Journal of Catalysis 340 (2016) 60–65

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Priority Communication

Improved promoter effect in NiWS catalysts through a molecular approach and an optimized Ni edge decoration

Thibault Alphazan [a], Audrey Bonduelle-Skrzypczak [a], Christèle Legens [a], Zoubeyr Boudene [a], Anne-Lise Taleb [a], Anne-Sophie Gay [a], Ovidiu Ersen [b], Christophe Copéret [c,*], Pascal Raybaud [a,*]

[a] IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, 69360 Solaize, France
[b] IPCMS-UMR 7504, CNRS, Université de Strasbourg, 23 rue du Loess, BP 43, 67034 Strasbourg cedex 2, France
[c] ETH Zürich, Department of Chemistry and Applied Biosciences, Vladimir Prelog Weg. 1-5, CH-8093 Zürich, Switzerland

ARTICLE INFO

Article history:
Received 3 January 2016
Revised 29 April 2016
Accepted 6 May 2016
Available online 6 June 2016

Keywords:
Hydrotreatment
Toluene hydrogenation
NiWS
Surface chemistry
Mixed edge sites

ABSTRACT

An efficient preparation method – based on the grafting and deposition of Ni and W molecular precursors onto partially dehydroxylated amorphous silica–alumina followed by a thermal treatment under H_2S/H_2 – generates supported NiWS catalysts exhibiting enhanced activities in toluene hydrogenation, by comparison with conventional samples, prepared from metallic salts. A careful analysis of these materials by IR, XPS, TEM, HAADF-STEM, together with DFT calculations, reveals that the improved activity probably originates from the lower sulfidation temperature of W that improves distribution of Ni–W mixed sites at the edges of NiWS crystallites. This provides an optimal compromise between intrinsic activity and surface concentration of active sites.

1. Introduction

In the context of the evolution of oil resources and environmental regulations, the expected expansion of catalytic hydrocracking and hydrotreating (HDT) processes for producing clean – sulfur free – fuels remains a crucial industrial challenge. Promoted molybdenum and tungsten phases (CoMoS, NiMoS, NiWS) are profitably used in industrial HDT processes [1]. Despite intense research in this area, a strong challenge resides in the continuous improvement of the intrinsic catalytic performance of these active phases, and more particularly for WS_2 based catalysts.

Recently, the preparation of HDT catalysts through a molecular approach [2] referred to as surface organometallic chemistry (SOMC) or in a more general term controlled surface chemistry (CSC) [3–7] allowed reaching high catalytic performances for non-promoted WS_2 phases supported on amorphous silica–alumina (ASA). In particular, the sulfide phase generated by CSC exhibits specific two-dimensional (2D) morphology features and unprecedented sulfidation level, even at temperatures as low as 23 °C [2]. However CSC non-promoted WS_2 catalysts remain much less active than their conventional Ni(Co)-promoted counterparts prepared from metallic salts in aqueous solution, which exhibit higher intrinsic hydrodesulfurization (HDS) or hydrogenation (HYD) activities by at least one order of magnitude [1]. In the early eighties, silica and alumina supported NiMoS and NiWS phases were prepared by a similar CSC approach, and revealed enhanced activity in thiophene HDS, by comparison with catalysts prepared with conventional Ni and W salts in aqueous solution [8]. Whatever the preparation method, it is expected that the fine tuning of the promoter (Ni, Co) to metal (W, Mo) ratio should provide optimized activities [8–12]. According to density functional theory (DFT) studies [10,13,14], modifying the promoter/Mo(W) ratio provides various structural configurations of the active sites located at the "M-edge" or "S-edge" of the NiMoS or NiWS nanocrystallites. However, quantitative structure–activity relationship between the Ni promoter edge location in each NiW(Mo)S nano-crystallite and the resulting intrinsic activity is still a challenging task. It is in particular difficult to tune the Ni/W ratio without modifying simultaneously other parameters such as particle sizes or stacking number [15]. In addition, such structure–activity relationships depend on the targeted reaction: HDS, HYD, hydrodenitrogenation (HDN), etc. Theoretical studies suggested that HYD or HDS active sites for MoS_2-based catalysts are located on M- or S-edge [10,13,14,16]. NiWS catalysts, however particularly efficient for reactions involving aromatic hydrogenation (including HDN) [17,18], remain far less studied at a molecular scale than their

---

* Corresponding authors.

