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Bulk phase charge transfer in focus – And in sequential along with surface steps

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ABSTRACT

In recent decades, catalysis has witnessed increasing interests in many catalytic reactions with bulk phase and interface charge transfer steps as a distinguished feature. Here, the charge can be cations, anions, electrons or holes. Research into both bulk phase and interface charge transfer has changed our understanding and in-focus design of catalysts and reactors, due to the clear difference in kinetics from those classical catalytic reactions, where only surface steps are concerned. This perspective selects several types of representative reactions and discusses the challenges and opportunities to innovations in catalytic technologies from the viewpoint of recognizing and accelerating the key step of the charge transfer at interface or in the catalyst bulk phase, as well as incorporating the surface steps into the overall kinetics.

1. Introduction

The understanding and development of catalytic processes have been of crucial importance for the advancement of modern industry. A catalyst allows chemical reactions to follow a more energetically favorable path without itself appearing in the overall stoichiometry of the reaction, thus significantly reducing the overall energy consumption [1]. There are two categories of catalytic reactions, homogeneous and heterogeneous catalytic reactions, of which the heterogeneous catalysis has been more favorable because of the ease of product separation and higher catalyst stability [1]. Fig. 1a illustrates a simplified scheme of the surface step of a heterogeneous catalytic reaction, which normally occurs in a real reactor with reactant fluid in a sequential order of reactant external/internal diffusion, adsorption, surface reaction, product desorption and internal/external diffusion [2].

From the perspective of charge transfer, heterogeneous catalytic reactions typically involve electron transfer in the surface reaction steps. Further, in a large number of heterogeneous reactions, the transfer of ions in the surface steps is also involved. The most well-known examples are the classical heterogeneous acid and base catalyzed reactions, which are two kinds of the most important reactions for modern hydrocarbon processing. For instance, the cracking of large molecules catalyzed by acidic zeolites has been recognized as the largest process in modern industry [3,4]. Other acid-catalyzed reactions include isomerization, alkylation/dealkylation, hydration/dehydration, esterification, halogenation and sulphonation reactions [5]. For these reactions, surface proton transfer is a key step (Fig. 1b). Taking the catalytic benzene ethylation reaction as an example, the proton residing on the surface of the acid catalyst is first transferred to ethanol to form an ethyl carbanion, which then reacts with benzene to form an aromatic carbocation. The carbanion finally turns into ethyl benzene while releasing a proton, which returns to the catalyst surface so that the proton does not appear in the overall stoichiometry of the reaction. Similarly, carbanion is formed via the surface transfer of hydroxide ion in a base catalyzed reaction [3]. The surface ion exchange steps are also involved in many other reactions (Fig. 1c), such as hydro-desulfurization and hydro-denitrogenation [6].

Clearly, the above-mentioned reactions are featured with the participation of surface charge transfer steps. Meanwhile, the development of catalysis has gradually posed an increasing interest towards catalytic reactions where not only surface charge transfer, but also considerable bulk phase charge transfer is involved (Fig. 1d). Catalytic processes such as selective catalytic oxidation, photocatalysis, and electrocatalytic reactions include essential charge transfer steps both within bulk phase and across interfaces, differing largely from those depicted in Fig. 1a–c. Charge transfer is very often sluggish both in bulk
phase and across an interface, which greatly influences the kinetics of the overall reaction. Thus, the understanding, modelling and promoting of bulk phase and interface charge transfer steps in these reactions become important. This article discusses several representative catalytic reactions with the characteristics of bulk phase and interface charge transfer in a general form, aiming to offer some insights into related fields. Summary and perspective on mechanism elucidations in these systems using advanced characterization methods can be found in other feature papers [7–14].

2. Heterogeneous catalytic oxidation

The Mars-van Krevelen (MvK) mechanism proposed in 1954 is by far the most widely acknowledged principal in establishing kinetic models for catalytic oxidation reactions [15]. Fig. 2 depicts the MvK mechanism of an oxidation reaction on the surface of an oxide catalyst. The reactant (R0) molecules are reduced and adsorbed on the oxide surface and oxidized by the lattice O2− to form either a selective oxidation product (RO3) or complete oxidation products, such as H2O and CO2, which are subsequently desorbed from the surface and diffuse to the bulk fluid phase. The oxygen vacancy sites generated accordingly are simultaneously replenished by the surface adsorption and dissociation of gaseous O2 molecules followed by the lattice O2− diffusion.

