Recent Advances in Solid Superacids

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Abstract: Recent advances in solid superacids are reviewed. The acid stronger than $H_0 = -11.93$, which corresponds to the acid strength of 100% $H_2SO_4$, is known as superacid. Solid superacid catalysts have many advantages such as an easy separation of products from catalyst, the repeated use and regeneration of catalysts, as compared with liquid superacids. The preparation methods, surface properties including acid amount and acid strength, structures of acid sites, and the applications of solid superacid catalysts for several chemical reactions are presented.

Keywords: solid superacid catalyst, preparation method, structure of acid sites, applications of catalysts

Introduction

Many kinds of solid acids have been found; their acidic properties, their catalysis, and the structure of acid site have been elucidated and those results have been reviewed by several workers [1-3]. A superacid is defined as a solid which exhibits an acid strength higher than the acid strength ($H_0 = -11.93$) of 100% sulfuric acid [4]. The acidity of highly acidic media can be determined by using appropriate Hammett indicators; the Hammet acidity function, $H_0$ [5], has been extensively used as a measure of acidity. Using various nitro compound indicators, which were first used by Brand and coworkers [6], Gillespie and coworkers determined the Hammett acidity function of superacid system [7,8], $H_2SO_4$, $H_2SO_4$$\cdot$FSO$_3$H, FSO$_3$H$\cdot$HF$\cdot$SbF$_5$, and FSO$_3$H$\cdot$SO$_3$F$\cdot$SbF$_5$. The acid strength of a solid is defined as the ability of the surface to convert an adsorbed neutral base into its conjugate acid. If the reaction proceeds by means of proton transfer from the surface to the adsorbate, the acid strength is expressed by the Hammett acidity function $H_0$ [5],

$$H_0 = pK_a + \log[B]/[BH^+]$$

(1)

where [B] and [BH$^+$] are, respectively, the concentrations of the neutral base (basic indicator) and its conjugate acid and $pK_a$ is $pK_{BH^+}$. If the reaction takes place by means of electron pair transfer from the adsorbate to the surface, $H_0$ is expressed by

$$H_0 = pK_a + \log [B]/[AB]$$

(2)

where [AB] is the concentration of the neutral base which reacted with the Lewis acid or electron pair acceptor, A. The $H_0$ of $H_2SO_4$ has been determined as -11.93, whereas that of FSO$_3$H was -15.07 [8].

<table>
<thead>
<tr>
<th>Acid</th>
<th>$H_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-10.2</td>
</tr>
<tr>
<td>BF$_3$$\cdot$H$_2$O (1:1)$^\dagger$</td>
<td>-11.4</td>
</tr>
<tr>
<td>$H_2$SO$_4$</td>
<td>-11.93</td>
</tr>
<tr>
<td>CF$_3$SO$_2$H</td>
<td>-13.0</td>
</tr>
<tr>
<td>$H_2$SO$_4$$\cdot$SO$_3$F (1:0.2)</td>
<td>-13.41</td>
</tr>
<tr>
<td>HF-NbF$_5$ (1:0.008)</td>
<td>-13.5</td>
</tr>
<tr>
<td>HSO$_3$Cl</td>
<td>-13.80</td>
</tr>
<tr>
<td>HF-SbF$_5$ (1:0.06)</td>
<td>-14.3</td>
</tr>
<tr>
<td>$H_2$SO$_4$$\cdot$SO$_3$F (1:1)</td>
<td>-14.44</td>
</tr>
<tr>
<td>FSO$_3$H</td>
<td>-15.07</td>
</tr>
<tr>
<td>HF-SbF$_5$ (1:0.14)</td>
<td>-15.2</td>
</tr>
<tr>
<td>FSO$_3$H-SO$_4$ (1:0.1)</td>
<td>-15.52</td>
</tr>
<tr>
<td>FSO$_3$H-AsF$_3$ (1:0.05)</td>
<td>-16.61</td>
</tr>
<tr>
<td>FSO$_3$H-TaF$_3$ (1:0.2)</td>
<td>-16.7</td>
</tr>
<tr>
<td>FSO$_3$H-SbF$_5$ (1:0.05)</td>
<td>-18.24</td>
</tr>
<tr>
<td>HF-TaF$_3$</td>
<td>-18.85</td>
</tr>
<tr>
<td>FSO$_3$H-SbF$_5$ (1:0.1)</td>
<td>-18.94</td>
</tr>
<tr>
<td>FSO$_3$H-SbF$_5$ (1:0.2)</td>
<td>-20</td>
</tr>
<tr>
<td>HF-SbF$_5$ (1:0.03)</td>
<td>-20.3</td>
</tr>
<tr>
<td>FSO$_3$H-SbF$_5$ (1:1)</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>

$^\dagger$ Figures in parenthesis are mole ratio.

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(e-mail: jrsohn@knu.ac.kr)
Table 2. pK\textsubscript{a} of Basic Indicators

<table>
<thead>
<tr>
<th>Indicators</th>
<th>pK\textsubscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,6 - Trinitroaniline</td>
<td>-10.10</td>
</tr>
<tr>
<td>p - Nitrotoluene</td>
<td>-11.35</td>
</tr>
<tr>
<td>m - Nitrotoluene</td>
<td>-11.99</td>
</tr>
<tr>
<td>p - Nitrofluorobenzene</td>
<td>-12.44</td>
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<tr>
<td>p - Nitrochlorobenzene</td>
<td>-12.70</td>
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<td>m - Nitrochlorobenzene</td>
<td>-13.16</td>
</tr>
<tr>
<td>2,4 - Dinitrotoluene</td>
<td>-13.75</td>
</tr>
<tr>
<td>2,4 - Dinitrofluorobenzene</td>
<td>-14.52</td>
</tr>
<tr>
<td>1,3,5 - Trinitrotoluene</td>
<td>-16.04</td>
</tr>
<tr>
<td>2,4 - Dinitrofluorobenzene</td>
<td>-17.35</td>
</tr>
<tr>
<td>2,4,6 - Trinitrotoluene</td>
<td>-18.36</td>
</tr>
<tr>
<td>p - Methoxybenzaldehyde</td>
<td>-19.50</td>
</tr>
</tbody>
</table>

pK\textsubscript{a} of the conjugate acid, BH\textsuperscript{+}, of indicator, B, (\(=\)pK\textsubscript{BH\textsuperscript{+}})

and 2 summarize H\textsubscript{0} values for some acidic media and pK\textsubscript{a} values of basic indicators, respectively. Butane can be protonated in a superacidic medium as follows:

\[
\text{C}_4\text{H}_{10} + \text{H}^+ \rightarrow \left(\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}\right)^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \tag{3}\]

\[
\text{C}_4\text{H}_{10} + \text{H}^+ \rightarrow \left(\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}\right)^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{SO}_4 \tag{4}\]

