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The surface structure of sulfated zirconia: Studies of XPS and thermal analysis

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Abstract

Sulfated zirconias were prepared using two kinds of amorphous zirconia gels, XZO 631 and 632 supplied by MEL Chemicals, and their thermal gravimetrical analyses were carried out. DTG of the former sample showed two peaks based on decomposition of the sulfate species on the surface, the first peak at 680 °C and the second broad one centered at 850 °C. The latter sample indicated only broad peak at 850 °C in the range from 700 to >1000 °C. The first peak for the former sample was ascribed to the decomposition of $Zr(SO_4)_2$ remained on the surface, and the broad one at 700 to >1000 °C for the both samples was attributed to the catalytically active species. The acidic character of sulfated zirconia calcined at 1000 °C was examined in acid-catalyzed reactions of cumene, ethylbenzene, and butane together with the adsorption heat of Ar, showing a solid acid with acidity higher than that of silica–alumina. It was indicated from the XPS analysis that the S species are composed of SO_4^{2-}. The results led to a structural model of the active surface to be polysulfate species containing mainly three or four S atoms with two ionic bonds of S—O—Zr in addition to coordination bonds of S═O with Zr, the active site being Lewis sites on the S atoms.

Keywords: Sulfated zirconia; DTG; XPS; Acidity; Structure; Polysulfate; Lewis site; Coordination

1. Introduction

In 1979, we reported that sulfated zirconia (SO_4/ZrO_2) shows extremely strong acidity to be capable of catalyzing the isomerization of *n*-butane to isobutane at room temperature [1,2]. Since then, the material has drawn much attention as a remarkable catalyst, and numerous studies have been achieved for its preparation, characterization, and catalytic performance; several reviews are available in literatures [3–8]. Following the same manner as the SO_4/ZrO_2, tungstated zirconia (WO_3/ZrO_2) was also synthesized and shown to be a potential catalyst [9,10].

In order to know how the sulfate species enhances the surface acidity of zirconia, we studied the surface using mainly X-ray photoelectron spectroscopy (XPS) and infrared (IR) [2], and proposed the surface structure to be SO_4 combined with Zr elements in the bridging bidentate state as shown in Scheme 1 [3]. The S═O double bond nature in the sulfate complex is much stronger than that of a simple metal sulfate; thus, the Lewis acid strength of Zr^{4+} becomes remarkably greater by the inductive effect of S═O in the complex, as illustrated by arrows. In the presence of water, the Lewis acid sites are converted to Bronsted aid sites via proton transfer. By means of CO adsorption, the analogous model was proposed by Bolis et al., but in their case H_2O dissociates on sites involving strongly acidic Zr^{4+} cations, next to a sulfate group; an interaction gives rise to a bridged OH group and to a protonated sulfate [11].

Afterward, a number of studies have attempted to determine the nature of acid sites in the catalyst. Similarly using XPS and IR spectroscopy, Tanabe and co-workers proposed a structure to be chelating bidentate complexes, in which the sulfate species chelates to a single Zr atom as in the model in Scheme 1 [12]. They suggested that Bronsted acid sites are generated by the interaction of hydrocarbons or water with Lewis acid sites;

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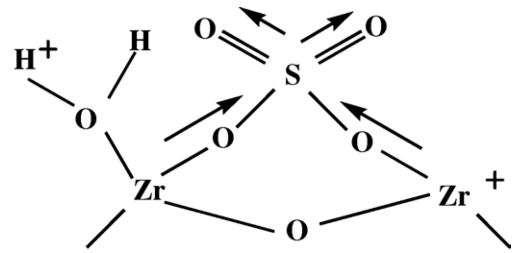


Scheme 1. A surface structure of sulfated zirconia.

the reaction of hydrocarbons proceeds through the formation of carbocations [13]. This model, a chelating bidentate, was also proposed by Ward and Ko, but in this case a hydroxyl group is bonded to a Zr atom adjacent to the Zr chelated with a sulfate species; thus, the proton is strengthened by the electron-inductive effect of two S=O bonds in the sulfate group [14].

