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Zeolite-based Photocatalysts: A Promising Strategy for Efficient Photocatalysis

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A photocatalyst is generally defined as a material that has the capability to induce chemical reactions of substances of interest adsorbed on the surface by light-generated active radicals [1]. The efficiency of the photocatalyst is a function of the balance between charge separation, ease of interfacial electron transfer and energy-wasting charge recombination [2]. With the inspiration of improving photocatalysis efficiency and selectivity, people are trying hard to develop new photocatalysts.

Zeolites are crystalline nanoporous inorganic materials with well-defined interconnected channels or cavities in the nanometre or subnanometer length scale, termed as micropores (0.5-2 nm) [3,4]. With the uniform pore size, polar environment, high surface area, the internal active sites and excellent adsorption capability [5], zeolites could enhance the efficiency and selectivity of photocatalysts either by photoactiving the zeolite framework or by encapsulating with semiconductor oxides.

Photoactiving the zeolite framework through the incorporation of heteroatoms (Ti and other transition metals) can make the structure a photocatalyst [6-9]. The most representative example of titanium containing zeolite is titanosilicalite TS-1, which has the MFI structure [10]. There is a characteristic absorption band at 225 nm, which originates from the incorporation of the tetrahedral Ti atoms and the electron transfer in ligand-to-metal (–O–Ti). The photocatalytic properties of TS-1 was further proved by the decomposition of 4-nitrophenol in aqueous solution when illuminated with a 500 W high pressure Hg lamp [11]. The tetrahedral Ti atoms tripodally connected to the TS-1 framework are able to form the titanohydroperoxy species when interacting with H_2O_2, photochemically generating the •OH radicals. It was found that Si/Ti ratios (from 3.3 to 26.3) in TS-1 can greatly affect the photocatalytic efficiency. The TS-1 with the highest Si/Ti ratio exhibited a remarkable enhancement of the photocatalytic activity in the presence of H_2O_2 [11]. TS-1 has also been used to degrade monoethanolamine in aqueous solution by forming ethanolamine-Ti complex [12]. It was found that the photocatalytic activity of TS-1 is comparable with TiO_2 per weight of photocatalyst and the intrinsic activity per Ti atom in TS-1 is higher than that in TiO_2.

Besides TS-1, Ti-Beta zeolite could be used for the selective oxidation of alkenes in the presence of organic hydroperoxides [13]. It was found that the hydrophilic or hydrophobic properties of the zeolite cavities could control the reactivity and selectivity in the photocatalytic reduction of CO_2 with H_2O to produce CH_4 and CH_3OH on these Ti-Beta zeolite catalysts [14]. This result opened a new way to improve the photocatalytic activity by modifying the surface properties of zeolite. Furthermore, a novel titanosilicate ETS-10 contains photoexcitable Ti–O–Ti 1-dimensional quantum wires and 3-dimensional 12-ring channel was reported recently [15]. It was found that this ETS-10 could act as a shape-selective photocatalyst for the degradation of a mixture of phenols of different sizes [16]. The compounds which are small enough to access the interior of the micropores become protected and are degraded more slowly, while the others that are too large to enter the pores are degraded preferentially.

It is relatively difficult to obtain zeolites with photocatalytically active framework, and the amount of these zeolites is pretty few. Another class of zeolite-based photocatalysts, which incorporates semiconductor oxides into the cavities either by ion exchange or by hydrothermal method, has been widely studied [17-20]. In this type of semiconductor @ zeolite photocatalysts, the unique characteristics of zeolite could be fully utilized, such as, the crystal structure determines the size of the encapsulated particles and the optical absorption bandgap, [21] the polar environment favors the photoinduced electron transfer and minimizes the electron-hole recombination [22]. The most representative semiconductor @ zeolitephotocatalyst is TiO_2 @ Zeolite, which has been widely studied recently. It was found that TiO_2 @ Zeolite is efficient for the decomposition of NO, [23] for the efficient removal of NH3 and H2S from air [24] and for the reduction of CO_2 [25]. TiO_2 @ Zeolite is also efficient for selectivity photocatalyze CH_3OH with minor product concentration of CO and O_2 [26]. Furthermore, it was suggested that different semiconductor oxides located in different cages of zeolite may further synergistically enhance the photocatalytic performance of semiconductor @ zeolitephotocatalyst [19]. For example, a maximum water splitting efficiency of (ZnS-CdS) @Y photocatalyst was achieved at a Cd/Zn ratio of 0.25 and when CdS and ZnS clusters were located in α-cages and β-cages, respectively [27,28].

The photocatalytic efficiency of zeolites could be further enhanced by incorporating the photoactive zeolite framework and semiconductor photocatalysts together. For example, microporous titanosilicates (ETS-4, ETS-10) have been utilized to incorporate CdS, in which the Ti-O-Ti backbone acts as a nanowire capable of accepting electrons from the photoexcited CdS [29,30]. The encapsulation of CdS in ETS zeolite is effective for improving the activity as well as the stability of CdS.

In conclusion, by photoactiving the zeolite framework and by encapsulating with semiconductor oxides, the efficiency and selectivity of zeolite-based photocatalysts could be enhanced effectively. However, little is known about the photocatalysis mechanism on a molecular level, to which people should pay special attention in the future.

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