

Precise Synthesis, Characterization, and Reactivity of Multi-functional Catalysts

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1. Introduction

Beyond the maximized atomic efficiencies and cost savings, atomically dispersed catalysts have attracted great attention in recent years due to the uniformity in active sites and careful regulation over local environments of active sites. Thus, it is interesting to investigate how the dispersed active site-support environment can be precisely engineered to control catalytic reactivity. In this work, we demonstrate control over the local coordination environment of atomically dispersed Rh on Al_2O_3 through a systematic tuning of interactions between Rh and ReO_x or WO_x species. Through this precise engineering of the local environment of atomically dispersed Rh species on an oxide support, it is shown that the local environment of the active site are significantly influenced, which in turn control ethylene hydroformylation reactivity. Whereas ReO_x were atomically dispersed on Al_2O_3 regardless of Re loading, the structure of WO_x on Al_2O_3 varied (atomically dispersed WO_x , polystungstate monolayer, to monoclinic WO_3 crystallites) by changing W loading, which influences the intrinsic reaction kinetics.

2. Experimental

Supported atomically dispersed Rh catalysts were prepared by a strong electrostatic adsorption method. Catalysts were characterized by a range of techniques, including UV-Vis and Raman spectroscopy, CO probe molecule infrared (IR), and transmission electron microscopy to understand the local structure and Rh charge state.

3. Results and Discussion

Figure 1 (a) and (b,c) show representative image of the $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$ and corresponding line scan intensity analysis of the two selected dimers, respectively. The difference in scattering intensity of Rh and Re species due to their different atomic mass (intensity $\propto Z^{1.5-2}$, where Z represents atomic number) evidences the formation of Rh-ReO_x atomically dispersed site pairs in $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$.

For ethylene hydroformylation, the propanal formation was greatly enhanced over $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$ and $\text{Rh}/\text{WO}_x\text{-Al}_2\text{O}_3$ relative to $\text{Rh}/\text{Al}_2\text{O}_3$, resulting in the higher selectivity toward propanal up to 63%. Interestingly, the selectivity toward propanal substantially changed depending on WO_x structure nearby dispersed Rh species. When Rh were localized with atomically dispersed WO_x ($\text{Rh}/1\text{WO}_x\text{-Al}_2\text{O}_3$), the selectivity toward propanal is the higher

(63%) than Rh on bare Al_2O_3 ($\text{Rh}/\text{Al}_2\text{O}_3$, 22%), a polystungstate monolayer ($\text{Rh}/2\text{WO}_x\text{-Al}_2\text{O}_3$, 43%) and monoclinic WO_3 crystallites ($\text{Rh}/8$ and $25\text{WO}_x\text{-Al}_2\text{O}_3$, 50%).

Kinetic experiments revealed that $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$ and $\text{Rh}/\text{WO}_x\text{-Al}_2\text{O}_3$ have higher CO reaction orders relative to $\text{Rh}/\text{Al}_2\text{O}_3$, indicating a decrease in the CO binding energy on Rh in Rh-ReO_x and Rh-WO_x co-localized structures, which was further evidence by CO temperature program desorption (TPD) characterization. This suggests that the promoted reactivity for $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$ and $\text{Rh}/\text{WO}_x\text{-Al}_2\text{O}_3$ was primarily due to an increase in the concentration of vacant sites under reaction conditions. As shown in Figure 2, the CO reaction orders increased and became positive over $\text{Rh}/1$ and $3\text{WO}_x\text{-Al}_2\text{O}_3$, potentially suggesting that C_2H_4 adsorbed on atomically dispersed WO_x reacts with CO on nearby dispersed Rh. Two classes of active sites consisting of Rh and WO_x with an atomic intimacy allow a cooperative bifunctional mechanism when Rh is coordinated with atomically dispersed WO_x , consistent with previous report studies reporting atomically dispersed WO_x as active sites for olefin metathesis.

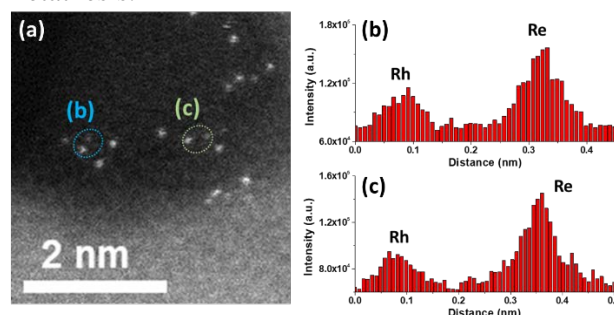


Figure 1. (a) HAADF STEM image of $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$. (b,c) Corresponding line scan intensity analysis of the two selected dimers shown in (a).

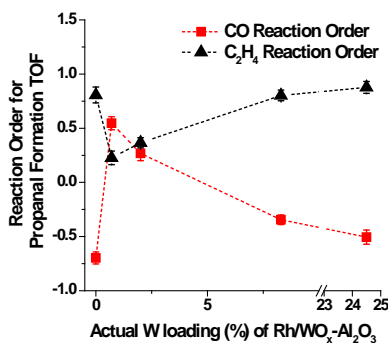


Figure 2. CO and C_2H_4 reaction orders for propanal formation TOF as a function of actual W loading of $\text{Rh}/\text{WO}_x\text{-Al}_2\text{O}_3$.