Review of $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid superacid catalysts

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Abstract  Some metal oxides modified with sulfate ions form highly acidic or superacidic catalysts. $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid superacid catalysts, play a vital role in more and more fields such as organic synthesis, fine chemicals, pharmaceuticals, and means for strengthening environmental safeguards. This review highlights the recent development of solid superacid catalysts based on $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$, including synthesis method, characterization of acid sites and acid strength, and applications.

Keywords  solid superacid catalyst, synthesis method, characterization, applications

1 Introduction

More than 90% of chemical processes employ catalysts. Among these processes, acid catalysts play a substantial role in organic synthesis and transformations. Currently, most of these acid-catalyzed reactions are catalyzed by conventional acids such as $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, and HF or Lewis acids such as $\text{AlCl}_3$ and $\text{BF}_3$, which exhibit significant disadvantages in handling, containment, and disposal because of their toxic and corrosive nature. On the contrary, solid superacids have some additional advantages over these conventional acids, such as strong acid sites, nontoxicity, noncorrosiveness, easily handling, low cost, and easy to recover and recycling. So solid superacid have attracted many attentions in theoretical research [1] and synthetic application, such as isomerization [2–4], cracking [5,6], dehydration [7,8], alkylation [9], acylation [10,11], dehydration and dealkylation [12,13], Friedel-Crafts [14,15], and other new applications.

With the increasing environmental awareness, chemical processes are facing challenges to reduce the use of environmentally hazardous chemicals. To this end, to find suitable solid superacids to substitute conventional acid catalysts has been of great interest to the scientists throughout the world.

In recent years, among different kinds of solid superacid catalysts, $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ is the most promising candidate to substitute the conventional acid catalysts and be widely used in a number of important industrial processes. In this paper, we presented the recent progress in synthesis methods of $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$, characterization of acidic properties of $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$, and application of $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ catalysts.

2 Preparation of $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid superacid

The strength of acidities of $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid superacids is strongly relied on the preparation methods and subsequently thermal treatment. The following highlights some latest development of preparation of $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid superacids.

2.1 Impregnating method

Impregnating method includes coprecipitation-impregnating method, mix-precipitation coprecipitation method [16], and gas phase dry impregnating method [17].

Coprecipitation-impregnating method is a conventional preparation method and is widely used. A series of sulfate-, molybdate-, and tungstate-promoted $\text{ZrO}_2$ catalysts were prepared via impregnation method [16]. The report showed that incorporation of sulfate, molybdate, and tungstate promoters has significant influence on the physicochemical properties of zirconia. Novel magnetic solid superacids $\text{ZrO}_2/\text{TiO}_2/\text{Fe}_3\text{O}_4$ were prepared by introducing $\text{TiO}_2$ and magnetic substrates by chemical coprecipitation method. The synthesized samples showed lamellar crystals with high purity and uniform size distribution [18].
Liao et al. reported a new type of superacid catalysts SO$_4$$^-$/$\text{ZrO}_2$-$\text{SiO}_2$ via mix-precipitation coprecipitation method [16]. The precursor ZrO$_2$-$\text{SiO}_2$ binary oxides were prepared by a precipitating/mixing-precipitate method. The activities of these catalysts is 6–10 times higher than that of traditional SO$_4$$^-$/$\text{M}_2\text{O}_3$ catalyst for the esterification of acetic acid with butanol. S$_2$O$_4$$^2$-$/$ZrO$_2$-$\text{SiO}_2$ superacids with various contents of rare earth oxides were prepared by an improved mix-precipitation coprecipitation method without calcination process. The activity and stability of the catalysts prepared by mix-precipitation coprecipitation method are better than that prepared by the traditional coprecipitation method [19].

As to gas phase-dry impregnating method, during the preparation of SO$_4$$^-$/$\text{M}_2\text{O}_3$, the amorphous ZrO$_2$ was treated with H$_2$S, SO$_2$, and CS$_2$ at 20 kPa and 20°C, followed by calcinating in O$_2$ at 400°C. The activity and the surface area of the catalysts prepared by gas phase-dry impregnating method are comparable with the catalysts prepared (Rozman, 1997) by precipitation method [17].

