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Recent conceptual advances in the catalysis science of mixed metal oxide catalytic materials

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Abstract

The catalysis science of mixed metal oxides (supported metal oxides, molecular sieves and bulk mixed metal oxides) has undergone dramatic paradigm changes over the past 25 years as new characterization techniques became available (X-ray absorption spectroscopy (EXAFS/XANES/soft XANES), Raman, solid-state NMR, HR-TEM, UV–vis DRS and LEISS) to catalysis researchers. The major advantages offered by these spectroscopic improvements are that (1) they can detect XRD inactive amorphous surface metal oxide phases as well as crystalline nanophases and (2) their ability to collect information under various environmental conditions. Application of these spectroscopic techniques to the investigation of mixed metal oxide catalysts have provided new fundamental insights into the electronic and molecular structures of mixed metal oxide catalytic active sites and how they control the catalytic activity and selectivity characteristics. The most significant discovery has been that amorphous metal oxide phases are always present and are the catalytic active sites for many applications of mixed metal oxide catalysts. This has resulted in a significant paradigm shift as to how mixed metal oxide catalytic materials function for different applications. This article reviews the instrumental advances and the resulting conceptual advances that have evolved over the past 25 years in the catalysis science of mixed metal oxide catalysts.

Keywords: Catalysts; Metal oxides; Supported; Molecular sieves; Bulk; Vanadium oxide; V_2O_5; Oxidation; CH_3OH; C_3H_8; C_4H_{10}; SO_2; CH_3SH; Thiophene

1. Introduction

The catalysis science of metal-based catalysts, bulk as well as supported, was significantly advanced in the 1970s by (1) introduction of selective chemisorption methods to determine the number of exposed metal sites, (2) transmission electron microscopy (TEM) for imaging the structure and morphology of the metallic components, (3) X-ray diffraction (XRD) for determining the volume average particle dimensions, (4) X-ray absorption spectroscopy (EXAFS/XANES) for determining local coordination, and (5) UHV model single crystal studies [1–5]. This allowed for the successful quantitative comparison of reaction rates between different catalysis laboratories as well as supported metal catalysts and model large single crystals [1–3]. In contrast, the catalysis science of mixed metal oxide catalysts was not sufficiently developed in the 1970s and significantly lagged the rapid advances being achieved in the catalysis science of metal catalysts [6,7]. The major reasons for the much slower development of the catalysis science of mixed metal oxide catalysts are (1) that mixed metal oxide catalysts are significantly more complex than metal-based catalysts (e.g., possible presence of multiple oxidation states, variable local coordination, coexisting bulk and surface phases as well as different surface termination functionalities such as M–OH, M=O, or M–O–M) and (2) the need for the development of new spectroscopic methods that can determine such fundamental electronic and molecular structural details. The objective of this article is to review the growth of mixed metal oxide catalysis science over the past three decades and to assess the current status of this important area of catalysis. Zeolitic materials will not be discussed in this article since by definition their structures are made up from Al and Si TO_4 units that are not metal oxides [8]. Molecular sieves containing transition metal

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oxides (e.g., Ti, V, Nb, etc.), however, will be covered in this article on mixed metal oxides. Another class of emerging mixed metal oxide catalysts is Keggin, Anderson and Dawson clusters, which has recently been reviewed [9,10].

