

Heterogeneous Catalysis at the Single-Atom Limit

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1. Introduction

Identification of the active catalytic site and design of catalysts with 100% atomic efficiency has been a long-standing goal in heterogeneous catalysis. Today, atomically dispersed supported metal catalysts can be prepared to test a reaction mechanism and may be further developed for industrial applications to low-cost fuel processing, and hydrogen and high value-added chemicals production [1]. The reaction landscape for application of single atom catalysts is rapidly expanding [2-8]. In this presentation, single metal atoms or cations of Pt and Au stabilized on various supports will be reviewed drawing examples from a variety of reactions, including the low-temperature water-gas shift reactions [2,3,7,8], methanol steam reforming [9,10], and several selective hydrogenation reactions [11-13]. It will be demonstrated that reaction mechanisms involving single metal atoms/cations transcend support structures and compositions as long as the metal atom-centered active site is allowed to form stably with the correct coordination. Novel synthesis methods will be discussed as will be the stability of atomically dispersed catalysts in various reaction environments. Single atom alloy (SAA) catalysts will also be discussed as a successful strategy to design highly selective hydrogenation and dehydrogenation catalysts that comprise trace amounts of a precious metal in a base metal like copper, the combination having largely improved activity and stability along with excellent selectivity [11-13].

2. Experimental

The preparation of supported atomically dispersed metals relies on the use of supports that contain a large number of anchoring points for the metal atom [1,2,5,7,8]. Often, shape effects are important as is the use of nanoscale supports. Typical methods of preparation include impregnation, anionic adsorption, and co-precipitation or some other one-pot synthesis. When the interest is in studying atoms on supports, in the absence of metal clusters or particles, very low metal loadings can be carefully added from the liquid phase or from the vapour phase using suitable metal precursors [1]. A novel method for preparing Au-Ox-Na- or Pt-O_x-Na-supported catalysts involves the addition of sodium hydroxide in the solid state to the support already impregnated with a solution of a compound containing platinum. Alkali metal cations are added to provide –OH groups to the active metal site, especially if the support lacks such capability, as was shown recently for Au or Pt/SiO₂ or m-SiO₂, TiO₂, and zeolites [7,8]. The single atom alloy catalysts are prepared by various techniques, a preferred one being galvanic replacement when a more noble metal is the minority component [12,13].

3. Results and Discussion

Similar TOF (per platinum atom) for the WGS reaction were observed over the sodium-containing platinum catalysts [8] on the various carriers shown in Fig. 1. The activities were

also similar to atomic Pt-O_x- species supported on ceria proving a similarly structured-active site [14]. Facile dissociation of water on the Na, Ce, Fe, or Ti cations surrounding the active Pt atom supplies the –OH for the reaction with CO. Pt(IV) is reduced to Pt(II) during the reaction. The catalysts were stable up to 300 °C under realistic conditions [8, 14]. For the SAA catalysts shown in Figure 2, the 1,3 butadiene hydrogenation activity of PtCu with atomic ratio 1:140 is markedly higher (10x at 70 °C) than the monometallic Cu sample, while both have high selectivity (~90%) to butenes at full conversion.

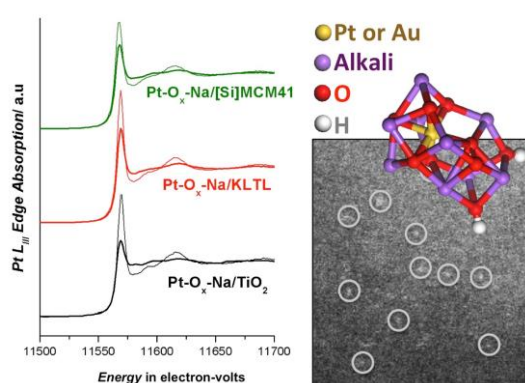


Fig. 1. XANES/EXAFS of similarly structured Na-O stabilized single- platinum atom clusters on titania, zeolites, and silica carriers, at RT (thin line) and after 275° C (bold line) in the WGS reaction [8].

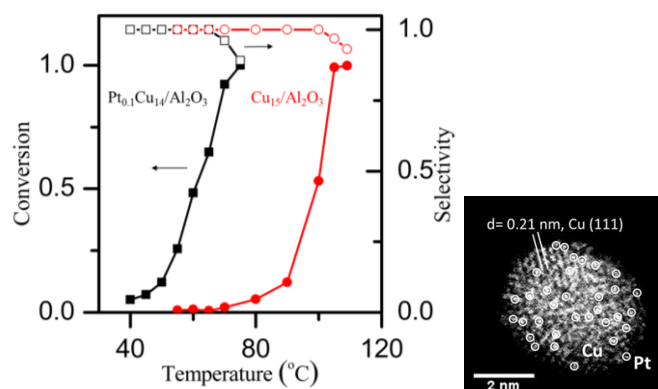


Fig. 2. Selective hydrogenation of butadiene over Cu₁₅/Al₂O₃ and Pt_{0.1}Cu₁₄/Al₂O₃ (SAA); 1, 3-butadiene (1.25%), H₂ (20%) and He (bal.). WHSV=0.09 h⁻¹ [13].

4. Conclusions

The era of designing heterogeneous single atom catalysts is upon us. These 100% atom efficient catalysts may be used to develop sustainable and cost-effective chemical processes.

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