



Contents lists available at ScienceDirect

Journal of Catalysis

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

Post-synthesis Sn β : An exploration of synthesis parameters and catalysis

Jan Dijkmans^a, Jan Demol^a, Kristof Houthoofd^a, Shuigen Huang^b, Yiannis Pontikes^b, Bert Sels^{a,*}

^a Center for Surface Science and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium

^b Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium

ARTICLE INFO

Article history:

Received 6 April 2015

Revised 23 June 2015

Accepted 29 June 2015

Available online xxx

Keywords:

Heterogeneous catalysis

Lewis acid catalysis

Sn-beta

Post-synthesis procedures

Synthesis parameters

Adsorption process

ABSTRACT

Sn β is probably one of the best water tolerating heterogeneous Lewis acids for liquid phase catalysis. Instead of applying the usual lengthy hydrothermal synthesis to prepare Sn β , this contribution uses a more hands-on two-step synthesis method, involving the grafting of Sn precursors in isopropanol under reflux conditions on a commercial β zeolite that was dealuminated in acid. Among several reference synthesis procedures, this Sn introduction method resulted in active Sn catalytic sites. Taking advantage of this practical method, several synthesis parameters were explored and their impact on the catalytic activity in four different Lewis acid catalyzed reactions is discussed. The adsorption isotherm of Sn^{IV} in isopropanol over a broad range of Sn salt concentrations at reflux temperature is presented and discussed in relation with FTIR spectroscopy, UV–vis absorption characteristics and the porosity of the materials. The study reveals a selective Sn uptake, up to 2 wt% Sn loading, into silanol nests of the dealuminated precursor, forming a diversity of mononuclear Sn^{IV}. Higher Sn loadings result in less active Sn (hydrous) extraframework oxide phases, which also cause partial blockage of the zeolite micropores. Depending on the reaction type under study, space time yield may increase with increasing Sn loading, but the activity per Sn is always lower. Therefore it is concluded that a preferred synthesis should form high contents of isolated Sn active sites, especially for sugar isomerization and intermolecular Meerwein–Ponndorf–Verley, while the other reaction types like Baeyer–Villiger is also sufficiently catalyzed by the small Sn oxide clusters, albeit less actively.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

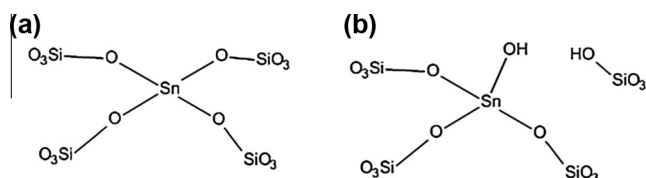
Sn-containing silica materials are widely studied in catalysis owing to their Lewis acid properties [1,2]. Tetrahedral Sn is able to expand its coordination with two extra ligands, forming an octahedral configuration [3,4]. Such expansion of coordination is useful for its interaction with organic reagents in a catalytic cycle. Formation of stable octahedral Sn sites, like in the framework of SnO₂, prevents such coordinative interaction rendering such materials catalytically inactive [5]. Therefore, homogeneous [6–12] and heterogeneous Sn-species with varying Sn geometry have been subject of many catalytic studies. The heterogeneous catalysts span from amorphous [13], over mesoporous [14–24] to highly crystalline zeolitic silica [1,2,25–29]. Among them, Sn β type zeolites show the highest catalytic activity, provided that not too large crystals or too bulky substrates are used [18,30,31]. According to literature, Sn β contains (in dried state) isolated and tetrahedrally coordinated Sn^{IV}, built into the framework [32]. The catalyst has been used successfully in several chemical transformations,

including hydrogen-shift, oxidation and carbon–carbon coupling reactions [25,30,33,34]. Though there is a general agreement on the presence of Lewis acidity because of Sn incorporation, the exact nature of the Sn active catalytic site is under debate. So far, two different Sn^{IV} active sites have been revealed showing a common 4–O inner-sphere complexation [4]: a perfect framework substitution leading to Sn(OSi)₄, also denoted as ‘closed’ site and a partly hydrated Sn species, formally written as Sn(OSi)₃(OH) and termed ‘open’ Sn sites [3,35]. A schematic representation of both sites is shown in Scheme 1. Multiple reports currently discuss the importance (or not) of SnOH and nearby SiOH groups for the catalytic properties [4,36,37]. Aside from the framework Sn-species, catalytic activity has also been ascribed to small extra-framework (EFW) oxidic Sn particles within the hydrophobic pores of the zeolite, whereas large Sn oxide particles on the crystal surface do not show this activity [5].