Morrow and co-workers showed a structure, in the experiment of ^{18}O exchange using $H_2{}^{18}O$ in addition to IR analysis, in which three oxygens of the sulfate are bonded to Zr elements in a tridentate form, whereas in the presence of H_2O the sulfate species is converted to a bridged bidentate sulfate, accounting for the Bronsted acidity [15]. They also pointed out possibility in the formation of a polysulfate structure with a high sulfate loading [16]. This structure was supported by Morterra et al. using IR data of adsorbed pyridine [17].

A monodentate structural model, which cotains a bisulfate group, has been proposed by several workers [18,19]. The bisulfate OH group is hydrogen-bonded to an oxygen on the surface of zirconia. A similar model was, recently, pointed out for the surface of sulfated alumina on the basis of NMR studies [20].

Another bisulfate structure was proposed by Riemer et al. using NMR and Raman spectroscopies; two oxygens are bonded to Zr atoms in a bridged bidentate state [21]. The strong Bronsted acidity based on the OH group is originated from the electron-withdrawing effect of neighboring Zr ions. The same model was also proposed by Lunsford and Clearfield, electrons being withdrawn through S–OH to adjacent Zr in their model [22,23].

Models in which SO_3 species are coordinated with zirconia are proposed. One of them is coordination of the SO_3 sulfur with lone pairs of the zirconia oxygen in addition to one of the SO_3 oxygens with a Zr suggested by Vedrine and co-workers [24], and the other is depicted in such a way that two of the SO_3 oxygens are coordinated with surface zirconium atoms, leaving a single S=O moiety, shown by White et al. [25].

A species of thionyl tetraoxide with four oxygens bonded to zirconia together with a single S=O is represented when loaded with a low sulfate [26].

In the present study, sulfated zirconia has been investigated by thermogravimetric (TG) and differential thermogravimetric (DTG) analyses in order to provide additional information on the surface. TGA-MS was also employed for TG experiments so that volatile products evolved could be identified when the sample was heated. We propose possible surface structures of sulfated zirconia on the basis of new observations investigated by the thermal analyses in addition to spetroscopic studies of XPS.

2. Experimental

The catalyst (SO_4/ZrO_2) was prepared using three kinds of zirconia gel. Two of them were supplied by MEL Chemicals (XZO 631/05 and 632/03). The third one was obtained by hydrolysis of $ZrOCl_2$ with aqueous ammonia to pH 8; the precipitates were washed several times with water, and dried. All gels were dried at 100 °C for 24 h followed by exposing to 1N H_2SO_4 and calcining in air for 3 h. The sulfated samples are denoted as SO_4/ZrO_2-l, -2 and -3 prepared from the samples of XZO 631, 632, and $ZrOCl_2$, respectively.

Thermal gravimetrical analysis (TGA) was performed using a Shimadzu model with an operating range from room temperature to 1000 °C at a programmed rate of 10 °C/min. X-ray photoelectron spectra (XPS) were determined by ULVAC-PHI 5600ci using Al Kα radiation; samples were evacuated at room temperature before measurement.

Reactions for alcohols, alkylbenzenes, and butane were carried out in a microcatalytic pulse reactor as described elsewhere (flow rate of He carrier gas 50 and 30 ml min^{-1} for alcohols and alkylbenzenes together with butane, respectively; pulse size 1 μl and 0.05 ml (gas) for alcohols together with alkylbenzenes and butane, respectively) [27]. Effluent products were directly introduced into a gas chromatographic column for analysis (Porapak R, 2 m, 110 °C for alcohols: Bentone 34 + DIDP, 2 m, 80–100 °C for alkylbenzenes: VZ-7, 6 m, 30 °C for butane). The catalyst was again heated at 300 °C for 1 h in the He flow before reaction. Activities were compared with the first pulse value.

The heat of Ar adsorption was determined by measuring the adsorption isotherm of Ar by means of a volumetric method using a conventional BET system. The adsorption temperature was controlled at −30 to −60 °C, along with a pressure of 2–100 kPa.