One characteristic feature of the protonation in superacidic media is that the protonation takes place on the C-H or C-C bonding to form two electron-three center carbonium ion which then converts to form carbonium ion by equation (3) and (4) [9]. Since the acidity of superacid is so strong that stable alkanes can be ionized even at low temperature, superacid has been utilized for the decomposition, polymerization, carboxylation, alkylation, isomerization, and oxidation of alkanes.

Homogeneous acidic media are widely used for organic reactions, for example, the acylation reaction using FeCl\(_3\), SnCl\(_4\), AlCl\(_3\), TiCl\(_4\), CF\(_3\)SO\(_2\)H, FSO\(_2\)H, and H\(_2\)SO\(_4\). However, they have several disadvantages for their applications to industrial processes. Replacement of homogeneous liquid acids by heterogeneous solid acids as catalysts in the chemical industry is expected to bring about the ease of separation from the reaction mixture, which allows continuous operation, as well as regeneration and reutilization of the catalyst. Furthermore, the use of solid superacid catalysts can lead to additional advantages, that is, no corrosion of the reactor and no environmental problem in the disposal of the used catalyst.

Surface and acidic properties, surface structures, generation mechanism of superacidic sites for solid superacid, and their applications to chemical reactions are reviewed herein.

**Liquid Superacid Supported on Metal Oxides**

The primary studies to obtain the solid superacid catalyst of liquid superacids supported on solid supports are found in the extensive patent literature [10-20]. BF\(_3\) attached to ion-exchanged resin; BF\(_3\) or SbF\(_5\) supported on graphite; AlF\(_3\) or HSBF\(_6\) supported on Al\(_2\)O\(_3\); SbF\(_5\) or TaF\(_5\) supported on SiO\(_2\), Al\(_2\)O\(_3\), zeolites, and SiO\(_2\)-Al\(_2\)O\(_3\); HF-SBF\(_5\) or HSO\(_3\)-SbF\(_5\) supported on metals, alloys, SiO\(_2\), Al\(_2\)O\(_3\), active carbon, graphite, SiO\(_2\)-Al\(_2\)O\(_3\), and polymer; and CF\(_3\)SO\(_2\)-SbF\(_5\) supported on Al\(_2\)O\(_3\) are examples of the system. On such carriers, at temperatures as low as 343 K, HF-SBF\(_5\) and HSO\(_3\)-SbF\(_5\) readily isomerize straight-chain alkanes such as n-hexane or n-heptane, and similar systems are also effective as alkylation catalysts for alkanes with alkenes, especially for isobutane with butenes for obtaining gasoline materials with high octane value.

Tanabe and coworkers provided a systematic investigation of Lewis acid-treated metal oxides [21-23]. The SBF\(_5\)-treated oxides such as TiO\(_2\) and SiO\(_2\), and mixed oxides such as SiO\(_2\)-Al\(_2\)O\(_3\), SiO\(_2\)-TiO\(_2\), TiO\(_2\)-ZrO\(_2\), were found to be effective in the isomerization and cracking reactions of butane and other alkanes. The catalysts were prepared by exposing the powdered metal oxides to SBF\(_5\) vapor followed by evacuation of excess SBF\(_5\); prior to exposure to the vapor of SBF\(_5\), all the metal oxides were outgassed at 773 K. The adsorption-desorption cycle was repeated several times in order to substitute the surface hydroxyl group with fluorine and to let SBF\(_5\) adsorb on the substituted surface.

The IR spectra of pyridine adsorbed on SBF\(_5\)/SiO\(_2\)-Al\(_2\)O\(_3\) showed that both Brønsted and Lewis acid sites were present on the surface when SiO\(_2\)-Al\(_2\)O\(_3\) was treated with SBF\(_5\) at low temperatures (below 373 K), but only Lewis acid sites were present when treated at 573 K [21,22]. The reaction of SBF\(_5\) with SiO\(_2\)-Al\(_2\)O\(_3\) is considered as follows (Scheme 1).

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Scheme 1.
Figure 1. Time dependence of composition in the reaction of pentane at 273 K over SbF$_5$/SiO$_2$-Al$_2$O$_3$. Catalyst, 0.1 g; initial pressure, 43 Torr; ○, pentane; ●, 2-methylbutane; △, 2-methylpropane.

Supercritical properties of the SbF$_5$/metal oxides are realized by their catalytic activities for alkane reactions. Over SbF$_5$/SiO$_2$-Al$_2$O$_3$, alkanes, except methane, ethane, and 2,2-dimethylpropane, undergo mainly skeletal isomerization at room temperature or below. As an example, time dependence of composition in the reaction of pentane is shown in Figure 1 [22]. At 273 K, pentane undergoes rapid isomerization to give 2-methylbutane in the initial stage of the reaction. In 30 min, 2-methylpropane begins to form. Relative conversion rates of straight-chain alkanes are in the order: butane < pentane < hexane. The conversion rate increases as the carbon number increases.

