



# Single-atom and small-cluster Pt induced by Sn (IV) sites confined in an LDH lattice for catalytic reforming



Yanru Zhu, Zhe An, Jing He\*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

## ARTICLE INFO

### Article history:

Received 17 February 2016

Revised 2 June 2016

Accepted 4 June 2016

### Keywords:

Pt dispersion

Single atoms

Small clusters

Hydrotalcite-like compounds

Catalytic reforming

## ABSTRACT

Conventional supported Pt for industrial catalytic reforming exhibits high conversion, but suffers low selectivity due to the hydrogenolysis reaction. The development of highly dispersed Pt offers the opportunity to settle this problem. Here, a supported Pt, with Pt dispersed in single atoms plus small clusters with fewer than 10 atoms (91%) on Sn-containing mixed metal oxides, has been prepared by the induction of a Sn component confined in the lattices of brucite-like layers of layered double hydroxides. Pt in single-atom and small-cluster dispersion effectively inhibits hydrogenolysis and significantly improves the selectivity to cyclization products in the *n*-heptane reforming reaction.

© 2016 Published by Elsevier Inc.

## 1. Introduction

Catalytic reforming is an important secondary processing procedure for crude oil, which converts the naphtha feedstock into high-octane reformates, playing a key role in solving the demand for gasoline consumption and quality upgrading [1]. The isomerization and cyclization reactions in catalytic reforming are value-enhancing because they provide high-octane products. But it is necessary to inhibit hydrogenolysis byproducts for the sake of atom economy. Aromatization needs to be avoided as well, since carcinogenic aromatic compounds are limited by environmental regulations [2]. On alumina-supported Pt, the reforming catalyst applied in industry [3–5] and of wide research interest [6–10], hydrogenolysis was favored on large Pt ensembles containing five atoms, the so-called B5 sites [6,7], and the aromatization requires Pt sites with threefold symmetry [8,9]. Therefore, highly dispersed Pt catalysts with abundant atomic sites are critical to inhibit the byproducts and could catalyze the reforming process better than large clusters or even particles [10]. Introduction of a second or even a third component, such as Sn, Re, Ge, or Ir, offers a way to enhance Pt dispersion [11–20].

More and more studies point to the importance of highly dispersed metallic catalysts because of their enhanced catalysis in a variety of significant reactions [21–26]. For example, Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts with smaller contiguous Pt islands [21,22] exhibit high

selectivity to isomerization and cyclization, but low selectivity to aromatization and hydrogenolysis in *n*-hexane reforming. Isolated Pd atoms dispersed onto Cu surfaces allow very selective hydrogenation of styrene and acetylene [23]. Alumina-supported single-atom alloy nanoparticle catalysts with low concentrations of individual Pt atoms on a Cu surface have been found to exhibit excellent activity for butadiene hydrogenation, with high butene selectivity under mild conditions [24]. An Ag-alloyed Pd single-atom catalyst supported on silica gel provides excellent catalysis in the selective hydrogenation of acetylene under ethylene-rich conditions [25]. The catalyst consisting of only single Pt atoms uniformly placed on an FeO<sub>x</sub> support shows extremely high activity for both CO oxidation and PROX reactions [26].

Many efforts have been dedicated to improving the dispersion of active metal sites [27–31]. A mass-selected soft-landing technique is powerful in the preparation of supported metal clusters or even single-atom catalysts, because of its exact control of the size of metal species using mass-selected atom beams [28]. A wet-chemistry approach is often used to anchor single-site metals to the support surface because the precursor already contains single-atom metal species, so long as an aggregation can be avoided in the post-treatment processes [29,30]. A few studies show that the support surface defects could serve as anchoring sites for metal clusters or even single atoms [26,31]. Nevertheless, to improve metal dispersion by a highly uniformly dispersed second element might be more controllable, suitable, and inexpensive. For example, either the iron oxide interface between Pt and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [32]

\* Corresponding author. Fax: +86 10 64425385.

E-mail address: [jinghe@263.net.cn](mailto:jinghe@263.net.cn) (J. He).

or the Pt–O–Ce bond in Pt/ceria-based oxide [33] could help promote Pt dispersion.