3. Results and discussion

Sulfated zirconia (SO_4/ZrO_2) is commonly prepared by obtaining an amorphous zirconia gel from zirconium salts followed by treatment of the amorphous gel with sulfate ion and calcination in air. The calcination temperature showing the maximum activity and acidity is often varied with the type of prepared gel. For instance, the maximum activity for the conversion of butane to isobutane and propane was observed with calcination at 575 and 650 °C for the materials prepared from $ZrO(NO_3)_2$ and $ZrOCl_2$ as starting reagents, respectively [2]. For the present SO_4/ZrO_2-1, the highest activity for the conversion of butane to isobutane and propane was observed at 575 °C of calcination. The TG analysis for this sample was carried out; both integral and differential profiles are shown in Fig. 1 together with those of other samples.

The figure shows three peaks based on the weight decrease, which is observed as peaks on the DTG profile. The first broad peak around 200 °C is attributed to desorption of water adsorbed on the surface; the broadness up to ∼400 °C indicates heterogeneity of strong acid sites. The second peak along with the third broad one at temperatures above 600 °C are ascribed to decomposition of the sulfate species on the surface. It is, how-

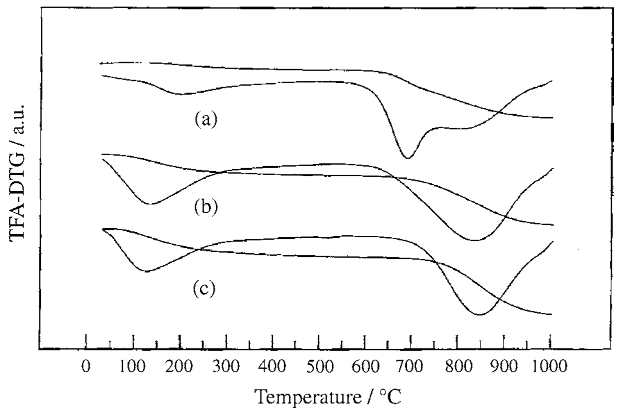


Fig. 1. TGA and DTG profiles of SO_4/ZrO_2-1 calcined at 575 °C (a), 600 °C (b), and 650 °C (c).

ever, seen that the former peak close to 680 °C disappears when calcined at 600 °C, and vanishes almost completely with calcination at 650 °C as is shown in Fig. 1(b and c), respectively. The materials obtained by calcination at 600–650 °C are still highly acidic and active for the butane conversion in comparison with the sample treated at 575 °C. Thus, it is indicated that the third peak centered at 850 °C is the active species.

In order to know further information about the active species, the TG analysis was employed for $Zr(SO_4)_2$, after heating at 150 °C for 3 h to remove hydrated water, the profile being in Fig. 2 together with those of other samples. A large weight decrease is observed at 760 °C, and this is caused by decomposition of $Zr(SO_4)_2$ itself; the weight decrease in the temperature range between 500 and 900 °C is 54.8 wt%: 56.5% for the theoretical value of decomposition of $Zr(SO_4)_2$ to ZrO_2.

The $Zr(SO_4)_2$ matter was impregnated on the zirconia gel 631 using 1N aqueous solution of the sulfate, and its TG analysis was performed, as shown in Fig. 2(b). The peak owing to the decomposition of $Zr(SO_4)_2$ is observed at the temperature 720 °C, it being 40 °C lower than that of $Zr(SO_4)_2$ (Fig. 2(a)). The difference in the decomposition temperature is probably caused by variations in the sulfate state, surface sulfates and crystallized bulk sulfates. The decomposition of an amorphous multilayer sulfate is shifted to lower range of temperature; that is, DTG peaks based on the decomposition of sulfate for crystallized $A1_2(SO_4)_3$ and multilayer sulfate in $SO_4/A1_2O_3$ samples are observed at 800 and 630 °C, respectively [28].

The zirconia gel 631 was impregnated with 1N H_2SO_4 followed by the TG measurement after drying at 150 °C, the profile being shown in Fig. 2(c). A peak observed at 670 °C is quite similar to the second peak for SO_4/ZrO_2-1 calcined at 575 °C, shown in Fig. 1(a), whose catalytic activity is highest. This peak is attributed to the decomposition of $Zr(SO_4)_2$ on the surface, though the temperature is lower than that of $Zr(SO_4)_2$ itself impregnated on the gel (Fig. 2(b)). It seems that zirconium sulfates formed by sulfate ions with Zr ions on the surface of zirconia gels are decomposed more easily than intact $Zr(SO_4)_2$. A broad peak centered at 250 °C is ascribed to decomposition of the adsorbed sulfuric acid.