Aluminum chloride supported on Inorganic Oxides

Many patents have been issued for the treatment of inorganic oxides with aluminum chloride [24-28]. The most common method of treating hydroxylated inorganic oxides with aluminum chloride is by vapor deposition [9,24-28]. Drago and coworkers have prepared a superacid catalyst by reacting an inorganic oxide with aluminum chloride [Al$_2$Cl$_3$] in refluxing carbon tetrachloride (Scheme 2) [29]. The reaction of aluminum chloride with silicon dioxide resulted in the evolution of 1.1 mol of hydrogen chloride for every mol of AlCl$_3$ used, suggesting that over 90% of the chloroaluminum species on the surface of this support has the composition (-O-) AlCl$_3$. The use of chloroform, methylene chloride, ethylene dichloride and saturated hydrocarbon did not produce a solid superacid catalyst with the properties described for CCL$_4$. The three major products from the cracking of n-hexadecane are propane, isobutene, and n-butane. As shown in Table 3, the most active catalysts were those prepared on SiO$_2$, Al$_2$O$_3$, high silica zeolite, and B$_2$O$_3$.

Table 3. Activities for Different AlCl$_3$-Functionalized Supports

<table>
<thead>
<tr>
<th>X$^a$</th>
<th>propane$^b$</th>
<th>isobutane$^b$</th>
<th>n-butane$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>4.2 × 10$^{-4}$</td>
<td>7.1 × 10$^{-2}$</td>
<td>5.4 × 10$^{-6}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>6.2 × 10$^{-3}$</td>
<td>5.3 × 10$^{-2}$</td>
<td>3.0 × 10$^{-6}$</td>
</tr>
<tr>
<td>silicalite$^e$</td>
<td>1.8 × 10$^{-2}$</td>
<td>1.1 × 10$^{-1}$</td>
<td>3.3 × 10$^{-1}$</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>1.1 × 10$^{-2}$</td>
<td>5.0 × 10$^{-2}$</td>
<td>1.5 × 10$^{-5}$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>5.0 × 10$^{-8}$</td>
<td>5.0 × 10$^{-5}$</td>
<td>None</td>
</tr>
<tr>
<td>MgO</td>
<td>2.4 × 10$^{-9}$</td>
<td>7.8 × 10$^{-5}$</td>
<td>None</td>
</tr>
</tbody>
</table>

$^a$Made in CCL$_4$. $^b$Units: moles of product/(moles of Al/18 h). $^e$A high-silica zeolite.

Scheme 2.
Sulfate Supported on Metal Oxides

Recently a new type of solid acid that is modified by a sulfate ion, such as SO$_4^{2-}$/ZrO$_2$, SO$_4^{2-}$/TiO$_2$, SO$_4^{2-}$/TiO$_2$-SiO$_2$, SO$_4^{2-}$/ZrO$_2$-SiO$_2$, and SO$_4^{2-}$/Fe$_2$O$_3$, has been developed and used as a powerful catalyst for various acid-catalysed reactions, such as the dealkylation of cumene, the skeletal isomerization of butane to isobutane, the acylation of benzene derivatives by acyl chlorides, and the ring-opening isomerization of cyclopropane [2,9,30-34]. The SO$_4^{2-}$ ion can be introduced from H$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, SO$_2$, CS$_2$, and H$_2$S. It was pointed out that the existence of covalent S=O bonds in sulfur complexes formed on metal oxides was necessary for the generation of acidity [31,35-37].

Titanium dioxide has moderate acidic strength ($H_0 = +1.5$) and weak basic strength [38]. The acidic and basic strengths of ZrO$_2$ are very weak [39]. Ferric Oxide is an almost neutral oxide [33]. However, these oxides begin to show superacidity when they contain a small amount of sulfate ion or if a small amount (0.5~8 wt%) of ammonium sulfate or sulfuric acid is added. The discovery of these solid superacids originated from the study of the effect of anions on the preparation of TiO$_2$ [40]. Since these superacids do not contain halogen atoms, they have advantages of not only low-energy synthesis, but also low corrosion and environmental problems when used as catalysts. Therefore, the use of the solid superacids instead of aluminum chloride or sulfuric acid as a catalyst is promising for chemical industry use.

The solid superacids such as SO$_4^{2-}$/TiO$_2$, SO$_4^{2-}$/ZrO$_2$, SO$_4^{2-}$/TiO$_2$-SiO$_2$, SO$_4^{2-}$/ZrO$_2$-SiO$_2$, and SO$_4^{2-}$/Fe$_2$O$_3$ are easily prepared by adding (NH$_4$)$_2$SO$_4$ or H$_2$SO$_4$ to Ti(OH)$_4$, Zr(OH)$_4$, Tit(OH)$_4$-Si(OH)$_4$, Zr(OH)$_4$-Si(OH)$_4$, and Fe(OH)$_3$, respectively, followed by calcining at 773~923 K. As an example, the preparations of SO$_4^{2-}$/ZrO$_2$, SO$_4^{2-}$/TiO$_2$-SiO$_2$, and SO$_4^{2-}$/ZrO$_2$-SiO$_2$ are described in more detail [33,34,37]. A commercially available ZrOCl$_2$ or ZrO(NO$_3$)$_2$ is hydrolyzed with 28% aqueous ammonia and the precipitates formed are washed with distilled water and dried at 373 K overnight to obtain Zr(OH)$_4$. The hydroxide, Zr(OH)$_4$, is immersed into an aqueous solution of (NH$_4$)$_2$SO$_4$ or H$_2$SO$_4$ and the suspended solution is evaporated to dryness, followed by calcinations in air or in vacuum at 773~923 K to obtain SO$_4^{2-}$/ZrO$_2$. The optimum temperature of calcinations depends on the kind of SO$_4^{2-}$ source [(NH$_4$)$_2$SO$_4$ or H$_2$SO$_4$]. In the acylation of chlorobenzene with chlorobenzoyl chloride, the optimum calcination temperature are 823 and 873 K for H$_2$SO$_4$/ZrO$_2$ and (NH$_4$)$_2$SO$_4$/ZrO$_2$, respectively [40]. The optimum content of SO$_4^{2-}$ changes from 1 to 8 wt% depending on the kind of reaction. An important point is to use Zr(OH)$_4$ instead of ZrO$_2$ as an adsorbent of SO$_4^{2-}$. Since the solid superacid loses superacidity by adsorbing moisture when exposed to air, calcinations in air and then storage in sealed tubes are recommended.