Sn β is usually synthesized by a traditional hydrothermal synthesis, that is above the water boiling point, in a closed vessel, reaching super-atmospheric pressure (Scheme 2, top pathway) [25,32]. During the synthesis process, Sn is gradually incorporated into the beta zeolite framework. Unfortunately, nucleation of Sn β from Sn-containing gels is difficult. To facilitate the crystallization

* Corresponding author.

E-mail address: bert.sels@biw.kuleuven.be (B. Sels).



Scheme 1. Schematic representation of a (a) closed tetrahedral Sn-site and (b) an open tetrahedral Sn-site.

process addition of seed crystals is often used [38]. In spite of successful synthesis of Sn β , long synthesis times and hazardous mineralizing agents like HF or NH $_4$ F are indispensable. More practical synthesis methods are therefore proposed. Modification of seeding procedures result in increased rate of crystallization, while other syntheses use steam to convert dry Sn gels into Sn β materials [39,40]. Unfortunately, these methods maintain the need for F-ions as mineralizing agents.

A different approach is followed in the so-called secondary (or post-) synthesis procedures. Instead of bottom-up synthesis, pre-formed zeolites like beta are doped with Sn (top-down approach, Scheme 2 bottom pathway). Usually, the parent zeolites are subjected to an acid treatment to remove (part of) framework Al (or Si or B), leading to dealuminated zeolites rich in silanol nests [41–44]. These silanol groups function as anchoring points for the Sn precursor. Among the top-down synthesis procedures, there is a large variety of ways to introduce Sn. A solid-gas reaction with gaseous SnCl $_4$ at elevated temperatures for instance results in a 6 wt% Sn β containing substantial amounts of framework Sn active sites but also catalytically inactive EFW SnO $_2$ [45,46]. A practical alternative, first introduced by the Hermans' group, describes a solid-state mixing method of the dealuminated beta zeolite with Sn $^{2+}$ acetate, followed by calcination. They showed the synthesis of Sn β with extremely high Sn content, up to 10 wt%, avoiding substantial content of EFW SnO $_2$ [47]. In a similar procedure, use of dimethyltin dichloride resulted in a 3.8 wt% of Sn β [48]. Finally, an adsorption process of SnCl $_4$ in dried isopropanol under reflux conditions, was recently communicated by our group, leading to an active 1.6 wt% Sn β [49,50].

The notion of turnover frequency (TOF) is used as a measure of the intrinsic activity of a catalytic site. In Sn-catalyzed materials too, efforts are reported to achieve maximal TOF values [4,49,51]. Though comparison between different reports is not always straightforward, as several reaction types are investigated at differ-

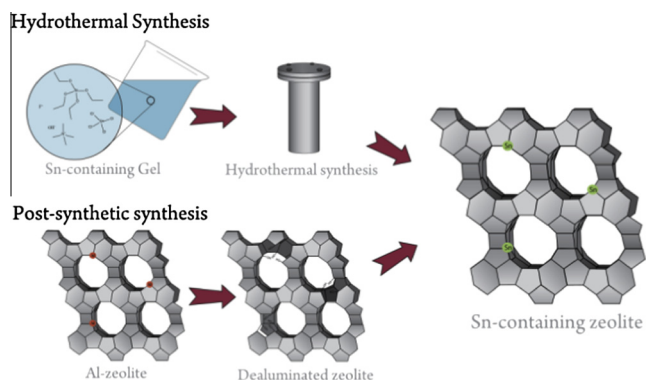
ent reaction conditions. In addition, use of TOF values implies the absence of any mass transfer rate limitation, causing underestimation of the true potential of the Sn sites and the determination of the concentration of the active site, provided the identity of the latter is known [14,31]. Also the heterogeneity of Sn sites makes the determination of genuine turn-over frequencies rather challenging. Alternatively, a property known as the space-time yield (STY) is often used to evaluate the practical potential of a catalytic material, as not the activity per site but per catalyst weight is involved. Careful inspection of Sn β literature indeed indicates that a high Sn content is mostly not a guarantee for a high STY, as often TOF gradually decreases with increasing Sn, even when the authors correctly identified the exclusive presence of isolated tetrahedral Sn IV [46,49,51].

