Coordination Chemistry Reviews 343 (2017) 220–255

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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

Review

Lewis acid catalysis on single site Sn centers incorporated into silica hosts

Paola Ferrini, Jan Dijkmans, Rik De Clercq, Stijn Van de Vyver, Michiel Dusselier, Pierre A. Jacobs, Bert F. Sels *

KU Leuven, Center for Surface Science and Catalysis, Celestijnenlaan 200F, 3001 Heverlee, Belgium

ARTICLE INFO

Article history:
Received 24 February 2017
Accepted 25 May 2017
Available online 29 May 2017

Keywords:
Snβ
Zeolite
Lewis acid
Biomass
Stannosilicates

ABSTRACT

Tetrahedral Sn built into microporous silica frameworks such as zeolites and structured mesoporous silica can be used as heterogeneous Lewis acid catalysts. These materials have recently attracted much attention, as they show remarkable activity and selectivity in a wide range of reactions. A prominent example is the conversion of carbohydrates into platform and commodity chemicals such as lactic acid or alkyl lactates, where the activity and selectivity of Sn-based materials remains unsurpassed compared to Sn-free catalysts. Some of the materials show water-tolerant behavior and can therefore also be used in aqueous systems. In this work, a literature overview regarding synthesis of Sn-containing silica materials is given, as well as a synopsis of the characterization tools which can be used to unravel the structure of the catalytic active site. The application of such Sn-containing materials for diverse catalytic reactions is reviewed, with special emphasis on the effects of the catalyst characteristics on the catalytic activity and stability.

Contents

---

* Corresponding author.
E-mail address: bert.sels@kuleuven.be (B.F. Sels).

http://dx.doi.org/10.1016/j.ccr.2017.05.010
0010-8545/

1. Introduction

The incorporation of heteroatoms into silica hosts has been widely used as a strategy for catalyst design, wherein the catalyst's properties depend on the metal that is incorporated. For example, the tetrahedral incorporation of trivalent Al atoms into a silica framework leads to an excess negative charge, which can be neutralized by protons, giving rise to Brønsted acidity [1]. Similarly, the incorporation of tetravalent metals such as Zr, Ti, Hf and Sn results in catalysts possessing Lewis acidic properties. Such solid Lewis acids have recently attracted increasing attention due to their ability to activate hydroxyl and carbonyl functional groups [2,3]. In particular, Sn-based catalysts have been shown catalytically superior for a variety of reactions, especially those involving biomass-derived substrates, for example sugar isomerization [4,5]; Meerwein-Ponndorf-Verley reductions [6,7]; Baeyer-Villiger oxidations [8,9]; 1,2-hydride shifts [10,11]; and aldol condensations [12–14]. Hence, the design of Sn-containing silica catalysts recently became a hot topic. Two major strategies can be distinguished for the preparation of stannosilicates, *viz.* bottom-up strategies, wherein a Sn precursor is added to the synthesis gel of a catalyst (*e.g.*, hydrothermal procedures), and top-down strategies, wherein Sn is deposited on an already-existing silica structure. Depending on the strategy chosen, different catalytic active sites may be produced (*e.g.*, open or closed, hydrated or dehydrated, framework species or extra-framework oxides), which can therefore lead to different activity, selectivity and stability of the materials.

The scope of this review is to summarize the synthesis techniques of Sn-containing silica catalysts proposed until now and, where possible, link the catalytic activity of the resulting catalyst with the structure of the Sn active site. Differences due to alternative synthesis procedures, even subtle ones, may significantly impact catalytic activity, selectivity or stability. For this, the first part will give an overview of the synthesis procedures reported so far, with a focus on the top-down synthesis approaches. Herein, Sn-containing silica will be distinguished based on pore size/structure. Then, different analytical techniques that have been commonly used to identify the Sn active sites will be briefly discussed, highlighting their limitations which still need to be overcome. Afterwards, different reaction types which have been reported to be catalyzed by Sn-containing silica will be reviewed. The catalytic activity of the Sn site will then be linked to its reported structure in the catalyst and to the pore architecture of the materials. Finally, the impact of various catalyst synthesis procedures and material characteristics on catalyst stability and deactivation mechanisms will be outlined.

2. Catalyst synthesis

Sn-containing silica catalysts can be divided into microporous (*i.e.*, zeolites), mesoporous and nonporous materials. Due to the different pore structures, the materials may exhibit varying physicochemical and catalytic properties [15], and offer different possibilities for Sn incorporation. For example, mesoporous silicates allow for direct grafting of Sn onto the Si—OH defects of the amorphous surface, whereas defect-free zeolites or nonporous silicates require, in most cases, a previous treatment for the introduction of anchoring points. Regardless of the topology of the materials, tin can be introduced either in the synthesis gel (bottom-up strategy), or onto preformed structures, by post-synthetic modifications (top-down approach). The scope and scalability of various approaches to introduce Lewis acid functionalities in zeolites have been well reviewed [16]. Here, an overview is given, with focus on the influence of the synthesis method and the catalyst topology on the efficient introduction of active Sn sites.

One of the main concerns in the synthesis of catalysts containing atomically dispersed Sn is the formation of polymeric SnO_x phases. For example, in SnO_2 crystals, the most common oxide form of tin in stannosilicates, the metal is octahedrally coordinated to six —O—Sn neighbors, and is thus in its highest coordination state. The absence of open coordination sites prevents Sn to interact with reactants, thus making SnO_2 a less active catalytic species. Ideally, catalytically active Sn-species have four (tetrahedral) or fewer bonds with the support structure to allow coordination with electron-donating groups of the substrate (*e.g.*, carbonyls). Depending on the synthesis method and parameters, the formation of Sn oxide species can be avoided or minimized.

2.1. Zeolites

Due to their shape-selectivity and acidic properties, zeolites have been industrially relevant since the '60 s, when they were first introduced as isomerization catalysts and later employed as hydrocarbon cracking catalysts [1]. Zeolites can be classified into three groups based on pore size, *viz.* small-pore zeolites, with 8 membered T-atom rings (*e.g.*, CHA topology, Fig. 1A), medium-pore zeolites, with 10-membered rings (*e.g.*, ZSM-5, with MFI