E-mail addresses: ccoperet@inorg.chem.ethz.ch (C. Copéret), pascal.raybaud@ifpen.fr (P. Raybaud).

http://dx.doi.org/10.1016/j.jcat.2016.05.004
0021-9517/© 2016 Elsevier Inc. All rights reserved.

NiMoS homologues [19], and their intrinsic performances, still far from being optimal, thus remain to be improved.

In what follows, we use a molecular approach to prepare a broad range of silica–alumina supported NiWS catalysts, where the Ni promoter distribution on WS_2 nanocrystallite edges is precisely quantified by various techniques: XPS, TEM, HAADF-STEM and DFT. In particular, we show that well-defined silica–alumina supported NiWS catalysts prepared by a molecular (CSC) approach display enhanced catalytic performances in toluene hydrogenation through a better control of the Ni promoter edge distribution.

2. Results and discussion

ASA-supported NiWS catalysts were prepared by post-treating the ASA-supported $[W(OEt)_5]_2$-based material, prepared by deposition of $[W(OEt)_5]_2$ on ASA [2], with a toluene solution of $Ni(acac)_2$ through an incipient wetness impregnation (IWI), yielding samples with about 1.6 (±0.1) W nm^{-2} and Ni/W atomic ratio ranging from 0.21 to 1.00 (Supporting Information). After activation through sulfidation, the catalytic performances were evaluated in toluene hydrogenation (see supplementary materials), and all activities (r_i) were firstly normalized per total atom of W (Fig. 1). It is one of the goals of the present work to evaluate turnover frequency (TOF) according to the atomic scale description of the active phase and sites as detailed in what follows.

Ni-promoted WS_2 materials (with Ni/W ∼ 0.2) exhibit improved reaction rates, which are one order of magnitude greater than for their non-promoted counterpart. This highlights the “synergy effect” between W and Ni when engaged in a mixed NiWS phase [1], similar to what is known for Co(Ni)MoS phases [20]. More strikingly, NiWS catalysts prepared by CSC are ∼1.5 times more active than dried or calcined samples synthesized from metallic salts according to conventional approaches, whether dried or calcined (Supporting Information). Catalytic performances expressed per catalyst weight (Fig. S1) illustrate this trend, and highlight the beneficial effect provided by the present molecular approach *vs.* conventional approaches.

To evaluate the influence of the different preparation methods on the physico-chemical properties of NiWS phases, samples were first characterized by XPS. For Ni/W ratio of ∼0.2, WS_2 catalysts exhibit close levels of sulfidation around 71–73 rel% WS_2, for samples prepared *via* CSC or by the conventional method using dried samples. The calcined sample undergoes sulfidation to a lesser extent (56 rel%), which is related to the formation of a refractory tungsten oxide phase during the calcination step. This incomplete sulfidation of W observed for all catalysts, for an industrially relevant sulfidation temperature (350 °C) is consistent with previous studies of ASA [21] or alumina [22–25] supported NiWS catalysts. However, CSC catalysts exhibit high levels of promotion, with up to 80 rel% NiWS (expressed in relative amount of Ni present in the NiWS phase, Table S1) *vs.* 57 rel% and 66 rel% for calcined and dried samples respectively. Thus the effective amount of NiWS active phase found on the CSC catalyst appears to be slightly higher than the dried sample and significantly higher than the calcined one (Table S1). Note also that for CSC samples, two higher Ni/W ratios (0.44 and 1.00) were studied. Results show that their amount of Ni_xS_y and NiWS phases increases, and that the $(Ni/W)_{slab}$ ratio (*i.e.* Ni/W ratio in NiWS slabs) reaches 0.50–0.57. XPS analyses thus show that the CSC method can efficiently generate Ni promoted WS_2 nano-crystallites.