A sulfated zirconia was prepared using another gel 632 by impregnation with sulfuric acid followed by the measurement of TG after drying at 150 °C; the profile is shown in Fig. 3. A sharp peak based on the decomposition of $Zr(SO_4)_2$, formed on the surface, is seen at 700 °C in addition to a peak at 250 °C, which is due to the decomposition of surface H_2SO_4. After calcination at 600 °C, whose temperature gave the highest activity for the butane conversion, the peak at 700 °C completely disappeared, and a quite broad peak was created in the range from 700 °C to temperatures over 1000 °C (Fig. 3). This broad peak is an active species for the reaction, and in this case the active catalyst is the materials without the surface $Zr(SO_4)_2$, different from the SO_4/ZrO_2-1 sample with both species (Fig. 1). It is of interest that the materials estimated as an active species are partially produced at the stage of drying at 150 °C before calcination for both the gels of 631 and 632 as shown in Figs. 2 and 3. Those must be formed while raising the temperature; the materials should be inactive at this stage.

In the consideration of the results, it is proposed that $Zr(SO_4)_2$ is formed on the surface of zirconia gel in monolayer followed by generation of the active species by calcination. It must be, however, that the $Zr(SO_4)_2$ matter is not a precursor for forming the active species, because the weight decrease in the temperature range between 500 and 1000 °C is 6.6 and 3.8 wt% for the samples calcined at 575 and 600 °C, respectively, in Fig. 1.

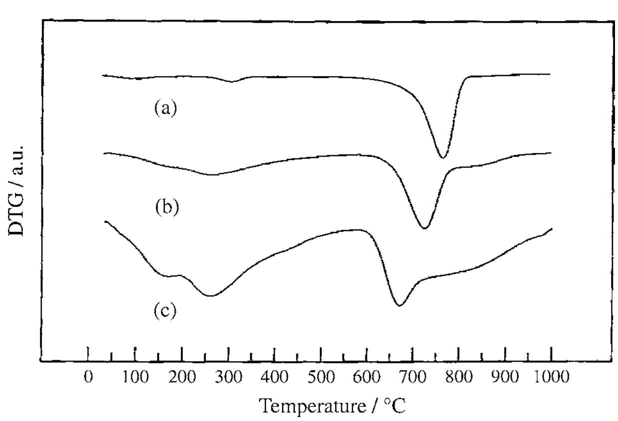


Fig. 2. DTG profiles of samples dried at 150 °C for 3 h. (a) $Zr(SO_4)_2$; (b) Zr-gel-1 impregnated with 1N $Zr(SO_4)_2$ solution; (c) Zr-gel-1 impregnated with 1N H_2SO_4 solution.

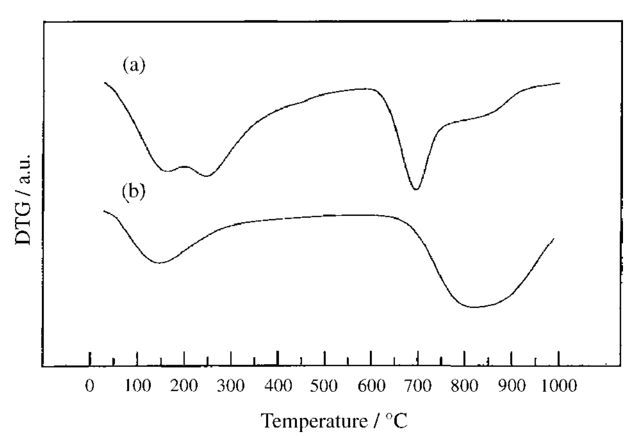


Fig. 3. DTG profiles of SO_4/ZrO_2-2 calcined at 150 °C (a) and 600 °C (b) for 3 h.