2. Development of spectroscopic instrumentation

2.1. 1950s–1970s

The past three decades has seen a revolution in the development of spectroscopic catalyst characterization techniques and many of these instrumental advances have had significant impacts on the challenging catalysis science of mixed metal oxide catalytic materials. These spectroscopic instruments serve are our "eyes" into the sub-nanometer molecular world of catalytic metal oxide surfaces and their novel surface chemistry with different molecules. Consequently, not surprisingly, many of the recent advances in catalysis science have paralleled the development of new spectroscopic instrumentation during this rapidly expanding period. There were several events prior to the past three decades that set the stage for the advances that occurred in this time period. Mapes and Eischens reported the first successful demonstration of in situ infrared (IR) spectroscopic measurements of chemisorbed molecules on catalytic metals and zeolites in 1954 [11]. These groundbreaking studies showed that with IR spectroscopy it was possible to discriminate between surface Lewis and Bronsted acids by chemisorption of NH_3 and measure the vibrational spectrum of $NH_{3(ads)}$ and $NH_{4(ads)}^+$, respectively. Lunsford and Kazasky were among the first catalysis researchers that were active in the 1960s in developing electron proton resonance (EPR) techniques for characterization of catalytic materials and surface intermediates [12]. It was shown by these and other researchers that were active in this area at the time that EPR can provide information about the presence and local coordination of paramagnetic species (e.g., Mo^{+5}, V^{+4}, Cr^{+5}, Cr^{+3}, etc.). Siegbahn also developed X-ray photoelectron spectroscopy (XPS) in the late 1950s and 1960s that allows determination of the surface region of catalytic materials [13]. These exciting developments in XPS led to the introduction of commercial XPS units in the 1970s [14]. Solid-state magic angle spinning-nuclear magnetic resonance (MAS-NMR) and intense monochromatic lasers were just being developed in the late 1960s. However, the discovery of XRD at the beginning of the 20th century to determine long range order of crystalline phases dominated the available catalyst characterization arsenal due to its sound scientific development over the century. This was the status of the spectroscopic characterization methods available to catalysis researchers ~30 years ago.

These spectroscopic capabilities, however, were not developed enough to significantly advance the catalysis science of catalytic mixed metal oxide materials with the exception of XRD. Although IR provided information about chemisorbed molecules on oxide surfaces, it was not able to provide fundamental molecular structural information about the metal oxide catalytic active sites on surfaces because such vibrations are typically obscured by the strong bulk or oxide support vibrations in the region of interest, usually appearing below $1000\,\mathrm{cm}^{-1}$, and many of the chemical probe molecules developed for metals only adsorbed with extreme difficulty on metal oxide surfaces (e.g., O_2, H_2, CO, etc.). The full potential of XPS was not fully tapped at that moment and EPR spectroscopy is only able to provide information about paramagnetic species that only represent a very small fraction, ~1/100, of the total catalytic sites. Furthermore, the small signals detected with EPR may not even be kinetically relevant in many cases or associated with the presence of impurities. It should also be noted that the escape depth of conventional XPS is typically ~3–5 nm, which means that many layers of the mixed metal oxide material are simultaneously being sampled by this spectroscopic technique and the surface component of the signal becomes diluted by the signal from the underlying layers. Thus, catalysis scientists were not equipped at that point in time to fundamentally address the molecular nature of the catalytic active sites, especially surface sites that do not possess long range order, present in mixed metal oxide catalysts and the influence of different environments on their electronic and molecular structures.

2.2. 1970s–1990s

This situation began to rapidly change during the 1970s and 1980s as several new electronic and molecular structural characterization techniques became available and were further advanced (intense monochromatic laser sources and faster detectors for Raman spectroscopy, high energy synchrotron X-ray sources for X-ray absorption spectroscopy (XAS), stronger magnetic fields for solid-state nuclear magnetic resonance (NMR)) and commercial instruments to measure UV–vis diffuse reflectance spectroscopy (DRS) spectra. In contrast to XRD that requires long range order for signal detection, these spectroscopic techniques do not require long range order for signal detection and provide local electronic and molecular structural information. Although these characterization techniques are bulk techniques that sample the entire sample volume rather than the surface, they are able to also yield surface information when the catalytic active component is highly dispersed (molecular sieves and supported metal oxides) in the catalyst sample. For example, the active metal oxide component is typically 100% dispersed throughout the sample volume in molecular sieves, either in framework or as extra-framework sites [8], and on the surface of supported metal oxide catalysts [7]. Recent advances, to be discussed below, have further extended these bulk characterization techniques to also provide surface information about bulk mixed metal oxide catalytic materials.

It cannot be overemphasized, even in the beginning of the 21st century, that heterogeneous catalysis is a surface