Similarly, as in the case of SO$_4^{2-}$, the addition of SO$_3$ to Fe$_2$O$_3$ causes the generation of superacidity [36]. However, the addition of SO$_3$, CS$_2$, or H$_2$S does not generate super acidity. It is interesting that SO$_3$, CS$_2$, and H$_2$S adsorbed on ZrO$_2$ or Fe$_2$O$_3$ do not show any acidity, but exhibit strong acidity when oxidized with O$_2$. The latter hand, SO$_4^{2-}$/ZrO$_2$ and SO$_4^{2-}$/Fe$_2$O$_3$ lose their acidity when reduced with H$_2$ at 773 K. These facts indicate that oxidation and reduction influence the acidity of a sulfur-containing superacid.

The SO$_4^{2-}$/Fe$_2$O$_3$ catalyst is also highly active for polymerization of alkylvinyl ethers [41]. The SO$_4^{2-}$/TiO$_2$ and SO$_4^{2-}$/ZrO$_2$ catalysts showed high activities for various esterification reactions [42-44]. As an example, SO$_4^{2-}$/TiO$_2$ calcined at 773 K is much more active than SiO$_2$-AlO$_2$ for esterification of terephthalic acid with ethylene glycol at 473 K, as shown in Figure 2 [42].

![Figure 2](image)

**Figure 2.** Esterification of terephthalic acid with ethylene glycol over SO$_4^{2-}$/TiO$_2$. Reaction temperature, 473 K; reaction time, 90 min.
reaction [46]. According to IR study of adsorbed pyridine, the acid sites on SO₄²⁻/NiO-TiO₂ are of Brønsted and Lewis types. However, upon the addition of water vapor to the catalyst, a considerable amount of Brønsted acid increased accompanied by a simultaneous decrease in Lewis acidity. This indicates that the Lewis site is converted to the Brønsted site by water molecules as shown in Figure 3 [46].

Using IR spectroscopy, Tanabe and coworkers proposed a structure for the acid site on sulfate-promoted metal oxides to be chelating bidentate complexes [32,36,47]. The central metal ion acts as a Lewis acid site, whose acid strength can be strongly enhanced by the inductive effect of S=O in the sulfur complex, as shown in Figure 4.

Arata and coworkers observed that Lewis and Brønsted sites on SO₄²⁻/ZrO₂ catalysts are easily changeable by adsorption or desorption of water molecules, the reaction of butane being also catalyzed by the Brønsted site [48, 49]. The surface structure appears to be SO₄ combined with Zr elements in the bridging bidentated state, as shown in Figure 5. The double-bond nature of the complex is much stronger compared with that of a simple metal sulfate. When water molecules are present, the Lewis acid sites are converted to Brønsted acid sites [3,49].

Sauer and coworkers studied the structure of sulfate-promoted alumina and titania and postulated that in the absence of water three oxygens of the sulfate are bonded to Al or Ti, whereas in the presence of H₂O this is converted to a bridged bidentate sulfate (Scheme 3), thus

![Diagram](image-url)
accounting for the increased amount of Brønsted acid site [50].

When adsorbing SO\textsubscript{2} on ZrO\textsubscript{2}, Sohn and coworkers found the bands at 1336 and 1148 cm\textsuperscript{-1} and a broad band at 1000-850 cm\textsuperscript{-1} at room temperature which are assigned to S-O stretching and SO\textsubscript{2}\textsuperscript{-} stretching vibrations, respectively [37,47,51]. However, as shown in Figure 6, successive oxidation with O\textsubscript{2} at 673 K gave new bands at 1210, 1134, 1060 and 990 cm\textsuperscript{-1}, whose intensities increased with oxidation time [37]. These bands are very similar in shape and absorption position to those of SO\textsubscript{2}\textsuperscript{-}/ZrO\textsubscript{2} [37], indicating the formation of SO\textsubscript{4}\textsuperscript{2-} species from the adsorbed SO\textsubscript{2} species due to the oxidation process. Similar oxidation results were obtained using other sulfur compounds, H\textsubscript{2}S and CS\textsubscript{2}[37]. Figure 7 show the variation of catalytic activity of SO\textsubscript{2}/ZrO\textsubscript{2} for 1-butene isomerization as a function of oxidation time at 673 K. The longer the oxidation time, the higher the catalytic activity becomes [37].

**Iron/manganese Sulfated Zirconia Catalysts**

Environmental concerns are leading to the replacement of aromatic hydrocarbons on gasoline with high-octane-number branched paraffins and oxygenated compounds such as methyl t-butyl ether, which is produced from methanol and isobutylene. The latter can be formed from n-butane by isomerization followed by dehydrogenation. To meet the need for improved catalysts for isomerization of n-butane and other paraffins, researchers identified solid acids that are noncorrosive and active at low temperatures. A new class of solid superacids, sulfated metal oxides containing Fe, Mn and Zr (SFMZ), has recently been developed and shown to be the most active non-halide catalyst for isomerization of n-butane and industrial applications [52-54]. These catalysts were shown to isomerize n-butane to isobutane at 308 K with rates approximately 2-3 orders of magnitude greater than sulfated zirconia as claimed by workers at Sun Refining and Marketing Company [55]. These catalysts usually contain 0.5-3 wt% Fe and Mn and exhibit catalytic activity even at room temperature (Table 4). These catalysts are suitable for either gas or liquid phase operations [56].