The MvK mechanism has been intensively verified via oxygen partial pressure monitoring and isotopic tracing experiments [16,17]. The participatory O2− is present within a few surface layers of the catalyst, where the bulk phase diffusion of lattice O2− from the inner layers to the surface occurs. The O2− transfer is via an O2− vacancy hopping mechanism (sometimes interstitial hopping) and is directly governed by the difference of O2− chemical potential between the inner layers and the surface layer. Therefore, it is correlated with the lattice defect concentration [18,19], as well as the metal-oxygen bonding strength [20]. The regeneration of the catalyst requires an inward diffusion, which is further correlated with the chemical potential of oxygen in the atmosphere. This suggests that all approaches that enhance the O2− transfer would be useful for accelerating the catalytic process, even though the initial activation of the first C–H bond is often believed to be the rate-determining step (RDS) for hydrocarbon oxidation [21]. Depending on the comparative rate of the sequential steps, the O2− transfer step may become the RDS as the surface steps are accelerated. The MvK mechanism has been the base for many practical selective and non-selective catalytic oxidation processes [22,23], and more recently, chemical looping [24–26] and rich oxygen combustion [27,28] have been observed in industrial practices. For instance, Dupont previously made an attempt in utilizing circulating fluidized-bed reactors for mass production of maleic anhydride with a vanadium phosphorus oxide catalyst, where the selective oxidation of n-butane and the re-oxidation of the catalyst occur in two separate reactors [29–31]. Even though this approach was eventually not adopted in the commercial practice, the concept behind has been intriguing. Except for lattice O2−, the MvK concept has been also practiced in understanding and developing other catalytic systems that involve lattice components, such as S, Cl, H and N, etc. [32].

3. Heterogeneous photocatalysis

Heterogeneous photocatalysis is another sort of catalytic reactions where bulk phase and interface transfer of charges (electrons and holes) are involved. The term “photocatalysis” has been referred to in a broad concept, which includes both thermodynamically favourable downhill reactions, such as organic pollutant oxidation, as well as thermodynamically unfavourable uphill reactions, such as hydrogen evolution reaction from water [34,35]. When the photon energy is higher than the band gap of the photocatalyst, the electrons in the valence band (VB) are excited into the conduction band (CB) of the semiconductor, leaving holes in the VB. The resultant photinduced electrons and holes transfer to the surface and take part in the reduction and oxidation, respectively (Fig. 3). However, the recombination of the electron-hole pairs, either in the bulk or at the surface/interface leading to a lowering of quantum yield, always accompanies the bulk phase and interface charge transfer [36].

The transfer of electrons and holes within a photocatalyst is intrinsically a physical process that occurs in microseconds, and can be enhanced with speedwing up the surface steps, as well as shortening the transfer length of charge carrier [37,38]. Forming an interfacial potential gradient accelerates the transfer of charges to the external surface and has been proved to be effective in enhancing the overall performance. Such a potential gradient has been realized via the formation of heterojunctions or surface states, at the interfaces of semiconductor-electrolyte [39], metal-semiconductor [40], semiconductor-semiconductor [41]. Even more than one junction has been applied in some designs [42,43]. Also, doping and tailoring the
nanostructure of the semiconductor bulk, interface and surface show positive effects due to the rate enhancement of both the physical and chemical steps, as well as the rate diminishment of electron/hole pair recombination. In addition, sacrificial agents (electron donors or acceptors) are often used to consume one unwanted charge (hole or electron) so that the favored reaction can be proceeded more efficiently. Detailed reviews on those approaches can be found in literature [33,41,44]. Since the surface steps are normally sluggish compared to the transfer of electrons and holes, cocatalysts and/or photo-electrocatalysts are also often incorporated on the surface of powders or photo-electrodes to enhance the reactions [38,45]. Such an effect has often been explained with the reduce of concentration overpotential. In fact, all these means, when applied on the RDS, would greatly improve the overall kinetics and energy efficiency.

4. Heterogeneous electrocatalysis

Similar to heterogeneous photocatalysis, heterogeneous electrocatalysis has also been applied in a broad scope, referring to catalysis in both downhill reactions in a Galvanic cell and uphill reactions in an electrolytic cell [46]. While ion transfer through both bulk and interfaces serves as key steps in conventional electrochemical devices, electrocatalytic reaction-based systems are further characterized by the involvement of at least one gaseous species, such as oxygen [47,48], hydrogen [49], carbon dioxide [50] and nitrogen [51]. Among them, the catalysis of oxygen molecules is essential in many energy conversion and storage devices. Herein, we focus on two types of heterogeneous electrocatalysis systems, where bulk phase and interface ion transfers are discussed together with surface reaction steps.