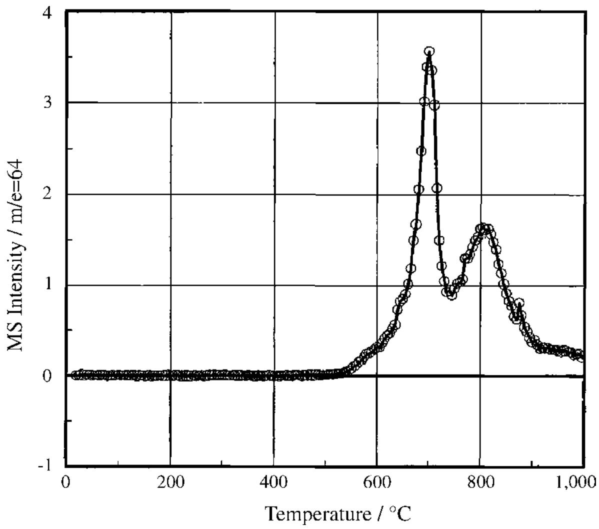


Fig. 4. TG-QMS analysis of SO_4/ZrO_2-3 calcined at 650 °C.

The third sulfated zirconia, SO_4/ZrO_2-3, was prepared using zirconia gel obtained by hydrolysis of $ZrOCl_2$ and calcined at 650 °C, whose temperature showed the highest activity for the butane conversion. Analysis of the thermal decomposition was carried out using a TG-MS apparatus; the profile is shown in Fig. 4. The figure indicates that the decomposition process is the evolution of SO_2 (m/e = 64), not SO_3; the literature reports the primary products to be SO_2 and O_2 in the ratio 2:1, a stoichiometric loss of SO_3 [25]. The surface of SO_4/ZrO_2-3 is quite similar to that of SO_4/ZrO_2-1, and the decomposition of the second species is observed with temperatures above 1000 °C analogous to the case of SO_4/ZrO_2-2 (Fig. 3).

In the process of thermal decomposition in Fig. 3, raising the temperature was stopped at 1000 °C, and the sample [SO_4/ZrO_2 (1000 °C)] was analyzed by XPS for comparison with an active sample of SO_4/ZrO_2-2 calcined at 600 °C [SO_4/ZrO_2 (600 °C)]. The spectra of S 2p and O 1s for SO_4/ZrO_2 (1000 °C) and SO_4/ZrO_2 (600 °C) are shown in Fig. 5. The spectra of S 2p for both materials are coincident with each other, whose binding energies are 168.9 and 169.2 eV for SO_4/ZrO_2 (1000 °C) and SO_4/ZrO_2 (600 °C), respectively; those values agree with that of $Zr(SO_4)_2$ [3]. The spectra of O 1s for both samples were also consistent, i.e., 530.1 and 530.6 eV for SO_4/ZrO_2 (1000 °C) and SO_4/ZrO_2 (600 °C), respectively, indicating the oxide oxygen. It is seen that a shoulder peak at 532 eV showing the sulfate oxygen is reduced in the SO_4/ZrO_2 (1000 °C) sample [3]. It is indicative from the XPS data that the sulfate species agree with each other, pointing out S^{6+} of SO_4^{2-} and resulting in the remarkable acidity on the surface of SO_4/ZrO_2 (1000 °C).

Since the XPS results showed the possibility of bearing high acidity on the surface of SO_4/ZrO_2 (1000 °C), its acidic character was examined in acid-catalyzed reactions, and the results are shown in Table 1. The dehydrations of methanol into dimethyl ether and of ethanol into diethyl ether and ethylene showed SO_4/ZrO_2 (1000 °C) to be inferior in activity to SiO_2-Al_2O_3. However, the former catalyst was superior to the latter for the cracking of cumene into benzene and propylene together with the less reactive ethtylbenzene into benzene and ethylene, in particular for the latter reaction. The superiority of SO_4/ZrO_2 (1000 °C) to SiO_2-Al_2O_3 was indicated by the least reactive butane among five tested reactions: 29.2% conversion into isobutane along with propane and pentanes compared with 0% by SiO_2-Al_2O_3. It can be stated that the present SO_4/ZrO_2 (1000 °C) is a solid acid with acidity higher than that of SiO_2-Al_2O_3. The catalyst, however, was inactive for the reactions when heat-treated for longer period, 1000 °C for 3 h. It is indicative that the active species slightly remained on the zirconia surface was removed during longer calcination.

