C. R. Physique 15 (2014) 258–268

Contents lists available at ScienceDirect

Comptes Rendus Physique

www.sciencedirect.com

Electron microscopy / Microscopie électronique

Using electron beams to investigate catalytic materials

Apports de la microscopie électronique à l'étude des matériaux catalytiques

Bingsen Zhang [a], Dang Sheng Su [a,b,*]

[a] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China*
[b] *Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4–6, 14195 Berlin, Germany*

ARTICLE INFO

Article history:
Available online 28 January 2014

Keywords:
Electron microscopy
Catalyst
Chemical composition
Surface
Dynamic process
Particle shape

Mots-clés :
Microscopie électronique
Catalyseur
Composition chimique
Surface
Processus dynamique
Forme des particules

ABSTRACT

Electron microscopy (EM) enables us, not only to reveal the morphology, but also to provide structural, chemical and electronic information about solid catalysts at the atomic level, providing a dramatic driving force for the development of heterogeneous catalysis. Almost all catalytic materials have been studied with EM in order to obtain information about their structures, which can help us to establish the synthesis–structure–property relationships and to design catalysts with new structures and desired properties. Herein, several examples will be reviewed to illustrate the investigation of catalytic materials by using electron beams.

RÉSUMÉ

Le microscope électronique à transmission (TEM) permet, non seulement de révéler la morphologie, mais aussi d'apporter des informations à l'échelle atomique sur les propriétés structurales, chimiques et électroniques de catalyseurs solides. Ceci en fait un outil majeur dans le développement de la catalyse hétérogène. Presque tous les matériaux catalytiques ont été étudiés par TEM afin de caractériser leur structure, ce qui aide considérablement à la recherche des relations synthèse–structure–propriétés, ainsi qu'à la production de nouveaux matériaux aux propriétés ciblées. Dans cette revue, plusieurs exemples ont été sélectionnés pour illustrer les méthodes et les résultats de l'étude des matériaux catalytiques, lorsque le faisceau d'électrons d'un TEM est utilisé comme faisceau sonde.

1. Introduction

Catalysis is central to the production of fuels and chemicals, including more than 70% of today's chemical products [1,2]. Nowadays, developing new catalyst with high activity, selectivity and stability constitutes an enormous challenge. Furthermore, it must be realized under sustainable conditions: the main constituents of new catalysts must be abundant in nature, cheap, and their production process must be environmentally friendly. Most importantly, new catalysts must be developed for processes that are not possible today such as artificial photosynthesis or hydrogen production from water. These new challenges for materials science and catalysis are seen as one of the major driving forces for the current revolution in

* Corresponding author at: Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China.
E-mail address: dangsheng@fhi-berlin.mpg.de (D.S. Su).

1631-0705/$ – see front matter
http://dx.doi.org/10.1016/j.crhy.2013.11.001

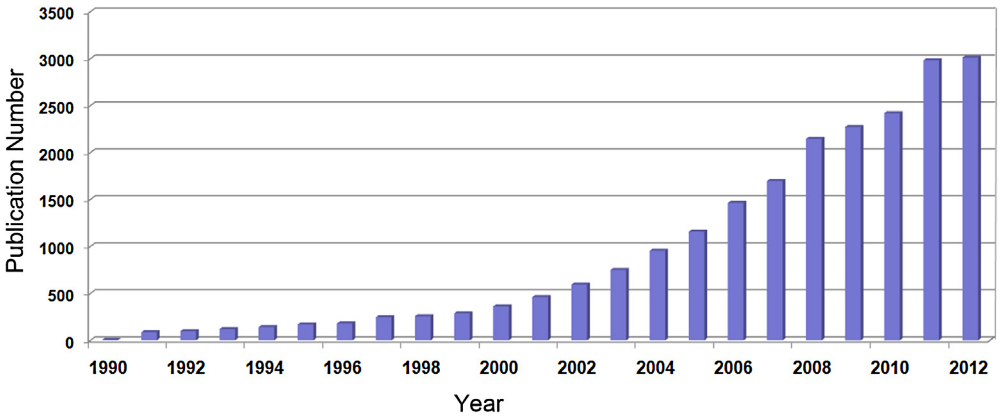

Fig. 1. The number of papers on catalysts investigated by TEM published annually, from 1990 to 2012. (Data from ISI Web of knowledge on February 10, 2013.)