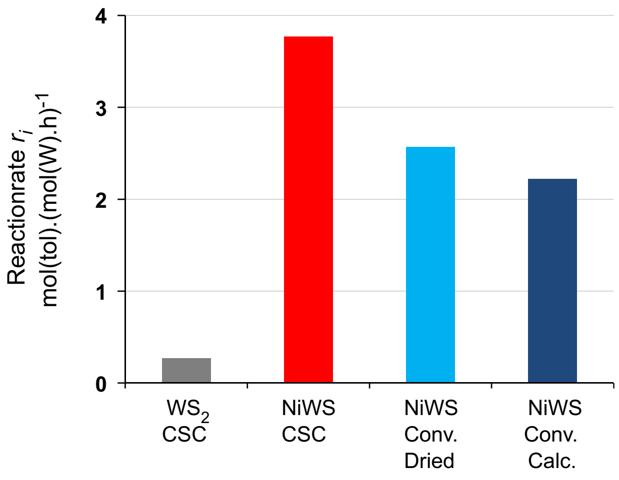

Fig. 1. Reaction rates, expressed in molecule of toluene converted normalized per total atom of W for ASA-supported WS_2 and NiWS catalysts, with W coverage ranging from 1.6 to 1.8 W nm^{-2}, and Ni/W atomic ratio of ∼0.2. Catalysts underwent sulfidation at 350 °C, under H_2S/H_2 mixture with 15 mol% H_2S for 2 h.

In our previous work [2], we have shown the ability of surface W ethoxy species to be sulfided at low temperature (23 °C). Therefore, the CSC NiW material was sulfided at 23 °C in order to get further insights into the genesis of the Ni_xS_y, NiWS and WS_2 phases. XPS analyses (Table S2) highlight first that at ambient temperature, the major part of Ni is sulfided as a Ni_xS_y phase (81 rel%), with no detectable incorporation of Ni in WS_2 slabs as in the so-called mixed NiWS phase. At 350 °C however, 80 rel% of Ni atoms are incorporated in WS_2. The high amount of W sulfide (42 rel%) initially generated at 23 °C on CSC samples probably allows for a better promotion of WS_2 slabs during sulfidation from 23 °C to 350 °C. Moreover, the mobility of Ni_xS_y species – the Hüttig temperature [26] of Ni_3S_2 is about 81 °C – enhances the incorporation of Ni in the WS_2 phase being simultaneously formed at lower temperature than through conventional methods. In conventional catalysts, which exhibit no W sulfide phase at 23 °C under similar conditions [2,27], incorporation of Ni in WS_2 slabs is likely delayed, and provides lower promotion levels (%NiWS), in particular for calcined samples [23]. These different genesis processes of NiWS also impact the Ni distribution at the crystallites' edges as it will be discussed with the help of DFT calculations (*vide infra*). Additional NiWS phases were also prepared by deposition of the $Ni(acac)_2$ onto preformed WS_2 (after sulfidation of $[W(OEt)_5]_2$ at 350 °C), as previously proposed in the literature [8,28–30]. XPS analyses and catalytic tests reveal that these catalysts exhibit lower amount of NiWS phase (45 rel% *vs.* 80 rel%) and lower catalytic activity (31% *vs.* 67% of toluene converted) than when prepared using successive impregnation of W and Ni molecular precursors, in spite of a high sulfidation level (84% WS_2). When WS_2 is preformed at 23 °C instead of 350 °C, higher amount of NiWS (53%) and catalytic activity (58% of toluene converted) is observed. Although more dedicated *in-situ* characterization analysis of the sulfidation process is required to precisely determine the origin of this improvement, we suspect that it may arise from a better interaction of $Ni(acac)_2$ either with the “nascent” WS_2 or with the W molecular precursor.

Interaction between the promoter and W thus appears to be of paramount importance in the genesis of the active phase, and the role of W surface species was further investigated. An additional NiWS catalyst was prepared by the successive IWI of a polyoxotungstate precursor and $Ni(acac)_2$. After sulfidation, this NiWS catalyst exhibits lower amount of NiWS phase (7 rel%) and lower catalytic activity (28% of toluene converted) than the sample prepared from $[W(OEt)_5]_2$ (*vide supra*). This clearly highlights that previous enhancements provided by the CSC method are linked to the highly reactive W ethoxy precursor. In this peculiar case, IR and GC/MS analyses (Supporting Information) performed on Ni(W) materials and the liquid phase after deposition, respectively, suggest a release of acac ligands from the Ni coordination sphere,