthermore, it is well veri-

fied that under ethylene epoxidation conditions, Ni exhibits mobility and segregates to the surface of Ag(111), which is thermodynamically driven by the oxophilicity of Ni. Notably, along with the Ni loading increases, EO selectivity rises while the ethylene conversion declines. Therefore, the optimal EO selectivity in $NiAg_{200}$ is mainly attributed to the inhibition of both ethylene and EO through Ni coverage on the surface, which is remarkably similar to that of Cl promoter. Then, in the presence of Cl promoter, $NiAg_{200}$ exhibits much higher EO selectivity (~90%, without the participation of other promoters like Cs and Re), ethylene conversion and stability compared to the pure Ag surface. This indicates that Ni and Cl on the Ag surface act synergistically to modify the epoxidation pathways, thus offering a promising approach to simplify catalyst formulations. Moreover, ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) reveals that the thermal stability of nucleophilic oxygen can reach up to 700 K in NiAg(111), while it is only 550 K on pure Ag(111). Hence, the improved thermal stability of nucleophilic oxygen induced by Ni incorporation favors minimizing the non-selective primary and secondary combustion rates. For this excellent work, we would like to highlight three key scientific issues on this Nickel-induced modulation of AgO catalysis:

(1) **Electronic property modification.** Inspired by the single-atom alloy (SAA) concept, different metal elements were introduced to enhance the dissociation and spillover of O_2 and weaken oxygen binding energy, thus decoupling activation energies at various stages. Benefited from its unique electronic structure and local coordination environment, Ni exhibits the disruption of the scaling relationship between $E_{a,diss}$ and $E_{ads,2O}$ for various dopant modification systems. Therefore, as confirmed by O_2-TPD method, Ni enables a near-barrierless dissociation of O_2 (< 0.05 eV), thus it enabled uptake of oxygen on Ag at low O_2 pressure, a feat not achievable with pure Ag.

(2) **Dynamic surface Ni mobility and segregation**. Under ethylene epoxidation conditions, abundant characterization data have firmly established that, within an oxygen-rich environment, Ni atoms display remarkable mobility and segregation preferentially to the surface of Ag(111), which is thermodynamically propelled by the high oxophilicity of Ni. Significantly, the segregation of Ni atoms enables them to interact more readily with surface-adsorbed oxygen species, similar as the role of Cl promoter, thereby altering the stabilization of oxygen intermediates and further reaction pathways.

(3) **Rationalize the stabilization of oxygen intermediates and reaction pathways**. Nickel, as a Cl-free promoter, doped on Ag(111) surface has the ability to stabilize nucleophilic oxygen species, causing stability of nucleophilic oxygen up to 700 K, in contrast to 550 K on pure Ag(111). This enhanced stability enables a more controlled orientation of ethylene and oxygen molecules. Meanwhile, it curtails the reactivity of nucleophilic oxygen towards the unwanted cleavage of C–C bonds. As a result, both non-selective primary ethylene combustion and secondary EO combustion reactions are mitigated, thereby enhancing EO selectivity.[5] The study also reports the cooperative effect of Ni and Cl, achieving ~90% EO selectivity without additional promoters like Cs or Re, showing much better industrial application potential.

Above all, Jalil et al.'s work exemplifies the power of combining theoretical predictions with surface science and catalytic studies. Under the background of decarbonization in industry, it redefines ethylene epoxidation catalysis through decoupling oxygen activation from combustion pathways over Ni alloyed Ag catalyst to minimize combustion reactions, which provides a high-performance and sustainable alternative to Cl-promoted systems. Thus. Ni-doped Ag catalysts could play a central role in reducing energy consumption and CO_2 emissions associated with EO production. Notably, Ni dopant not only functions independently but also complements existing industrial Cl-promoter practice, offering a pathway to simplify catalyst formulations. Further exploration concerning the coordination of Ag active sites and promoters could be conducted by integrating advanced characterization techniques (e.g. *in-situ* X-ray absorption spectroscopy, surface-enhanced Raman spectroscopy) and AI-driven theoretical calculations (e.g. machine learning, deep learning), to clarify the synergic mechanism in EO production, and hence promote catalyst design. The mechanistic insights into Ni's role in oxygen stabilization modulation provide a guidance for future catalyst development, as well as other oxidation processes. Additionally, to enhance the stability of dynamic oxygen intermediates, the electronic metal-support interactions could be altered via modifying the pore textile, surface properties and matrix substitution of α-Al_2O_3. Meanwhile, the kinetics on the combination of novel catalysts and highly efficient reactors, such as membrane reactor and microchannel reactor, warrants greater attention, especially for large scale industrialization. As a consequence, those efforts will further improve the efficiency of ethylene epoxidation and catalyst stability.

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All authors contributed to and approved the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.