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Research Paper

An overview on strategies towards clay-based designer catalysts for green and sustainable catalysis

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ABSTRACT

Remarkable strategies for constructing clay-based catalysts are critically overviewed. Clay minerals provide distinct nanometer-scaled layers and interlayers for engineering them as active catalysts. As such, strategic design and preparation has led to a variety of catalysts, including ion exchanged catalysts, acidic activated clay catalysts, intercalated catalysts, pillared clay catalysts, clay-supported catalysts, inorganic and inorganic–organic composites and hybrids, and hierarchically structured solid catalysts. In many cases, the combination of several protocols was implemented so that the resultant materials functioned with synergetic effects. Electric, optical, photonic, and magnetic functionalities can also be endowed on the resulting clay-based catalysts. Synthetic clay minerals and their derivatives, including layered double hydroxides, have peculiar features in purity and composition to be designed and transformed to catalysts, showing a complementary relationship with their naturally-occurring counterparts. The clay-based heterogeneous catalysts have many practical and potential applications in green catalysis. A review of the literature indicates that precise determination of microstructure and in situ observation of reactions at the molecular and atomic levels remain essential tasks. Prospects for the preparation of clay-based catalysts and their catalytic applications are briefly discussed.

1. Introduction

The discovery of functional solid materials of high catalytic performance is crucial to most chemical processes by allowing the replacement of polluting homogeneous catalysts by reusable heterogeneous catalysts (Poliakoff and Licence, 2007) or by innovating the production of fuels and chemicals from sustainable resources like biomass and biomass-derived feedstocks (Holm et al., 2010; Zhou et al., 2008). To this goal, well-engineered solid catalysts offer excellent potential for minimizing the screening of catalysts which is usually time-consuming (Thomas and Klinowski, 2007; Thyme et al., 2009; Wootton and deMello, 2010). In this context, clay minerals are just a class of inorganic layered compounds, which can be engineered into various functional solid catalysts due to their inherent features in composition and structure. Therefore, the rational design and preparation of novel catalysts based on clay minerals has received many a scholar's concern over the past four decades. Nowadays, there is a great need for creative strategies which should enable clay minerals to be engineered to "designer catalysts" for applications in green and sustainable catalysis, including chemical, photonic, electric, and biological processes.

Microscopically, naturally-occurring clay minerals are typically composed of ultrathin crystalline aluminosilicate layers (around 1.0 nm) superimposed on interlayers of hydrated ions. Therein, each aluminosilicate layer generally consists of one (for 1:1 type) or two (for 2:1 type) Si—O tetrahedral sheets and one Al—O (or Mg—O for some clay minerals) octahedral sheet. In other words, each layer in a 1:1 type clay mineral (T–O layer) is built by one octahedral sheet bonded to one tetrahedral sheet whereas each layer in a 2:1 type clay mineral (T–O–T layer) takes shape from one octahedral sheet sandwiched between two tetrahedral sheets through chemical bonds (Bergaya et al., 2006). The interlayer and the T–O–T layers are bound together by both electrostatic and hydrogen-bonding forces. Isomorphous substitution by other metal ions of different valence readily occurs to the central metal ion either in the octahedral (e.g., Mg for Al) or tetrahedral sheets (e.g., Al for Si), thereby leading to negative charges on the layers (Sainz-Diaz et al., 2000). Accordingly, positive-charged cations exist within the interlayer space necessary to compensate negative-charged aluminosilicate layers and such cations are hydrated like macro-counteranions. Besides, on either 1:1 or 2:1 clay minerals, the broken-edge of each layer acts as a second source of charge which is generally negative and pH-dependent (Churakov, 2006; Tournassat et al., 2003). Consequently, clay minerals possess unique physicochemical properties such as

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large surface areas, swelling, ion exchange, and active broken-edge M—O^- bonds. Therefore, clay minerals exhibit peculiar capacities for absorption, adsorption, and catalysis (Cornelis et al., 1991). Engineering clay minerals into catalysts primarily takes advantage of these characteristics, mainly arising from their nanoscale layers and interlayer space. Thus, the formulations, structure, and surface properties of the resulting clay-based catalysts could be finely tailored.

In view of the design and preparation, herein, the term "clay-based catalysts" can at least refer to the catalytic materials involved in the use of clay minerals from four angles: (1) the framework of clay minerals itself contains active species; (2) the ions within the interlayer space are judiciously exchanged with active components for catalysis purpose; (3) functional nanoparticles (NPs) or clusters are forged onto or within the clay nanostructure; and (4) clay minerals or their derivatives are used as catalyst supports. In general, the clay-based catalysts could be categorized into seven types as follows: ion exchanged catalysts, acidic activated clay catalysts, intercalated catalysts, pillared interlayer clay catalysts, clay-supported catalysts, composites and hybrids, and hierarchically structured catalysts. In many cases, several interactions and structures are integrated so as to enhance their performances in respective ways or to make them act in a synergic fashion. The properties of pillared clay, for instance, can be further tuned by ion exchange. Pillared clay can also act as a support or a promoter. Moreover, many clay-based catalysts, like the formation of nanometer-sized particles, the replica of nanosheets, and the fabrication of nanohybrids, are rightly viewed as exquisite architecture premised on a nanoscale platform of clay minerals.