Layered double hydroxides (LDHs), also known as hydrotalcite-like materials, accommodate a wide range of divalent ( $M^{2+}$ ) and high-valence ( $M^{3+}$  or  $M^{4+}$ ) metal cations in brucite-like layers [34]. The metal cations are distributed uniformly at the atomic level within the brucite-like layers, owing to the absence of continuous  $M^{3+}$ –O– $M^{3+}$  bonds [35]. Thus, LDH materials, with great flexibility in chemical composition, prove inexpensive and versatile precursors for supported metal catalysts in which the metal components are highly dispersed [36–39]. For instance, well-dispersed and embedded metallic iron nanoparticles with a high density ( $10^{14}$ – $10^{16}$  m<sup>2</sup>) have been produced using  $MoO_4^{2-}$ -intercalated  $FeMgAl$ -LDHs as a precursor [38]. Uniform Ni–Fe alloy nanoparticles supported on mixed metal oxides (MMOs) are prepared by calcination and reduction of a  $NiFeMgAl$ -LDH precursor [39]. For noble metals such as Pt or Pd, which are difficult to insert into the lattices of brucite-like layers of LDHs, high dispersion could be achieved through the interactions between the supported noble metal component and another component confined in LDH or MMO lattices [36,40–43]. Bimetallic PtIn particles with an average diameter of 1 nm have been prepared by dispersing Pt on the surface of a calcined In-containing LDH support,  $Mg(In)(Al)O$  [42]. Highly dispersed bimetallic Pd–Ga/ $MgO$ – $Al_2O_3$  catalysts have been produced by introducing  $[PdCl_4]^{2-}$  anions into positively charged  $MgGaAl$ -LDH layers [43]. Our previous work has demonstrated that electron-rich (Sn) or electron-defect (Zr) sites, derived from Sn (or Zr)-containing LDHs, could induce oppositely charged Pt precursors to facilitate Pt dispersion [44]. In this work, Pt–Sn reforming catalysts, with Pt sites dispersed in single atoms and small clusters, have been produced by the electrostatic induction of highly dispersed and negatively charged Sn sites to cation Pt precursors, in which the highly dispersed Sn sites are confined in the brucite-like layers of Sn-containing LDHs as the precursor (Scheme 1). The negatively charged Sn sites are selectively controlled by the deprotonation of hydroxy groups by use of the extremely low isoelectric point ( $\sim 4.3$ ) [45] of Sn (IV) oxide or hydroxide. Owing to excellent dispersion of Pt, the resulting catalyst effectively inhibits the hydrogenolysis and promotes the cyclization in the *n*-heptane reforming reaction.

## 2. Experimental

### 2.1. Materials

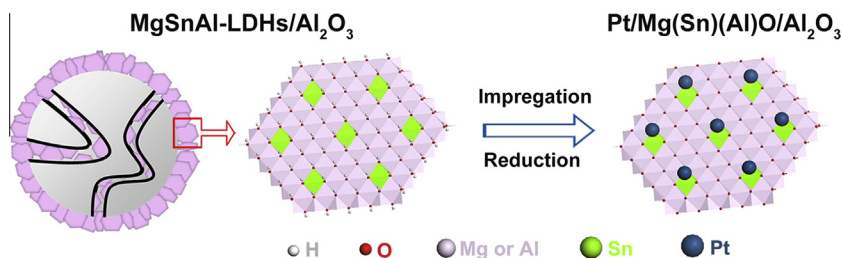
$Mg(NO_3)_2 \cdot 6H_2O$ ,  $SnCl_4 \cdot 5H_2O$ , urea, and sodium citrate were all of analytical purity.  $[Pt(NH_3)_4](NO_3)_2$  powder with 99.6% purity was purchased from Alfa Aesar. Methylcyclopentane (MCP) and *n*-heptane (J&K Scientific) were of HPLC purity. Commercial  $\gamma$ - $Al_2O_3$  as support (in 20–40 mesh and with a BET surface area of 228 m<sup>2</sup> g<sup>−1</sup>) was donated by SASOL (Sewula Africa).