In addition to activity for hydrocarbon isomerization, these catalysts are reported to be capable of catalytically converting methane into ethane at temperature less than 573 K [57]. These authors believe that the reaction proceeds through an acid-catalyzed oligo-condensation mechanism as suggested by Olah and Schlossberg [58]. Along similar lines, Scurrell [59] reports that methane-ethene mixtures are converted to higher hydrocarbons using SO\textsubscript{2}/ZrO\textsubscript{2}; initially C\textsubscript{6} and C\textsubscript{7} products dominated but with increasing reaction time the products become lighter weight.
Table 4. Conversion of n-Butane with Fe, Mn-SO_4^2-/ZrO_2 Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Run No</th>
<th>Reaction temperature(K)</th>
<th>Isomerization product composition(wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat ZrO_2</td>
<td>26</td>
<td>298</td>
<td>0.61</td>
</tr>
<tr>
<td>Neat ZrO_2</td>
<td>27</td>
<td>323</td>
<td>3.98</td>
</tr>
<tr>
<td>Neat ZrO_2</td>
<td>28</td>
<td>348</td>
<td>10.74</td>
</tr>
<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>29</td>
<td>298</td>
<td>1.67</td>
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<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>30</td>
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<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
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<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
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<tr>
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<td>323</td>
<td>13.42</td>
</tr>
<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>40</td>
<td>348</td>
<td>40.69</td>
</tr>
<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>41</td>
<td>298</td>
<td>1.02</td>
</tr>
<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>42</td>
<td>323</td>
<td>17.89</td>
</tr>
<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>43</td>
<td>348</td>
<td>37.96</td>
</tr>
<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>44</td>
<td>298</td>
<td>1.70</td>
</tr>
<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>45</td>
<td>323</td>
<td>26.05</td>
</tr>
<tr>
<td>1.5%Fe, 0.5% Mn on ZrO_2</td>
<td>46</td>
<td>348</td>
<td>45.57</td>
</tr>
</tbody>
</table>

Kinetics of the isomerization of n-butane and of isobutene catalyzed by sulfated zirconium oxide containing 1.5 wt% Fe, 0.5 wt% Mn, and 4.0 wt% sulfate at 333 K were well represented by a Langmuir-Hinshelwood equation accounting for the reaction equilibrium and for adsorption of both butanes [60]. The adsorption equilibrium constants estimated from the kinetics data are nearly the same for the two butanes. The form of the rate equation and the observation that disproportionation accompanies isomerization suggested that the reaction proceeds via a C5 intermediate.

Ethane was converted in the presence of FMSZ at temperature less than 573 K, but it was not converted in the presence of the other solid acids such as sulfated zirconia, HZSM5, and USY zeolite [61,62]. This comparison suggests that the other materials may be less strongly acidic than FMSZ. The observed gas-phase products were methane, ethane, and butane, which are the same as those observed at temperatures >573 K (H2 was observed at the higher temperatures but not at the lower temperatures).

Lin and Hsu [57] reported a temperature programmed desorption technique to determine the acidity of these sulfated Fe, Mn and Zr (SFMZ) catalysts and use this technique to compare their catalyst formulations to the conventional sulfated zirconia (SZ) catalysts. Alkyl or fluoro substituted benzenes are weak Lewis bases and are believed to function as bases because of interactions between the 2π-electrons of the benzene ring and acidic protons.

Data for a SFMZ (1.5% Fe, 0.5% Mn and 4.0% SO_4^2-) and SZ (4.0% SO_4^2-) are shown in Figure 8. For the
SFMZ sample without adsorbate, the only peak observed was at 1053 K; this corresponds to the decomposition of SO$_4^{2-}$ in the catalyst. The TPD for the SZ sample with benzene as adsorbate exhibited a peak at 1058 K due to SO$_4^{2-}$ decomposition, a weak peak at 800 K and an asymmetric peak at 500 K. The 500 K peak was due to desorption of weakly adsorbed benzene and is characteristic of all catalysts tested. The peak at 800 K is due to benzene adsorbed on an acidic site. In contrast to SZ, the SFMZ catalyst showed a large well-defined peak at 835 K. This peak was not generated by the adsorption of benzene on iron or manganese oxides since a catalyst containing these metals but no sulfate did not exhibit the 835 K peak (curve d, Figure 8). Thus, they concluded that SFMZ contained additional strong acid sites whose strength was high enough to adsorb a very weak base like benzene. These authors also found a striking correlation between the amount of acidity measured by TPD, the C$_4$ isomerization activity and the sulfate content [57].

Pt-SO$_4^{2-}$/Metal Oxides

Skeletal isomerization of normal paraffins is of great importance in the petroleum refining industry to increase the octane number of synthetic gasoline, and to synthesize branched paraffins which react with olefins under mild conditions to give highly branched hydrocarbons.

For these reactions, the activity of SO$_4^{2-}$/metal oxide catalysts is lowered as the reactions proceed, probably due to coke formation. To prevent the catalyst from deactivating, a catalyst on which a small amount of Pt, Rh, and Ni was added has been developed. It has been reported by several groups that the addition of platinum to ZrO$_2$ promoted by sulfate enhances catalytic activity in the skeletal isomerization of alkanes without deactivation when the reaction is carried out in the presence of hydrogen [63-66]. Hosoi and coworkers [63] reported amazing conversion data for C$_5$/C$_6$ isomerization using Pt-SO$_4^{2-}$/ZrO$_2$ catalysts. They found that the addition of Pt caused the catalyst to maintain its activity for a much longer period compared to the SO$_4^{2-}$/ZrO$_2$ catalyst without Pt. They explained the hydrogen effect as removal of carbonaceous residue formed during the reaction by hydrogenation. To avoid the deactivation, a solid superacid, Pt-SO$_4^{2-}$/ZrO$_2$, was prepared by impregnating ZrO$_2$ with SO$_4^{2-}$ and then Pt. The catalyst exhibits a high activity as well as a high selectivity for the skeletal isomerization in the presence of H$_2$, no deactivation being observed, as shown in Figure 9. The catalyst is quite stable even after 1000 h [67]. Platinum was the best among Pd, Rh, Ni, Ru, W, Mo, and Fe. Since a simple Pt/ZrO$_2$ was inactive as shown in Figure 9, superacidity formed by the reaction of ZrO$_2$ with SO$_4^{2-}$ is necessary for the high activity and selectivity. In fact, the acid strength of Pt-SO$_4^{2-}$/ZrO$_2$ is $H_0 = -12.7$. A

![Figure 9. Isomerization of pentane to 2-methylbutane at 413 K over SO$_4^{2-}$/Pt/ZrO$_2$. Pressure, 20 kg cm$^{-2}$; LHSV, 1.5 h$^{-1}$; H$_2$/pentane, 1.5 mol/mol.](image)

SO$_4^{2-}$/Pt/ZrO$_2$ which was prepared by impregnating with Pt and then SO$_4^{2-}$ showed the same acid strength and almost the same activity as those of a Pt-SO$_4^{2-}$/ZrO$_2$ catalyst [67].

