Asymmetric Ru-In Atomic Pairs Promote Highly Active and Stable Acetylene Hydrochlorination

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ABSTRACT

Ru single-atom catalysts have great potential to replace toxic mercuric chloride in acetylene hydrochlorination. However, long-term catalytic stability remains a grand challenge due to the aggregation of Ru atoms caused by over-chlorination. Herein, we synthesize an asymmetric Ru-In atomic pair with vinyl chloride monomer yield (>99.5%) and stability (>600 h) at a gas hourly space velocity of 180 h^{-1}, far surpassing those of the Ru single-atom counterparts. A combination of experimental and theoretical techniques reveals that there is a strong *d-p* orbital interaction between Ru and In atoms, which not only enables the selective adsorption of acetylene and hydrogen chloride at different atomic sites but also optimizes the electron configuration of Ru. As a result, the intrinsic energy barrier for vinyl chloride generation is lowered, and the thermodynamics of the chlorination process at the Ru site is switched from exothermal to endothermal due to the change of orbital couplings. This work provides a strategy to prevent the deactivation and depletion of active Ru centers during acetylene hydrochlorination.

KEY WORDS

acetylene hydrochlorination; Ru-In dual-atomic centers; excessive chlorination; asymmetric catalysis; orbital couplings

1. INTRODUCTION

Acetylene (C_2H_2) hydrochlorination is a critical industrial process for the production of vinyl chloride monomer (VCM), which accounts for 35% of global poly(vinyl chloride) (PVC) output. The conventional catalysts, activated carbon-supported mercuric chloride ($HgCl_2$/AC), have faced strong restrictions due to the Minamata Convention on Mercury, thus demanding green, Hg-free alternatives such as noble metal catalysts (e.g., Au, Pd, Ru, etc.). In recent years, ruthenium single-atom catalysts (Ru SACs) have emerged as promising candidates due to their excellent chlorine affinity and flexible control of active site architectures. However, Ru SACs always suffer from easy deactivation due to metal aggregation induced by over-chlorination and simultaneous coke deposition. In addition, the steric hindrance of the transition state during the reaction at the atomic site substantially impedes the further improvement of activity. Therefore, the rational design of Ru SACs with high activity and stable performance towards acetylene hydrochlorination remains a grand challenge.[1~3]

Recently, the synthesis efforts have been expanded to neighboring sites of single-atom metal that give rise to the bifunctional site at the atomic level and unlock excellent performance for acetylene hydrochlorination. Inspired by these previous studies, the fabrication of dual-atom catalysts offers an effective strategy to enhance the reactivity and stability as a result of optimizing the activation behavior of acetylene and hydrogen chloride (HCl) through orbital coupling between two adjacent metal atoms (e.g., *d-p* hybridization). In addition, the *p* block element indium (In) is known to have abundant empty 5*p* orbitals and exhibit a high degree of electrophilicity. In this regard, the assembly of a single In site next to atomic Ru (i.e., In–Ru DAC) is expected to manipulate the electron configuration of Ru and deliver a desired environment to balance the trade-off between reactivity and stability, resulting in highly stable acetylene hydrochlorination.[4~6]

2. RESULTS

Ru-N-In/NC showed an excellent initial activity of ~99.51% in comparison with the lower acetylene conversions of RuN_4/NC (~76.35%), InN_4/NC (~18.15%), and NC (~15.69%). Subsequently, we compared the turnover frequency (TOF) of Ru-N-In/NC with the recently reported catalysts. Intriguingly, the activity of Ru-N-In/NC was not only far exceeded by those of other Ru-based catalysts, but also higher than that of several Au- and Pt-based samples. Such a stable catalysis for Ru-N-In/NC in terms of time on stream (TOS, 600 h) and deactivation rate (0.001%/h) in the present study was apparently superior to other recently reported catalysts. However, the completed deactivation was observed for RuN_4/NC within 120 hours.

To unlock the intrinsic mechanism of the promising stability of Ru-N-In/NC, we first calculated the dissociation energy of Ru atom to be

1.86 and 1.27 eV for Ru-N-In/NC and RuN_4/NC, respectively, suggesting a higher binding strength between single atom Ru and the substrate in the case of a dual-atom catalyst. Then, in-situ DRIFTS NH_3 adsorption characterization indicated that the Lewis acidity of Ru-N-In/NC was weakened compared to RuN_4/NC, which could potentially prevent over-chlorination on the atomic Ru site.