This work evaluates variously prepared Sn β zeolites for four different reaction types and their catalytic data, expressed in both TOF and STY. The selected reactions are glucose isomerization (ISOM) to fructose, Meerwein–Ponndorf–Verley (MPV) of cyclohexanone with 2-butanol to cyclohexanol, Baeyer–Villiger (BV) oxidation of cyclohexanone to caprolactone and a multi-step conversion (via dehydration – MPV (DH/MPV)) of 1,3-dihydroxyacetone in ethanol to ethyl lactate (Scheme 3). The products of these reactions have applications as sweetener (fructose) or polymer building blocks [52,53,54,55]. First, a set of reported post-synthetic procedures is evaluated and compared, and the best method is used to exploit the effect of numerous synthetic parameters such as Sn precursor type and concentration and water content on the catalytic properties. Interestingly, the results will show that the best parameter set differs for some of the tested reactions, pointing to a diversity of Sn sites and different Sn active site requirements. Catalytic data are finally linked with Sn active site characteristics, as provided by electronic and vibrational spectroscopy, and with pore blockage phenomena.

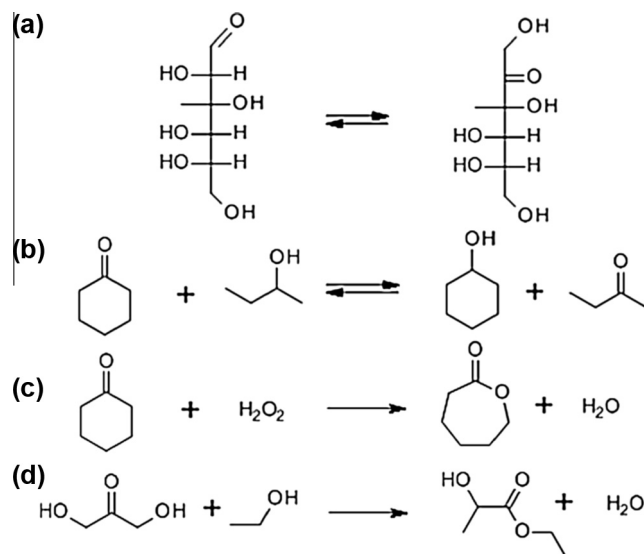
2. Experimental

2.1. Material synthesis

Commercial β zeolite (CP814e, Zeolyst International, SiO $_2$ /Al $_2$ O $_3$ = 25) was dealuminated by stirring the zeolite powder



Scheme 2. Schematic representation of synthesis pathways of Sn-containing zeolites. The top pathway shows the traditional (bottom-up) hydrothermal synthesis; a Sn-containing gel in an autoclave is placed in an oven for a period of time and the molecular building blocks assemble to form the Sn-containing zeolite at high temperature and pressure. The bottom pathway shows the post-synthetic or secondary synthesis. An Al-containing zeolite is dealuminated during an acid treatment or steaming operation. The dealuminated zeolite is then modified with a Sn precursor.



Scheme 3. Overview of the reactions studied. (a) Isomerization of glucose to fructose; (b) Meerwein–Ponndorf–Verley reaction of cyclohexanone and 2-butanol forming cyclohexanol and 2-butanone; (c) Baeyer Villiger oxidation of cyclohexanone with hydrogen peroxide yielding ϵ -caprolactone and water; (d) transformation of 1,3-dihydroxyacetone in ethanol to ethyl lactate.

Download English Version:

<https://daneshyari.com/en/article/6527132>

Download Persian Version:

<https://daneshyari.com/article/6527132>

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