electron microscopy. Apart from nanoscience and nanotechnology, catalysis is one of the most important areas, where EM, specially TEM and STEM, have found their applications [3–23]. It can be said that the evolution of catalysis science is based on the ability to cope with the structural complexity of solid catalysts, which is largely made possible by the advancement of electron microscopy [24,25]. Fig. 1 shows the number of papers on solid catalysts investigated by TEM annually from 1990 to 2012 as reported by ISI Web of Science. The spectacular rise in the annual total of papers clearly indicates that TEM and its associated techniques have significantly contributed to the investigation in the field of solid catalysts.

This article focuses on the applications of advanced TEM techniques to the fundamental study of solid catalysts. Herein, we will only show some selected examples due to the offered limited space. They have been selected to demonstrate how different forms of advanced TEM can be used to investigate solid catalysts. It is expected that better understanding of the nature of the solid catalyst in chemical reactions can help to design and develop catalysts with tailored properties.

2. TEM investigation of catalytic materials

Many characterization tools are widely used to analyze solid catalysts, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and so on. All these powerful tools, however, do not exhibit high spatial resolution. Scanning probe microscopes can provide images of a flat surface with a spatial resolution equivalent to that of a TEM/STEM. But they require a special treatment of the surface in many cases, and sometimes the application is limited; e.g., scanning tunneling microscope cannot image the surface of an insulator. TEM/STEM is not simply a complementary tool of the aforementioned methods. As we will see below, it has become a quite robust and versatile tool for catalysis research. It provides essential information (both static and dynamic) on solid catalysts, which cannot be obtained with any other characterization method [26,27].

2.1. Determination of the chemical composition of catalysts (EDS—Energy-Dispersive X-ray Spectroscopy—and EELS—Electron Energy-Loss Spectroscopy)

In many cases, revealing the elemental distribution in a catalyst or tracing the elements in a catalytic reaction is crucial for probing phase composition, understanding chemical processes, and detecting the growth history of the reaction-driven intermediates. Therefore, it is of paramount importance to reveal the composition distribution for the design of catalytic nanomaterials and for unraveling the catalytic mechanism that is involved [28–31]. EDS is a standard technique on a modern TEM for qualitative and quantitative elemental analysis, which is suitable for heavy elements with high fluorescence yield [32–34]. On the other hand, the use of core-level EELS spectroscopy is more suited to the analysis of light elements, such as boron, carbon, nitrogen, oxygen, and phosphorus [35–37]. Both EDS and EELS analysis can be carried out with very high resolution, allowing chemical analysis of individual nanoparticles (NPs) across surfaces or in interfacial areas [38–42].

EDS elemental maps are suitable for mapping the composition of metal or metal oxide nanomaterials, especially bi- or multi-metallic NPs, such as AuPd catalysts [34]. An experiment using physically mixed Au/AC and Pd/AC (AC = activated carbon) as the catalyst has been designed in the liquid-phase oxidation of benzyl alcohol by aerobic oxygen. The evolution of the physically mixed catalyst structures at different stages in the catalytic reaction was studied by spatially resolved elemental mapping techniques. Fig. 2 shows the results of EDS spectrum imaging on a few particles from one piece of original Au/AC in the physically mixed catalyst after 0.5 h of reaction. It includes the HAADF–STEM image, Au and Pd maps and the two maps superimposed. The integrated spectrum of all the pixels in the scanned area is shown in Fig. 2(b). It clearly indicates the migration of Pd atoms onto the Au particles, thereby forming bimetallic particles. The quantitative