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Recent development of heterogeneous catalysis in ring-opening, biocatalysis, and selective partial oxidation reactions on metal oxides

Ioana Fechete ^{a,*}, Jacques C. Védrine ^{b,**}

^a Université de Strasbourg, Institut de chimie et procédés pour l'énergie, l'environnement et la santé – ICPEES, UMR 7515 CNRS, 25, rue Becquerel, 67087 Strasbourg cedex 2, France

^b Université Pierre-et-Marie-Curie, Sorbonne Université, Laboratoire de réactivité de surface, UMR CNRS 7197, 4, place Jussieu, 75252 Paris cedex 05, France

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ABSTRACT

In this review article, we analyze the state of the art and future developments in three important domains of heterogeneous catalysis, namely ring opening, biocatalysis, and partial oxidation on metal oxides. After recollecting the scientific bases of each domain, we consider several examples, some recent improvements/developments, and some prospective views.

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R É S U M É

Nous considérons dans cette revue trois domaines importants de la catalyse hétérogène, à savoir l'ouverture de cycle, la biocatalyse et l'oxydation sélective. Après avoir rappelé les fondements scientifiques de chaque domaine, nous analysons plusieurs exemples et présentons les améliorations/développements récents ainsi que quelques perspectives.

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1. Introduction

Metal oxide nanostructures are intensively studied [1]. The behavior of nanostructured oxide is governed by both the oxidation process and the size reduction process [2]. The electronic processes of oxidation destroy the initially metallic bonds to create new kinds of bonds with specific

* Corresponding author.

** Corresponding author.

E-mail addresses: i_fechete@yahoo.com (I. Fechete), jacques.vedrine@upmc.fr (J.C. Védrine).

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properties, such as polarization, localization, and transportation of charge, which determine the behavior of the oxides to vary from their parent metals [3]. Oxygen interaction with atoms of metals relates to the technical processes of corrosion, bulk oxidation, heterogeneous catalysis, and so forth [4]. For examining nanostructures, many concepts developed in both molecular chemistry and solid-state physics have to be considered. It is possible to develop a “top-down” theory on the behavior of nanostructures starting from a solid and confining it to a limited size. Another chemical-like “bottom-up” approach is to start with a molecular system and expand its size [2].

Nanostructured materials are advantageous in offering huge surface to volume ratios, favorable transport properties, altered physical properties, and confinement effects resulting from the nanoscale dimensions, and have been extensively studied for several applications. The major domains of heterogeneous catalysis applied industrially concern:

- oil refining, energy, and transport;
- bulk chemicals;
- polymers and materials and detergents and textiles;
- fine chemicals, pharmaceutical and medical chemicals, and food and feed;
- plant design/engineering and realization, catalyst design, and subsequent development of catalysts and of catalytic processes;
- commercial production of catalysts in sufficient quantities;
- monitoring and control of chemical reactions and plant operations; and
- environmental issues.

Among these domains, this review describes recent developments of heterogeneous catalysis in ring opening of methylcyclopentane (MCP), selective partial oxidation reactions, and biodiesel on metal oxide catalysts.

2. Catalytic selective oxidation of hydrocarbons

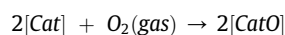
This is an attractive *field of reactions* because the reaction produces valuable chemicals such as alcohols, aldehydes, acids, and so forth, and accordingly ca. 25% of the chemicals and intermediates are industrially produced by the catalytic oxidation processes [5,6]. Partial oxidation reactions have been largely studied since the 1960s both in the industry, particularly by researchers at SOHIO Co., and at the academia level, using mixed metal oxides in the form of the so-called multicomponent catalysts.

For instance, in the SOHIO process of propene oxidation to acrolein, the base catalyst was bismuth molybdate (α -phase Bi_2MoO_3), but Fe and comolybdates were added for better performances. This was assigned to epitaxial growth between both types of molybdates [7], which favors electron transfer through the solid catalysts as required in the redox mechanism, Mars and van Krevelen, and demonstrated by electrical conductivity measurements.

Recently, the selective catalytic oxidation of light alkanes has attracted much attention due to the shale gas

revolution and the concern about petroleum [8,9]. Success in the reactions, however, has been limited so far despite tremendous efforts. This is due to the difficulty of the light alkane catalytic selective oxidations, which is derived from the chemical properties of light alkanes. Generally, C–H bonds of hydrocarbons are the most affective parameters for its reactivity in catalytic oxidation, and in the case of light alkanes, severe reaction condition like high reaction temperature is usually required because of their low reactivity due to the strong C–H bond. The severe reaction condition, however, often causes undesirable side reactions and consecutive reactions of the desired products, which makes it difficult to achieve high selectivity toward the desired products.

For a selective oxidation reaction, the main reaction mechanism is the Mars and van Krevelen mechanism, schematized below, which involves cations in variable oxidation states, such as Cr, Cu, Fe, Mo, V, and so forth.



where [CatO] represents the oxidized catalyst surface and [Cat] its reduced state, r_{red} is the rate of catalyst reduction by a reactant and r_{ox} is the rate of its reoxidation by cofed oxygen, and RCH and R–C–O are the reactant and the product. The kinetic equation involves the relative concentration of reduced (θ) and oxidized ($1 - \theta$) sites of the catalyst. At the steady state, $r_{\text{red}} = r_{\text{ox}}$ or $k_{\text{red}}P_{\text{HC}}(1 - \theta) = k_{\text{ox}}P_{\text{O}_2}\theta$, where P_{HC} and P_{O_2} are partial pressures of HC and O_2 , k_{red} and k_{ox} are rate constants of reduction of catalyst (first step), and r_{ox} is the rate of oxidation by O_2 (second step). The relative rate value of r_{red} and r_{ox} is important for the selectivity in the product and involves lattice oxygen anions, which may be incorporated into the reactant, and the corresponding vacancy created is then replenished by gaseous oxygen in the reoxidation step. If $k_{\text{red}}P_{\text{HC}} \gg k_{\text{ox}}P_{\text{O}_2}$, reoxidation of the surface is the rate-determining step; if $k_{\text{red}}P_{\text{HC}} \ll k_{\text{ox}}P_{\text{O}_2}$, reduction of the surface is the rate-determining step. Thus, reoxidizability and reducibility of the catalyst will lead to different kinetic expressions. According to this mechanism, the substrate is oxidized by the catalysts and not directly by the gaseous oxygen, and the role of oxygen is to regenerate or maintain the oxidized state of the catalyst. Lattice oxygen is introduced into the substrate or into H_2O for the oxidative dehydrogenation reaction. This process involves two active sites: an active cationic site and a site active for oxygen reduction. The process starts with the abstraction of a proton, accompanied by a two-electron transfer that reduces the transition metal cations. This step is followed by a nucleophilic addition of an oxide ion from the catalyst to the oxidized hydrocarbons with formation of oxygen vacancies, which are filled by oxygen with reoxidation of the metal cation, as schematized below for propene oxidation to acrolein and propane to propene. Note that on V-based catalysts, it is well accepted that the V^{5+} ion activates the

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