It has been found recently that the effect of Pt addition on SO$_4^{2-}$/ZrO$_2$ is not only to prolong the catalyst life by removing coke, but also to enhance the acidity of the catalyst [68]. According to IR and TPD studies of adsorbed pyridine, the acid sites on Pt-SO$_4^{2-}$/ZrO$_2$ are mostly of Lewis acid type and stronger than those of SO$_4^{2-}$/ZrO$_2$. Based upon isotopic studies, the following mechanism was proposed for the catalytic behavior. Hydrogen molecules are dissociated homolytically into hydrogen atoms on Pt and spill over to SO$_4^{2-}$/ZrO$_2$ where the conversion of an H atom to H$^+$ occurs, with concomitant formation of H$^+$ on a Lewis acid site. The H$^+$ acts as a catalytic site for skeletal isomerization of pentane. Therefore, the presence of H$_2$ in the reaction system over Pt-SO$_4^{2-}$/ZrO$_2$ is necessary for formation of H$^+$ and hence for enhancement of catalytic activity. The effect of the presence of hydrogen gas during the reaction on catalytic activity of Pt-SO$_4^{2-}$/ZrO$_2$ is remarkable compared with inert nitrogen gas [68].
Metal Sulfates Support on Metal Oxides

Many metal sulfates generate fairly large amounts of acid sites of moderate or strong strength on their surfaces when they are calcined at 946-1246 K [69,70]. The acidic property of metal sulfate often gives high selectivity for diversified reactions such as hydration, polymerization, alkylation, cracking, and isomerization [69,70]. However, structural and physicochemical properties of supported metal sulfates are considered to be in different states compared with bulk metal sulfates because of their interaction with supports [71]. Sohn and coworkers studied in detail the acidic catalytic activities and properties of metal sulfates [NiSO₄, Ti(SO₄)₂, Fe(SO₄)₃, CoSO₄, and Zr(SO₄)₂] supported on ZrO₂, TiO₂, Al₂O₃, and SiO₂-Al₂O₃ [72-79]; most of the catalysts showed the maximum catalytic activity by calcinations at temperatures around 873 K, with respect to the acid-catalyzed reaction.

The crystalline structures of 15-Ti(SO₄)₂/ZrO₂ having 15 wt% Ti(SO₄)₂ calcined in air at different temperatures for 2 h were examined [72]. For the sample of 15-Ti(SO₄)₂/ZrO₂ the transition temperature of ZrO₂ from amorphous to tetragonal phase was higher by 623 K than that of pure ZrO₂. X-ray diffraction data indicated that an orthorhombic phase of Zr(SO₄)₂ was predominantly observed together with a tiny amount of orthorhombic phase of Ti(SO₄)₂ at 673-973 K, indicating that zirconium sulfate between titanium sulfate and zirconia was formed during the catalyst preparation. The calcination, a tiny amount of tetragonal and monoclinic phases of zirconia was observed at 973 K due to the transition of ZrO₂ from amorphous to tetragonal phase. However, as shown in Figure 10, from 1073 K a large amount of monoclinic phase of zirconia was observed due to the decomposition of zirconium or titanium sulfate, showing a good agreement with the results of DSC described later.

The thermal analysis of precursors for Ti(SO₄)₂/ZrO₂ samples are illustrated in Figure 11. For pure ZrO₂, the DSC curve shows a broad endothermic peak below 453 K due to water elimination, and a sharp and endothermic peak at 711 K due to the ZrO₂ crystallization[80]. As Figure 11 shows, the exothermic peak due to the crystallization appears at 711 K for pure ZrO₂, while for Ti(SO₄)₂/ZrO₂ samples it is shifted to higher temperatures due to the interaction between Ti(SO₄)₂ and ZrO₂. The
Table 5. Specific Surface Area and Acidity of Ti(SO)$_4$/ZrO$_2$ Calcined at 873 K for 2 h

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m$^2$/g)</th>
<th>Acidity ($\mu$mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>56.1</td>
<td>41.3</td>
</tr>
<tr>
<td>0.5-Ti(SO)$_4$/ZrO$_2$</td>
<td>107.4</td>
<td>96.2</td>
</tr>
<tr>
<td>1-Ti(SO)$_4$/ZrO$_2$</td>
<td>108.2</td>
<td>185.4</td>
</tr>
<tr>
<td>3-Ti(SO)$_4$/ZrO$_2$</td>
<td>113.3</td>
<td>187.3</td>
</tr>
<tr>
<td>5-Ti(SO)$_4$/ZrO$_2$</td>
<td>137.2</td>
<td>189.0</td>
</tr>
<tr>
<td>10-Ti(SO)$_4$/ZrO$_2$</td>
<td>132.3</td>
<td>183.0</td>
</tr>
<tr>
<td>15-Ti(SO)$_4$/ZrO$_2$</td>
<td>126.5</td>
<td>137.3</td>
</tr>
<tr>
<td>20-Ti(SO)$_4$/ZrO$_2$</td>
<td>108.3</td>
<td>123.0</td>
</tr>
<tr>
<td>25-Ti(SO)$_4$/ZrO$_2$</td>
<td>91.7</td>
<td>120.5</td>
</tr>
</tbody>
</table>

shift increases with increasing titanium sulfate content. Consequently, the exothermic peaks appear at 746 K for 3-Ti(SO)$_4$/ZrO$_2$ and 790 K for 5-Ti(SO)$_4$/ZrO$_2$. These results are in good agreement with those of X-ray diffraction results described above. The endothermic peaks around 1003 K for Ti(SO)$_4$/ZrO$_2$ samples are due to the evolution of SO$_3$ decomposed from sulfone bonded to the surface of zirconia [71,81]. For 10-Ti(SO)$_4$/ZrO$_2$ and 20-Ti(SO)$_4$/ZrO$_2$, three endothermic peaks below 573 K are due to the dehydration of zirconium sulfate which was confirmed by X-ray diffraction [Figure 11(d)and(e)], indicating that the dehydration occurs in three steps. However, for 25-Ti (SO)$_4$/ZrO$_2$, four endothermic peaks below 573 K was observed, indicating that the dehydration of zirconium sulfate penta-hydrate occurs in four steps. For 25-Ti (SO)$_4$/ZrO$_2$, zirconium sulfate penta-hydrate was also confirmed by X-ray diffraction [Figure 11(f)].