2. Pristine clay mineral catalysts

Because of their Brønsted and Lewis acidities, clay minerals in their natural form function as efficient catalysts for certain organic transformations. It was found, for example, that natural kaolinites as catalysts can catalyze the transesterification of β-keto esters (Bandgar et al., 2001) and that the chlorite-group mineral chamosite can catalyze the acylation of alcohols and amines, the cyclization of arylaldehydes with O-phenylenediamines, and C—O bond formation reactions (Arundhathi et al., 2010). Moreover, these pristine clay mineral catalysts are non-corrosive and low-cost. In addition, they can be separated and reused. Therefore, wastes can be minimized.

It is noteworthy that, because clay minerals abound in nature and have good adsorptive and catalytic properties, scientists have been advocating linking the origin of life on earth with the formation of biomolecules catalyzed by natural clay minerals over the last few decades (Ertem and Ferris, 1996; Gabel and Ponnamperuma, 1967; Lynch et al., 1957). In this regard, there has been an emphasis on smectitic montmorillonite (hereafter referred to as mmt), a clay mineral typically formed by the weathering of volcanic ash, which is apt to adsorb organic compounds and catalyze organic reactions associated with the origin of life. Experimental results suggested that certain mmt minerals have a tendency to bind and catalyze small molecules to form larger molecules and oligomers like ribonucleic acid (RNA) (Ferris et al., 1996). Also, they could facilitate the transformation of RNA into vesicles (Swadling et al., 2010). These findings partly supported the RNA world hypothesis that life based on RNA predated current life based on deoxyribonucleic acid (DNA), RNA, and protein (Szostak, 2010). Although "life-from-clay" is still under debate, it is undoubted that raw clay minerals inherently possess super-selective adsorption (Komarneni et al., 2001) and a certain catalytic activity. Nevertheless, for catalytic use in practice in many cases, further strategic modification is necessary with the clear objective of improving and intensifying the performances of clay-based catalysts. Hence, a large class of clay-based catalysts emerges from different preparation approaches.

3. Ion exchange reaction

Cations in the interlayer space of clay minerals can be changed to various inorganic or organic cations via an ion-exchange reaction. Such a principle affords a facile way to prepare a clay-based catalyst with the desired ions as catalytically active species. The monovalent (Na^+) and divalent (Ca^{2+}) cations, which commonly occupy the interlayer region in natural mmt, for example, can be readily replaced by other ions. In this way, either homoionic or heteroionic mmt, in principle, can be produced. In this respect, cation exchange capacity (CEC) plays a leading role in an ion-exchange reaction. The CEC is mainly dependent on layer charge density. Nevertheless, it is worth noting that, the larger the amount of cations in the interlayer, the more strongly the platelets of mmt are bound together. This might hinder catalytic efficiency by means of hampering intercalation of reactants between the platelets because most sites within the interlayer of mmt have been filled with cations (e.g., Na^+) (Joshi et al., 2009). Therefore, clay minerals with CEC in a certain range should be chosen and then treated under a set of proper conditions for the ion exchange reaction. As a result, the ion exchanged clay catalysts might offer better catalytic performance for a specific reaction. Moreover, the interlayer cations can perform a reversible hydration–dehydration (Hendricks et al., 1940). Therefore, besides the selection of the parent clay minerals with a desired range of CEC and the conditions of ion exchange, CEC and subsequently the extent of ion exchange can also be controlled by pretreatments such as calcination (Sadek and Mekhamer, 2000). Furthermore, hydrophilic clays can be changed into hydrophobic clays once the charge-compensating interlayer cations sandwiched between the negatively charged aluminosilicate layers are exchanged with organic cations such as quaternary ammonium cations NR_4^+, where R is an alkyl group or an aryl group (Churchman, 2002; Tong et al., 2010a). Hence, the interlayer cations can be designed both qualitatively and quantitatively through a wide range of strategies for "designer catalysts."

Hydrogen ion exchanged clay minerals, which are generally produced by the treatment of clay minerals with acids, are an exclusive case among ion exchanged clay minerals. This is because such a process proves to be influential at least in three ways rather than merely in the way of ion exchange. The first is the ion-exchange reaction between interlayer cations with H^+; another is the part or thorough breakdown of the layers, leading to more broken-edge M—O^- bonds and a reduced particle size of clay platelets; the third is the selective leaching of central atoms in tetrahedral and octahedral sheets (Okada et al., 2006). Therefore, acid treatment might result in more acidic sites together with larger surface areas on the resultant products than the starting clay materials. Both outcomes are favorable for catalysis.

Such clay-based materials treated by acids are often called acid activated clays. Of this type of clay-based catalysts, mmt K-10 is representative of a commodity product that has actual applications in some organic syntheses (Baran et al., 2007). The concentration and the types of acid, and reaction time and temperature are major factors decisive to the physicochemical properties of the resultant acidified clay minerals. The use of concentrated inorganic acids, however, leads to environmental issues owing to the generation of a great deal of acidic wastewater, in addition to equipment corrosion and operational dangers. Organic acids such as carboxylic acids and sulfonic acids, instead of inorganic acids, can provide an alternative route to activated clay minerals. In addition, organic acid could lead to different degrees of changes in the layer, interlayer, and the edge compared with those attacked by mineral acids (Steudel et al., 2009).

4. Host–guest chemistry

Due to the ion exchange capacity and the swelling of the expandable interlayer space, in particular in smectitic clay minerals, guest species of different sizes from several angstroms to a few