4.1. Solid oxide fuel cells (SOFCs)

Charge transfer processes are key steps in fuel cell reactions and sometimes one of them may become the RDS. Many efforts have been devoted to enhancing both charge transfer and surface reaction steps for fuel cells that operate in a temperature range from ambient temperature to 300 °C. These systems include alkaline fuel cells [52,53], proton exchange membrane fuel cells (PEMFCs) [54,55] and solid acid fuel cells [56,57], and great success has been demonstrated in commercial scale with PEMFCs. Comparatively, SOFCs normally operate at high temperatures (600–1000 °C), and are thus more adaptive to achieving highly efficient cogeneration and flexible fuel choice from hydrogen, to hydrocarbon, and even carbon [58-60]. Fig. 4a shows a general configuration of a typical SOFC device, where two separate electrode compartments sandwich around a dense O2−-conducting electrolyte layer while the electrodes being connected through an external circuit. During operation, the anode catalyzes the oxidation of the fuel and releases electrons via the external circuit, while the cathode undergoes a catalytic oxygen reduction reaction (ORR) with the electrons from the external circuit. The cathode catalytic ORR process is directly correlated to the oxygen incorporation and subsequent bulk O2− transfer steps, where the former can be sufficiently enhanced by increasing the three phase boundary area and/or by leveling up the surface oxygen vacancy concentration [61-65]. The bulk O2− transfer, on the other hand, is generally based on the O2− vacancy hopping mechanism that occurs in the above mentioned heterogeneous catalytic oxidations, thus also varying with the chemical potential of O2−. In addition, achieving a sufficiently high bulk O2− transfer rate within the electrolyte becomes more crucial as the operating temperature decreases. It has been intensively demonstrated that, at high temperatures (800–1000 °C), the yttria-stabilized zirconia (YSZ) electrolyte with a bulk O2− conductivity of ~0.1 S cm−1 is capable of delivering a practically acceptable power output [66,67]. However, decrease of the operating temperature to an intermediate range (600–800 °C) causes significant drop in the bulk O2− conductivity, which can be compensated either by thinning the YSZ electrolyte layer or utilizing higher O2− conductive electrolytes (such as doped ceria materials) so as to ensure a comparable power output [67]. Further decrease of the operating temperature to a low range (400–600 °C) has been confronted with major challenges in drastically grown resistance of bulk O2− transfer through the electrolyte, as well as the oxygen incorporation step at the cathode side [68,69]. Even though improvement has been achieved by utilizing either oxide-molten carbonate composite electrolyte or proton conducting electrolyte, a satisfactory performance comparable to that at high operating temperature has not yet been realized [70-74]. Currently, the bulk phase O2− transfer is still the major focus in further improving the SOFC technology.

4.2. Lithium-oxygen batteries (LOBs)

Rechargeable batteries have long been following an advancing path
where charge (electrons and ions) transfer steps both in bulk phase and across interfaces form the fundamental basis [75,76]. This has led to the commercial success of lithium ion batteries (LIBs) from 1991, with ever-since continuation on the system optimization [77]. Metal oxygen batteries couple the charge transfer steps similarly to conventional rechargeable batteries further with the catalytic steps at the cathode, where a bi-functional catalyst is commonly included to catalyze both the ORR and oxygen evolution reaction (OER) processes. Compared with other metal (Na, Al, Mg, Fe, Zn, etc.)-oxygen batteries, lithium-oxygen batteries (LOBs) have been receiving more attention owing to their high specific energy and rechargeability [48]. The most focused subtype of LOBs [70], non-aqueous LOBs, are used here as an example to illustrate the bulk phase charge transfer, as shown in Fig. 4b. Similar to SOFCs, Li+ transfer in LOBs also includes interface and bulk phase steps. The ion transfer occurs between lithium metal anode and solid electrolyte interface (SEI), SEI and electrolyte, as well as electrolyte and cathode. The transfer of Li+ from SEI into the electrolyte typically involves a solvation process where an anion (from the electrolyte) shell encompasses Li+ and subsequent diffusion and migration to the cathode. At cathode, the solvated Li+ further experiences a de-solvation process before catalytic cathode reactions occur. In non-aqueous LOBs, the most well-established electrolytes for Li2O2- and Li2O-based chemistries are 1 M lithium bis (trifluoromethanesulfonyl) imide in tetraethylene glycol dimethyl ether and eutectic molten nitrate (LiNO3-KNO3), which have Li+ conductivities of ~0.01 and 0.1 S cm$^{-1}$, respectively [78–80]. The Li+ conduction in these systems are based on free ion motion driven by the chemical potential gradient of Li+ and is fast enough to assist a fast electrochemical process, whereas the intrinsically slow cathode catalysis in these systems is mainly responsible for the overall low power output, viz. an areal current density of several mA cm$^{-2}$ or even less [81]. This contrasts well with LIBs, where the electrode intercalation process (bulk phase Li+ transfer within the electrode materials) is often the RDS [82]. Even though the bulk ion transfer is not the central concern for the current LOBs, future derivatives such as high-temperature LOBs, operated at a temperature that is comparable to SOFCs, would likely to confront a situation where the bulk phase or interface ion transfer becomes the RDS.

5. Summary and outlook

Bulk phase charge transfer has turned out to be a fundamentally important step in a series of catalytic systems, including heterogeneously catalyzed selective oxidation, heterogeneous photocatalysis and heterogeneous electrocatalysis (such as SOFCs and LOBs). This article scratches the very surface of such a theme by briefly presenting the selected systems with a focus on the need to recognize and accelerate the RDS in the sequential charge transfer and surface reaction steps. The involvement of bulk phase and interface charge transfer implies the necessity of establishment models to incorporate charge transfer and surface steps when designing respective catalytic reactions and reactors. Even though in some cases, the charge transfer step may not be the RDS, it might turn to be the one under certain conditions. Thus, the RDS principle applies, and the research orientation is cleared up. This perspective has intended to present such a concept.

Credit author statement
Zhengze Pan initiated the writing under the instruction of Yongdan Li. Yicheng Zhao, Cuijuan Zhang and Hong Chen discussed and polished the manuscript. Yongdan Li proposed the topic.

Declaration of Competing Interest
The authors declare no competing interests.

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Appendix A. Supplementary data
Supplementary material related to this article can be found, in the