Analysis of the surface acidity using Ar as a probe was performed. There exist problems when temperature-programmed desorption (TPD) technique is applied to solid acids with high acidity such as sulfated zirconia and zeolites by using probes such as ammonia and pyridine. Ar was found to be applicable as a probe for the TPD. The acid strength can be estimated by the activation energy of Ar desorption from solid acids or by the adsorption heat of Ar [29,30]. The adsorption heat of SO_4/ZrO_2 (1000 °C) was calculated from a temperature dependence of amount of Ar adsorption at temperatures from −30 to −60 °C to be −22.0 kJ mol^{-1}, compared with −22.4 and −14.4 kJ mol^{-1} for SO_4/ZrO_2 (600 °C) and SiO_2-Al_2O_3, respectively [30,31];

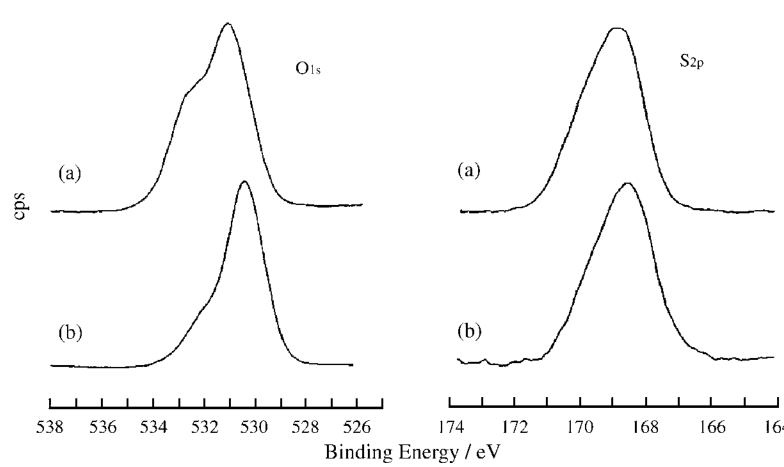
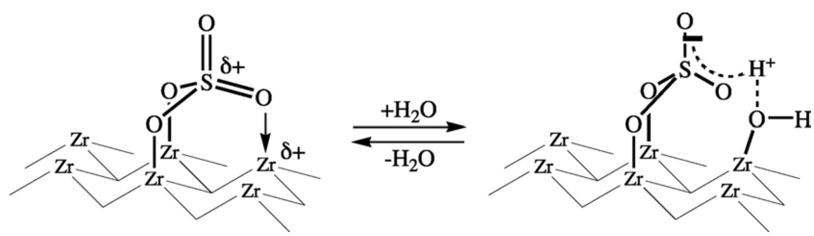


Fig. 5. XPS spectra of SO_4/ZrO_2-2 calcined at 600 °C (a) and 1000 °C (b).

Table 1
Activities of SO_4/ZrO_2 catalysts heat-treated at 1000 °C for reactions of methanol, ethanol, ethylbenzene, cumene, and butane

Catalyst	Conversion (%)				
	Methanol[a]	Ethanol[b]	Cumene[b]	Ethylbenzene[c]	Butane[d]
SO_4/ZrO_2-1[e]		2.2	20.8	1.9	
SO_4/ZrO_2-2[e]	14.8	22.8	27.5	12.5	29.2[f]
SO_4/ZrO_2-2[g]		0 (7.3)[h]	0 (1.4)[h]		0
SiO_2-Al_2O_3[i]	78.8	87.6	10.8	0.4	0

[a] Reactions with 0.05 g of catalyst at 280 °C.
[b] Reactions with 0.05 g of catalyst at 250 °C.
[c] Reaction with 0.2 g of catalyst at 280 °C.
[d] Reaction with 0.5 g of catalyst at 300 °C.
[e] Heat-treated from room temperature to 1000 °C at 20 °C min^{-1}.
[f] Yields: 7.6% C_3, 19.4% i-C_4, 2.2% C_5.
[g] Calcined at 1000 °C for 3 h.
[h] Reaction with 0.2 g of catalyst at 300 °C.
[i] Reference catalyst supplied from the Catalysis Society of Japan (JRC-SAL-2, 560 $m^2 g^{-1}$), heat-treated at 500 °C for 3 h.