The acid strength of Ti(SO)$_4$/ZrO$_2$ was estimated to have H$_3$O$^+ = 14.5$, indicating the formation of superacidic sites [72]. The acidity of catalysts calcined at 873 K, as determined by the amount of NH$_3$ irreversibly adsorbed at 503 K [71,82,83], is listed in Table 5. The acidity increases abruptly upon the addition of titanium sulfate [0.5 wt% of Ti(SO)$_4$] to ZrO$_2$, and then the acidity increases very gently with increasing titanium sulfate content up to 5 wt% of Ti(SO)$_4$. In view of Table 5, it is clear that the acidity runs parallel with the surface area. The catalytic activities for cumene dealkylation and 2-propanol dehydration correlated to the acidity of Ti(SO)$_4$/ZrO$_2$ [72].

Nickel sulfate supported on metal oxide catalysts, that is, NiSO$_4$/γ-Al$_2$O$_3$, NiSO$_4$/ZrO$_2$, NiSO$_4$/TiO$_2$, and NiSO$_4$/SiO$_2$–Al$_2$O$_3$ were tested for their effectiveness in ethylene dimerization [75,77,78,84,85]. Over these catalysts, ethylene was selectively dimerized to n-butene. NiSO$_4$/γ-Al$_2$O$_3$ was very effective for ethylene dimerization, but γ-Al$_2$O$_3$ alone without NiSO$_4$ was completely inactive. The catalytic activities for 1-butene isomerization at 20°C were also measured to examine the sulfonation effect using 20-NiSO$_4$/γ-Al$_2$O$_3$ and γ-Al$_2$O$_3$. 20-NiSO$_4$/γ-Al$_2$O$_3$ exhibited catalytic activity 15 times higher than that of pure γ-Al$_2$O$_3$ without NiSO$_4$, showing the high effect of sulfonation on the 1-butene isomerization activity.

The catalytic activities of NiSO$_4$/γ-Al$_2$O$_3$ containing different NiSO$_4$ contents were examined; results are shown as a function of acid amount in Figure 12 [71], where catalysts were evacuated at 673 K for 1.5 h before reaction. Figure 12 shows good correlation between the catalytic activity and the acid amount. The acid amount of NiSO$_4$/γ-Al$_2$O$_3$ calcined at 873 K was determined by the amount of NH$_3$ irreversibly adsorbed at 503 K [86-88]. As shown in Figure 12, the higher the acid amount, the higher the catalytic activity.

Infrared spectra of 20-NiSO$_4$/γ-Al$_2$O$_3$ after evacuation at 373-873 K for 1 h are shown in Figure 13. There are sharp peaks at 1362-1398 cm$^{-1}$ accompanied by four broad but split bands at 1250, 1157, 1038, and 941 cm$^{-1}$, indicating the presence of two kinds of sulfated species [77]. However, the frequency shift of this band at 1362-1398 cm$^{-1}$ differs depending on the evacuation temperature, as shown in Figure 13. At 273 K an asymmetric stretching band of S=O bonds was not observed because the water molecules are adsorbed on the surface of 20-NiSO$_4$/γ-Al$_2$O$_3$ [50,89]. However, from 473 K the band began to appear at 1362 cm$^{-1}$ as a shoulder, and the band intensity increased with the evacuation temperature and the position of band shifted to a higher wavenumber. It is likely that the surface sulfur complexes formed by
activity closely correlates to the asymmetric stretching frequency of the S = O bonds. An asymmetric frequency in the S = O bonds is a measure of the ability (acid strength) of a sulfur complex to pull basic molecules such as H₂O and NH₃ and is a driving force in generating highly acidic properties, acid strength and acid amount [32,50,89].

**Superacids Modified with Metal Oxides**

The sulfate-promoted catalysts sometimes suffer from dopant loss during thermal treatment and they undergo significantly deactivation during catalytic reaction, especially in a solid-liquid system. Another type of superacids, not containing sulfate ion but consisting of metal oxides such as WO₃, MoO₃, and Cr₂O₃, have been developed [90-99].

WO₃/ZrO₂ catalyst was prepared as follows. Zr(OH)₄ was impregnated with aqueous ammonium metatungstic [(NH₄)₅(H₂W₁₂O₄₁):nH₂O] followed by evaporating water, drying, and calcining in air at high temperatures [3,90]. WO₃/ZrO₂ catalysts were quite effective for the benzoylation of toluene with benzoic anhydride, for the reaction of pentane and heptane, and for the isomerization of o-xylene [96,99]. The catalyst was active for isomerization of butane at 327 K and pentane at 303 K. The addition of WO₃ up to 20 wt% to zirconia shifted the phase transition of ZrO₂ from amorphous to tetragonal to higher temperature due to the interaction between WO₃ and zirconia, and the specific surface area and acidity of catalysts increased in proportion to the WO₃ content [90].

The acid strength of this catalyst was estimated to be Hₒ ≤ -14.5 by a color change method using Hammett indicators. The high acid strength and high acidity were responsible for the W = O bond nature of complex formed between WO₃ and ZrO₂ [90]. The crystal structures of WO₃/ZrO₂ (having 5 and 13 wt% WO₃) calcined in air at different temperatures for 1.5 h were examined. In the case of supported WO₃ catalysts, the crystal structures of the samples were different from that of the ZrO₂ support as shown in Figure 14. The higher the content of WO₃, the higher the phase transition temperature of ZrO₂ from amorphous to tetragonal.

Over NiO-ZrO₂/VO₂, ethylene was selectively dimerized to n-butenes [87,93]. NiO-ZrO₂ without WO₃ was inactive for the ethylene dimerization, but NiO-ZrO₂/VO₂ was found to be very active even at room temperature. The high catalytic activity of NiO-ZrO₂/VO₂ was closely correlated with the increase of acidity and acid strength due to the addition of WO₃ [87,93].

