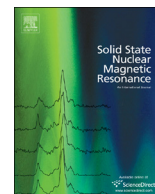




ELSEVIER

Contents lists available at ScienceDirect

Solid State Nuclear Magnetic Resonance

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

Trends

Solid-state NMR concepts for the investigation of supported transition metal catalysts and nanoparticles



Torsten Gutmann, Anna Grünberg, Niels Rothermel, Mayke Werner, Mohamad Srour, Safaa Abdulhussain, Shulin Tan, Yeping Xu, Hergen Breitzke, Gerd Buntkowsky*

Institute of Physical Chemistry, Technical University Darmstadt, Petersenstrasse 22, D-64287 Darmstadt, Germany

ARTICLE INFO

Article history:

Received 23 May 2013

Received in revised form

20 June 2013

Available online 2 August 2013

Keywords:

Solid state NMR

Heterogeneous catalysis

Transition metal nanoparticles

 ^2H solid-state NMR

Immobilized catalyst

ABSTRACT

In recent years, solid-state NMR spectroscopy has evolved into an important characterization tool for the study of solid catalysts and chemical processes on their surface. This interest is mainly triggered by the need of environmentally benign organic transformations (“green chemistry”), which has resulted in a large number of new catalytically active hybrid materials, which are organized on the meso- and nanoscale. Typical examples of these catalysts are supported homogeneous transition metal catalysts or transition metal nanoparticles (MNPs). Solid-state NMR spectroscopy is able to characterize both the structures of these materials and the chemical processes on the catalytic surface. This article presents recent trends both on the characterization of immobilized homogeneous transition metal catalysts and on the characterization of surface species on transition metal surfaces.

© 2013 Elsevier Inc. All rights reserved.

Contents

1. Introduction	1
2. Homogeneous catalysts immobilized on solid support carriers	2
3. Immobilization of Wilkinson's catalyst on silica	3
4. Immobilization of $\text{RuCl}_2(\text{PPh}_3)_3$ catalyst on silica	5
5. Ligand stabilized metal nanoparticles	6
6. Future, challenges and directions	6
6.1. Hyperpolarization techniques	7
6.2. Fast MAS-NMR and indirect detection	8
7. Summary	9
Acknowledgments	9
References	9

1. Introduction

Every year millions of tons of solvents are employed in the fine chemical and pharmaceutical industries for reactions or product isolation. Most of these solvents are small, volatile organic molecules. They constitute a major source of industrial pollution and cause severe environmental problems. Reducing the amount of solvents by designing new, environmentally benign reaction schemes which use a minimum of resources and energy, is one of

the major challenges of 21st century chemistry. One of the important steps in this concept of “Green Chemistry” is the development and optimization of efficient catalysts. Despite many favorable features of homogeneous catalysis, as for example high substrate selectivity and catalytic efficacy, heterogeneous catalysts still remain more productive and many large-scale industrial production processes depend strongly on them. Main reasons are that heterogeneous catalysts can be easily separated and reused in continuous flow reactions.

A hypothesis-driven rational design of new and improved heterogeneous catalysts necessitates detailed knowledge, both of the structure of the active sites on the surface of the catalyst and on the state of the reactants on the surface. Owing to the complexity of

* Corresponding author. Fax: +49 6151 16 4347.

E-mail address: gerd.buntkowsky@chemie.tu-darmstadt.de (G. Buntkowsky).

these materials neither the typical ultra-high vacuum (UHV) characterization techniques nor UV/VIS or IR spectroscopy are really suited for their study. For this reason several groups started to develop solid-state NMR techniques to solve this quest.

In the present trends article we will focus on transition metal based hydrogenation and hydroformylation catalysts. Hydrogen conversion at metal complexes or nanoparticles is the essential step in technically important processes like Haber–Bosch, [1,2] Fischer–Tropsch, [3–5] or arene hydrogenation, [6–8] which form one basis of our current economy. The detailed knowledge of the catalytic pathways in hydrogenation reactions plays a key role in the optimization of such technical processes. As important examples, in the following two different classes of transition metal catalysts are discussed, namely supported homogeneous catalysts, [9–24] and ligand stabilized metal nanoparticles [25–28].

Supported homogeneous catalysts represent a first class of transition metal catalysts. In many of these catalysts, linker molecules containing functional groups are tethered to a solid inorganic support by covalent binding to the surface, and the homogeneous transition metal catalyst is attached via these linker groups [9,29].

The main demands on a good carrier material are its stability in multiple reaction cycles, its easy separability from the reaction mixture, its harmlessness to the environment, and that its chemical and physical properties have no negative influence on the catalytic activity [30]. These conditions can be fulfilled both by organic polymers or inorganic oxides. Inorganic oxides and polymeric materials [31,32] are the most common carriers, especially for immobilizing homogeneous metal catalysts (see Fig. 1). Since the frameworks of inorganic oxides like zeolites, silica nanoparticles or mesoporous silica materials are chemically and thermally stable under different reaction conditions and their structure is not influenced by swelling processes, [33] these oxides are

often preferred to polymeric materials. Suitable support materials are inorganic oxides like silica or titania which contain reactive surfaces. This property displays a simple starting point for the immobilization of homogeneous catalysts.