Scheme 2. A mono-sulfate structure.

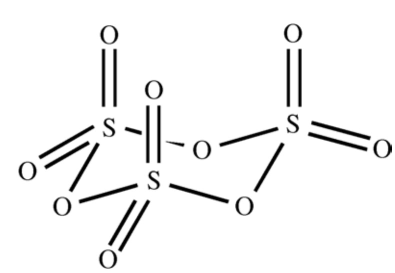
the sample calcined at 1000 °C for 3 h showed −13.5 kJ mol^{-1} (measured at −100 to −130 °C). Thus, the acid strength is in harmony with the activities for decompositions of cumene and ethylbenzene and for the butane isomerization.

3.1. Structural model of sulfated zirconia

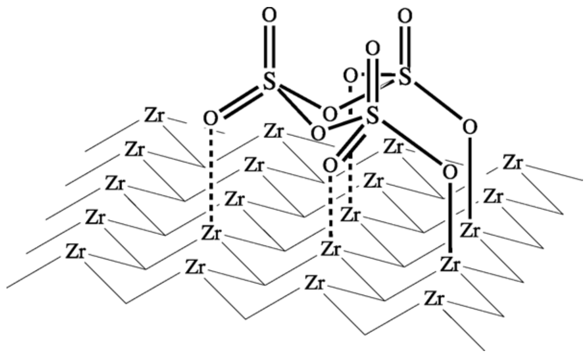
It has been mentioned above that the active species of sulfated zirconia, prepared by impregnation of zirconia gels with sulfate ions followed by calcination, are decomposed in the quite broad range of temperature, from 700 °C to temperatures more than 1000 °C. It is also indicated from the XPS data that the S species are composed of SO_4^{2-}. This high temperature of decomposition suggests additional formation of bonds to two ionic ones for the SO_4^{2-} species. Thus, an example of the models is shown in Scheme 2, where two oxygens are bonded to Zr in addition to coordination of a S=O group with Zr, indicating three bonds in the total.

In support of this assignment it is noted that the SO_4 group consists of a tetrahedron structure [32], and that the strength of coordination bond is quite large acoording to circumstances, for instance, 134 kcal/mol for the coordination strength between NH_3 and Co^{3+} [33]. Although the binding energies of C–H and C–C are less than 100 kcal/mol, the thermal decomposition of hydrocarbons requires temperatures over 200 or 300 °C. In our case the S=O bond nature is electron-rich by the electron-attractive effect; thus, the present coordination seems to be highly strong. Ardizzone and Bianchi studied the XPS characterization of sulfated zirconia to be the formation of a Zr(IV) species bonded to a more electron-attractive species, although being relative to a $Zr(SO_4)_2$ species [34]. The addition of water causes the breaking of this coordination to bring about Bronsted acid sites.

In the chemical properties of SO_3, it is readily polymerized by traces of water [32]. An ice-like solid formed by condensation of vapors at −80 °C or below containes cyclic trimers with structure shown in Scheme 3. A more stable solid has infinite herical chains of linked SO_4 tetrahedra. S in SO_3 reveals affinity for electrons, and SO_3 functions as a fairly strong Lewis acid; the trioxide gives crystalline complexes with pyridine and trimethylamine [32]. The solutions of SO_3 in H_2SO_4 are known as oleum or fuming sulfuric acid, and the increase in acidity on addition of SO_3 to sulfuric acid is marked, going up to an Ho value of −14.5 in the range of high superacid with 50 mol% SO_3. Similarly, SO_3 behaves as a non-electrolyte in HSO_3F, and the acidity reaches a maximum of −15.5 on the Ho scale for 4 mol% SO_3. This is the same system as magic acid such as SbF_5-HSO_3F or TaF_5-HF, which is a mixture of Lewis and Bronsted acids [35].