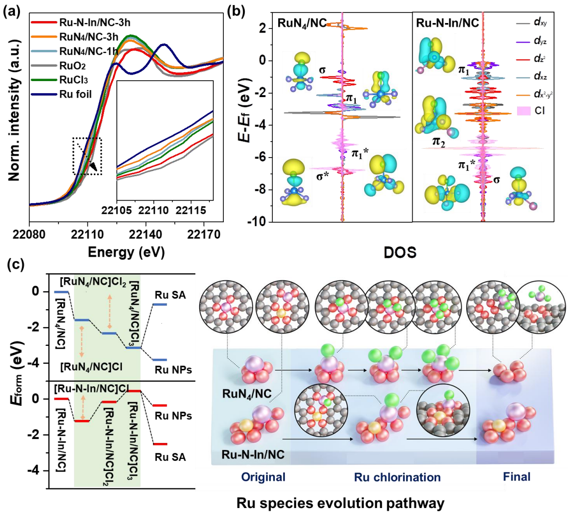

Fig. 1 (a) The normalized Ru K-edge XAFS plots of the post-hydrochlorination samples of Ru-N-In/NC-3h, RuN_4/NC-3h, and RuN_4/NC-1h. (b) PODS of the Ru p orbitals and Cl* d orbitals after Cl* adsorption over the interface of RuN_4/NC and Ru-N-In/NC. (c) The formation energy of various Ru chlorinated species and the illustration of the evolution pathway of Ru species over Ru-N-In/NC and RuN_4/NC.

Next, we utilized Ru K-edge XANES to track the chemical and geometric states of Ru after chlorination of three hours for Ru-N-In/NC and RuN_4/NC. The FT k^3-weighted $\chi(k)$-function and structural parameters analysis based on the fitting of EXAFS spectra showed that the coordination number of Ru–Cl over Ru-N-In/NC-3h was kept ~1, while the coordination number of Ru–Cl on the post-hydrochlorination RuN_4/NC presented an increasing trend, from ~1.3 (RuN_4/NC-1h) to ~2.6 (RuN_4/NC-3h), verifying that the asymmetric Ru-N-In/NC configuration inherently blocked the over-chlorination of Ru (**Fig. 1a**).

To obtain insights into bonding information for Ru–Cl interactions, we conducted PDOS analysis for Ru d orbitals before and after Cl* adsorption. Generally, the $H^{\delta+}$ and $Cl^{\delta-}$ species in HCl can be seen as Brønsted acid and Lewis base, respectively. Thus, the Ru atom (Lewis acid) can accept the $Cl^{\delta-}$ atom (Lewis base) of HCl to form Ru–$Cl^{\delta-}$ and promote the scission of the H–Cl bond. As illustrated in **Fig. 1b**, upon the adsorption of Cl*, the interaction between the p orbital of Cl and the d_{z^2} orbital of Ru gives the σ bonds on both Ru-N-In/NC and RuN_4/NC. However, the π bonds are derived from the coupling between the p orbital of Cl and the d_{x2-y2} orbital of Ru for Ru-N-In/NC, while the involved orbitals are changed to p(Cl) and d_{yz}/d_{xz} for RuN_4/NC.

To reveal the evolution pathways of the chlorination process on the atomic Ru of Ru-N-In/NC and RuN_4/NC, the formation energies of chlorinated species and the related PDOS analysis were carried out. For RuN_4/NC, the gradual addition of *Cl to Ru centers was observed, giving a stable three Cl-coordination configuration (denoted as $[RuN_4/NC]Cl_3$) eventually. Most importantly, the entire chlorination process from RuN_4/NC to $[RuN_4/NC]Cl_3$ is highly exothermic (**Fig. 1c**). That is because once the original symmetrical confinement of RuN_4/NC was broken with the adsorption of the first Cl*, the subsequent chlorination process became more energy favorable. In contrast, although the evolution of [Ru-N-In/NC]Cl was easily obtained, the addition of second Cl* turned to be highly endothermic, as evidenced by the emergence of several obvious antibondings, such as the σ* bond (p orbital of Cl and d_{z^2} orbital of Ru) and π* bond (p orbital of Cl and d_{x2-y2} orbital of Ru). Therefore, the over-chlorinated structures such as $[Ru\text{-}N\text{-}In/NC]Cl_2$ and $[Ru\text{-}N\text{-}In/NC]Cl_3$ ($E_{form} > 0$ eV) are unstable (**Fig. 1c**). Overall, the strong d(Ru)-p(In) interaction orbital couplings in Ru-N-In/NC promote the thermodynamic transition of the chlorination process from exothermal to endothermal compared to RuN_4/NC, intrinsically avoiding the over-chlorination of Ru and ensuring its excellent stability.

3. CONCLUSIONS

In summary, we developed an asymmetric Ru-N-In/NC catalyst to efficiently address the over-chlorination of Ru for highly active and stable acetylene hydrochlorination. Accordingly, Ru-N-In/NC exhibited exceptional C_2H_2 conversions and long-term stability, which was evidently far superior to that of the symmetrical RuN_4/NC counterpart, state-of-the-art metal-based moieties, and commercial $HgCl_2$ catalysts. The enhanced performances result from the electronic delocalization and electron transfer induced by d-p hybridization between Ru and In atoms. The orbital couplings promote the thermodynamic transition of Cl* intermediates interacting with Ru from endothermal to exothermal, lowering the energy barrier for Cl* addition. Eventually, the selective adsorption of C_2H_2 and HCl on different sites to suppress coke accumulation.

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