While conventional disordered silica materials are known for a long time, in the last years ordered modifications of these oxides became largely available. Typical representatives of these ordered modifications are periodic mesoporous silica (PMS) like MCM-41, SBA-15 and related materials [30,34,35]. PMS materials combine large pore spaces, ordered pore arrangements, narrow well-defined pore sizes, large surface areas and tunable physical properties of their inner surfaces, such as surface acidity or hydrophobicity [36]. They consist of pseudo-crystalline powders, where each crystallite constitutes a large number of more or less parallel cylindrical pores. The silica formation takes place in aqueous media using surfactants or amphiphilic block copolymers as structure-directing agents (templates). PMS based supported homogeneous catalysts were successfully applied in a number of catalytic reactions [24,37–42].

There are two main strategies for the immobilization of a metal complex on a solid support [43–45]. It can be bound by substitution of its ligands with functional groups of a suitable linker attached to the surface, or it can be attached directly to the oxide surface. In the latter case the metal complex loses its molecular character [46].

Ligand stabilized metal nanoparticles (MNPs) represent a second class of transition metal catalysts. They display colloidal particles consisting of an inner core of metal atoms stabilized by surface molecules such as aliphatic alcohols, amines, phosphines, thiols, carbenes, or polymers [25,26]. These particles can be synthesized under mild conditions from metal-organic precursors, following a route developed by Chaudret and Philippot [27,28]. These MNPs catalyze interesting organic transformations, including asymmetric hydrogenation, [47,48] oxidation and C–C coupling reactions [7,49]. Owing to their large specific surface they are ideally suited for solid-state NMR studies of both their ligands and the catalytically active species on their surface.

2. Homogeneous catalysts immobilized on solid support carriers

Owing to the presence of surface-silanol groups permitting convenient functionalization by organic linkers silica supports are very popular for the immobilization of homogeneous catalysts [50,51]. Since these systems contain several NMR-active nuclei (typically ^1H , ^{13}C , ^{29}Si , and ^{31}P), MAS NMR techniques have evolved into a powerful tool for the characterization of the immobilization process and the structure of the immobilized catalyst [50,52–55]. A more detailed overview about the relevant literature is given in the recent reviews by the Blümel group and some of us [33,51].

In the following, for two recent examples the binding of differently coordinated transition metal catalysts employing mesoporous silica as support is monitored by solid-state NMR. The first example [55] shows the immobilization of the four-fold coordinated $\text{RhCl}(\text{PPh}_3)_3$ complex (**1**, Fig. 2) also known as Wilkinson's catalyst, and the second example [56] the related five-fold coordinated $\text{RuCl}_2(\text{PPh}_3)_3$ complex (**2**, Fig. 2). In both cases APTES (3-aminopropyltriethoxysilane) (**3**, Fig. 2) [57] is employed as linker [55,56]. The crucial step after synthesis of these catalysts is the exact characterization of the binding of APTES to the silica surface.

$\text{RhCl}(\text{PPh}_3)_3$ (**1**) is probably the most widely investigated of all known homogeneous hydrogenation catalysts [60]. Its applications in many organic reactions have induced a strong demand for the efficient separation of catalysts from the product stream [61]. Various attempts towards catalytic applications of the immobilized

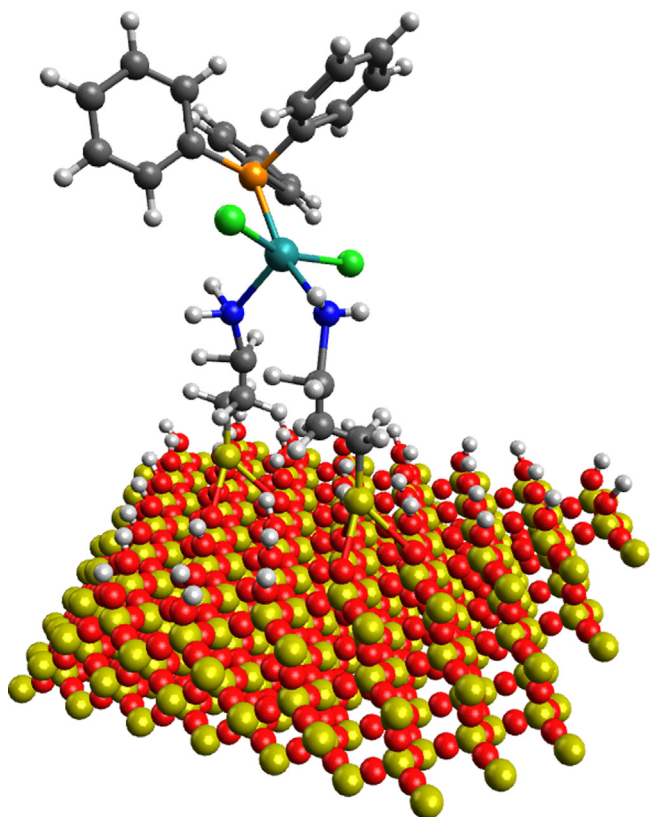


Fig. 1. Graphical illustration of an immobilized homogeneous transition metal catalyst at a silica surface.

Download English Version:

<https://daneshyari.com/en/article/5420461>

Download Persian Version:

<https://daneshyari.com/article/5420461>

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