### 2.2. Preparation

An  $MgSnAl$  LDH sample was synthesized on the surface of  $\gamma$ - $Al_2O_3$  by an in situ growth method [46]. Typically, 41 mg of sodium citrate and 49 mg of  $SnCl_4 \cdot 5H_2O$  were dissolved in 0.50 mL deionized water to form a  $Sn^{4+}$  citrate solution. Portions of 2.56 g of  $Mg(NO_3)_2 \cdot 6H_2O$  and 2.40 g of urea were dissolved in 4.5 mL deionized water to form a  $Mg^{2+}$  urea solution.  $Sn^{4+}$  citrate solution and  $Mg^{2+}$  urea solution were mixed well and then moved to a Teflon autoclave with 5.0 g of  $\gamma$ - $Al_2O_3$ . After aging at 120 °C for 12 h, the sample was filtrated, washed with deionized water till neutrality, and dried at 70 °C overnight, to give a  $MgSnAl$ -LDHs/ $Al_2O_3$  sample. Similar procedures were used to prepare  $MgAl$ -LDH/ $Al_2O_3$  samples in the absence of Sn citrate solution.  $Sn^{4+}$  was loaded on as-prepared  $MgAl$ -LDH/ $Al_2O_3$  or  $Al_2O_3$  by the incipient wetness impregnation method. A portion of 1.8 mL of  $SnCl_4 \cdot 5H_2O$  acetone solution (the concentration of  $Sn^{4+}$  is 3.7 g L<sup>−1</sup>) was impregnated onto 2 g of  $MgAl$ -LDH/ $Al_2O_3$  or  $Al_2O_3$  support; then the sample was oscillated for 2 h at ambient temperature and dried at 120 °C overnight.  $Pt^{2+}$  loading was achieved by the incipient wetness impregnation method. A portion of 13 mg of  $[Pt(NH_3)_4](NO_3)_2$  was dissolved in 1.8 mL of deionized water. This solution (pH 8) was then poured onto 2 g of an as-prepared  $MgSnAl$ -LDHs/ $Al_2O_3$  sample,  $Sn^{4+}$ -loaded  $MgAl$ -LDH/ $Al_2O_3$ , or  $Sn^{4+}$ -loaded  $Al_2O_3$ . The resulting sample was oscillated at ambient temperature for 2 h and dried at 120 °C overnight. A  $PtO_2/Mg(Sn)(Al)O/Al_2O_3$ ,  $PtO_2/SnO_2/Mg(Al)O/Al_2O_3$ , or  $PtO_2/SnO_2/Al_2O_3$  sample was produced by calcining  $Pt^{2+}$ -loaded  $MgSnAl$ -LDHs/ $Al_2O_3$ ,  $Sn^{4+}/MgAl$ -LDH/ $Al_2O_3$ , or  $Sn^{4+}/Al_2O_3$  at 550 °C for 2.5 h in flowing air (40 mL min<sup>−1</sup>). The temperature was raised from ambient temperature to 550 °C at 2 °C min<sup>−1</sup>. After calcination at 550 °C for 2.5 h, the temperature was decreased to 500 °C in  $N_2$  flow (40 mL min<sup>−1</sup>). Then a  $H_2$  flow (40 mL min<sup>−1</sup>) was introduced and the temperature was maintained at 500 °C for 2.5 h, affording  $Pt/Mg(Sn)(Al)O/Al_2O_3$ ,  $Pt/SnO_x/Mg(Al)O/Al_2O_3$ , and  $Pt/SnO_x/Al_2O_3$ . For comparison, 0.3 wt.%  $Pt/Al_2O_3$  or 2 wt.%  $Pt/Al_2O_3$  was produced following the above procedures, except for the loading of Sn element. For the temperature-programmed reduction (TPR) evaluation of Sn (IV),  $Mg(Sn)(Al)O/Al_2O_3$ ,  $SnO_2/Mg(Al)O/Al_2O_3$ , and  $SnO_2/Al_2O_3$  were produced by calcining  $MgSnAl$ -LDHs/ $Al_2O_3$ ,  $Sn^{4+}/MgAl$ -LDH/ $Al_2O_3$ , and  $Sn^{4+}/Al_2O_3$  at 550 °C for 2.5 h.

### 2.3. Characterizations

Elemental analysis for Pt and Sn was performed using a Shimadzu ICPS-75000 inductively coupled plasma optical emission spectrometer (ICP-OES). Before the measurements, 30 mg of the sample was put into a Teflon autoclave with 5 mL of nitromuriatic acid at 100 °C until completely dissolved. The solution was transferred to a 10 mL volumetric flask and diluted to volume with deionized water. Powder X-ray diffraction (XRD) patterns



**Scheme 1.** Schematic illustration of the preparation of highly dispersed Pt catalyst.

Download English Version:

<https://daneshyari.com/en/article/60485>

Download Persian Version:

<https://daneshyari.com/article/60485>

[Daneshyari.com](https://daneshyari.com)