Supported chromium oxide catalysts are being used for the polymerization, hydrogenation, and oxidation-reduction reactions between environmentally important molecules such as CO and NO [100-106]. Upon the addition of only a small amount of chromium oxide to ZrO₂, both the
acidity and acid strength of CrO$_x$/ZrO$_2$ increased remarkably, showing the presence of Brønsted and Lewis acid sites on the surface of CrO$_x$/ZrO$_2$. The acid strength of CrO$_x$/ZrO$_2$ was found to be H$_0$ = -14.5 [107]. The superacidic property was attributed to the double bond nature of the Cr = O in the complex formed by the interaction of ZrO$_2$ modified with sulfate ion and WO$_3$ [46,87,93].

The difficulty in the study of supported chromium oxide comes from the simultaneous presence of oxidation states. The XPS in the Cr 2p$_{3/2}$ region was analyzed by appropriate curve fitting and the results of quantitative analysis for the chromium oxidation state are listed in Table 7 [107]. It is noted that the number of Cr(III)

Table 7. Percentage of Chromium Species from the Area of the Fitted Bands in the Cr 2p$_{3/2}$ XPS Region

<table>
<thead>
<tr>
<th>treatment condition</th>
<th>Cr$^{6+}$</th>
<th>Cr$^{3+}$</th>
<th>Cr$^{0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncalcined sample</td>
<td>65</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>calcined at 873 K</td>
<td>54</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>after reduction with H$_2$ at 823 K</td>
<td>19</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>after oxidation with O$_2$ at 823 K</td>
<td>59</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>after reaction with n-hexane at 823 K</td>
<td>3</td>
<td>89</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure 14. X-ray diffraction patterns of ZrO$_2$, 5-WO$_3$/ZrO$_2$, and 13-WO$_3$/ZrO$_2$ calcined at different temperatures for 1.5 h: T, tetragonal phase ZrO$_2$; M, monoclinic phase ZrO$_2$.

Figure 15. Cyclic behavior of catalytic property of 1-CrO$_x$/ZrO$_2$-600 for cumene cracking reaction, where (↑) indicates the interval of 20 mL O$_2$ injection and (•) indicates catalytic activity after reduction with 20 mL H$_2$ at 723 K.

As seen in Table 7, the Cr(VI)/Cr(III) ratio increased or decreased, depending on the process of oxidation or reduction. Figure 15 shows cyclic behavior of catalytic activity for cumene cracking reaction at 723 K [110]. At the first pulse cracking activity is very high, but from the second pulse cracking activity drops suddenly because Cr$^{6+}$ species are reduced to Cr$^{3+}$ species during cumene reaction. Figure 15 also indicates the cracking activity of CrO$_x$/ZrO$_2$ after reduction with 20 mL H$_2$ at 723 K, showing very low cracking activity. However, after the fifth pulse the sample was treated with 20 mL of O$_2$ at 773 K and then at the sixth pulse the cracking activity was measured. The arrow in Figure 15 indicates the interval of 20 mL O$_2$ injection. At the sixth pulse the cracking activity was completely recovered, but at the seventh pulse the cracking activity dropped suddenly due to the reduction of Cr$^{6+}$ species, as it occurred at the second pulse. As shown in Figure 15, catalytic behavior like this was repeated at every pulse after 20 mL O$_2$ injection, indicating that redox cycles of chromium species are reversible [108,109]. In view of the XPS
results, acid strength measurement, and the above cyclic behavior of cracking activity, it is concluded that the catalyst having Cr⁺³ species is responsible for the cracking reaction of cumene.

Supported molybdenum oxide catalysts are extremely important for industrial applications. These systems are active for various reactions, such as partial oxidation of hydrocarbon [110-112], metathesis of alkenes [113], and hydrotreatment [114-116]. Several authors have shown the hydrotreating properties of $\text{Mo/ZrO}_2$ catalysts to be better than those of classical systems [117-121]. Zhao and coworkers [122] reported that Mo-O-Zr surface species in $\text{MoO}_3/\text{ZrO}_2$ should be responsible for its superacidity and that $\text{MoO}_3/\text{ZrO}_2$ was active for cumene cracking at 473 K which can be catalyzed at this temperature only by superacid [70]. A series of zirconia-supported molybdenum oxide catalysts with different molybdenum loading using conditions reported to generate superacidity have been evaluated for their performance as catalysts for methane oxidation [123]. A marked dependence of molybdenum content on catalytic activity has been observed, with the most active material being that with intermediate molybdenum content. 5 wt% $\text{MoO}_3/\text{ZrO}_2$ compared favorably with $\text{Zr}_6\text{Ce}_{1-x}\text{O}_2$ for methane combustion.

**Conclusion and Prospects**

I have tried to present the recent reports on the preparations of solid superacid catalysts, surface and acidic properties, surface structures, generation mechanism of superacidic sites for solid superacids, and their applications to chemical reactions. As mentioned above, liquid acid-catalyzed reaction processes have disadvantages such as difficulties of product separation and catalyst recovery, corrosion of reaction vessels, and pollution by acidic waste water. These processes should be replaced by a homogeneous process. However, solid superacids are much lower in acid strength compared to liquid superacids. The Hammett acidity function of liquid super-acids such as $\text{HSO}_3\text{F-SbF}_5$ and HF-SbF$_3$ reaches about -25, being more than 10$^9$ times stronger than the solid superacids. However, solid superacid catalysts can be used at elevated temperatures, although their acid strength is much weaker than that of liquid ones.

A new type of sulfated metal oxides is stable because of pretreatment at high temperatures, but elimination of sulfate is sometimes observed during reactions. Thus it is expected to prepare solid superacids modified with metal oxides. Another types of superacid catalysts, tungsten or molybdenum oxide supported on carriers such as $\text{ZrO}_2$, $\text{TiO}_2$, and $\text{Al}_2\text{O}_3$ have been prepared by new preparation methods, and their stability is satisfactory so far. It is hoped that the preparation methods will be extensively applied to other metal oxides for new solid superacids. There are many reactions where solid superacids might be expected to perform as highly active catalysts.

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**References**