2.2 Sol-gel method

Compared with impregnating method, sol-gel method was easy to control the size of the catalyst. Christian et al. [20] reported the potential of using sol-gel methods to tailor microporous and mesoporous structures.

Mixed oxides of alumina and zirconia were synthesized by means of sol-gel methods. The catalytic properties of the Al$_2$O$_3$-$\text{ZrO}_2$ series were studied using dehydration of 2-propanol at 180°C and isomerization of n-hexane at 250°C, 1 atm as probe reaction. The results showed that these sulfated solids possess high surface acidity and low crystallinity, as well as high activity for alcohol dehydration (i.e., 2-propanol) [21]. Zhao et al. [22] and Guo et al. [23] prepared SO$_4$$^-$/$\text{SnO}_2$-$\text{TiO}_2$ and SO$_4$$^-$/$\text{SnO}_2$-$\text{CeO}_2$ by sol-gel method and used them to catalyze the reaction of preparing terpinyl acetate from terpineol and acetic anhydride. The results showed that the conversion of terpineol is over 98%; selectivity to terpinyl acetate reaches 88%.

2.3 Double hydrolysis method

Guo et al. introduced a novel method to prepare solid superacid SO$_4$$^-$/$\text{SnO}_2$-$\text{SiO}_2$ via double hydrolyzation process [24]. The structure of SO$_4$$^-$/$\text{SnO}_2$-$\text{SiO}_2$ was studied using Fourier transform infrared (FTIR), thermogravimetry-differential thermal analysis (TG-DTA), and X-ray diffraction (XRD). The catalyst prepared by the double hydrolyzation method seems to have bigger particle size and easy to treat while filtering, and the preparation process is simple which could reduce the cost while the catalysts have higher catalytic activity and acid strength.

2.4 Hydrothermal method

SO$_4$$^-$/$\text{ZrO}_2$ solid acid catalyst synthesized via hydrothermal method was first prepared by Xu et al. [25]. The catalyst was phase esterification of acetic acid with n-butanol preformed to confirm the optimal conditions of preparation of SO$_4$$^-$/$\text{ZrO}_2$ solid acid catalyst through hydrothermal modification experiments made in comparison with normal preparation method. Compared with conventional methods, the SO$_4$$^-$/$\text{ZrO}_2$ catalyst prepared by hydrothermal method is more active in esterification reaction, and the conversion of acetic acid is up to 99.1%.

2.5 Supercritical fluid drying method

Ultrasound titania-zirconia composite aerogel materials were prepared by supercritical drying of alcogels formed in sol-gel process using cheap and convenient Ti(SO$_4$)$_2$ and ZrOCl$_2$ as the Ti and Zr sources, respectively [26]. The results showed that nanometer-sized and high surface area TiO$_2$-$\text{ZrO}_2$ can be prepared by a sol-gel technique combined with the supercritical drying method without any expensive organic precursors. The XRD and Raman analysis showed that the Zr-containing compound is TiZrO$_4$. They found that Zr presented in the form of TiZrO$_4$ could increase the mesoporosity, textual, and thermal stability.

2.6 Neutral templating method (or LCT method)

Mesoporous sulfated zirconia was synthesized via liquid-crystal templating (LCT) method [27]. Extremely strong acidity was formed on the surface of mesoporous zirconia after being treated with sulfuric acid. Mesoporous sulfated zirconia with strong acidity is capable of catalyzing the isomerization of n-butane at room temperature. The conventional microporous sulfated zirconia is not suited for liquid-phase reactions of larger molecules because of its small pore size. Mesoporous sulfated zirconia with narrow pore-size distributions and high acidity could be used in the selective reactions of large molecules. Debra showed that it is possible to synthesize mesoporous sulfated zirconia via LCT method, and it is also possible to alter the size of the mesopores by changing synthetic parameters, such as surfactant concentration and cosolvent. Preliminary catalytic testing has shown that the diameter of the pores of the catalyst does affect the reaction rate for a specific large-molecule alkylation reaction in the liquid phase.

2.7 Refluxing method

Risch et al. [28] found that a high surface area mesoporous zirconia could be formed in the absence of surfactant by refluxing a solution of zirconyl chloride and ammonium.