Scheme 3. A cyclic trimer of SO_3.



Scheme 4. A structural model of trimer.

Sulfated alumina was prepared by adsorption of SO_3 gas onto the surface of activated gamma-alumina by heating at temperatures above 300 °C [20]. Sulfated iron oxide was prepared by simply heating the oxide in the presence of SO_3 [36,37].

In the above-mentioned observations and by analogy to the structural model of mono-sulfate shown in Scheme 2, another example formed by the cyclic trimer is shown in Scheme 4, where two terminal S–O anions are bonded to Zr cations including three coordinations of S=O with Zr. These coordination sites of Zr are also the positions for water molecules to give rise to Bronsted acid sites just shown in Scheme 2 in the case of mono-sulfate species.

It is considered that the present surface is the same as that of tungstated zirconia, judging from both preparation procedures as well as their catalytic action. Knozinger and co-workers studied the structural model of tungstated zirconia to be oligomeric WO_x clusters with detection of WO–W linkages, and Bronsted acidity is presumably caused by delocalized protons that are connected with the WO_x network [38]. High-resolution TEM images revealed the formation of subnano-sized (0.4–0.7 nm) polytungstate cluster containing 3–5 W atoms on the zirconia surface with uniform dispersion for tungstated zirconia [39]. Several workers suggest the existence of polysulfate species on the sulfated zirconia. Thus, it is concluded that the surface is composed of coordinated olygomerous species in the wide range of olygomers, probably three or four S atoms as the chief species, with two ionic bonds between S–O– and Zr identical to the models for monomer and trimer (Schemes 2 and 4). In the point of the atomic size, W is 1.25 times as large as S, and thus the main polytungstate might be composed of 4 or 5 W atoms. As shown in Fig. 3, the active species contain quite wide range of the decomposition temperature from 700 to over 1000 °C. This indicates the surface acidity to be heterogeneous; in fact the acidiy of sulfated zirconia covers a wide range of strength [40]. However, the number of active sites required to actually catalyze the butane isomerization is very small [41]. Comelli et al. pointed out that the total acidity determined by IR spectroscopy of adsorbed pyridine is not related to the catalytic activity, much small [42]. In fact, the amount of Ar adsorbed on sulfated zirconia is much smaller than those of zeolites [31].

Recent studies clarified sulfated zirconia to be Lewis acid type by comparison of adsorption heats of nitrogen and argon [43]. In addition, reactions of C5–C6 linear and branched alkanes showed that sulfated zirconia has superacidic Lewis acid sites [44]. The Lewis acidity was also indicated by Davis and co-workers; XPS analysis showed the increased presence of a surface sulfate species with the increased catalytic activity for *n*-hexadecane [45]. The acid strength of sulfated zirconia is the highest among the sulfated oxides of Zr, Ti, Fe, and Al. This strength is mostly explained by the origin of the high electronegativity of Zr^{4+}. However, the Pauling electronegativity of Zr^{4+} is not higher than Ti^{4+}, Fe^{3+}, and Al^{3+}. As for the generation of Lewis site, it seems that the active site is not on the metals, but on the S atoms. The present method of preparation was applied to selenate and tellurate ions belonging to the same group as S in the Periodic Table; the materials caused the oxidative dehydrogenation of alcohol without acidic action [46]. This observation seems that the active site is not on the support, ZrO_2, but on the additives. The possibility in generation of strong Lewis acidity on the S site for sulfated zirconia is indicated by Vedrine and co-worker [47].

In the active point of view, the Lewis-acidic sites of tungstated zirconia are also the W elements; tungstated zirconia is known to give strong Lewis acid sites [48]. Recently, molybdenum oxides reduced at high temperature were reported to show activity for the isomerization of heptane and are classified into superacids, indicating creation of the highly acidic sites on the Mo species [49]. Molybdated zirconia was also prepared as a highly acidic catalyst in the same manner as tungstated zirconia [50].

The addition of water causes the breaking of the coordination bonds to bring about Bronsted acid sites which strengthen Lewis acid sites, as shown in Scheme 2 as an example. Many research groups report the simultaneous existence of Bronsted and Lewis acid sites or the reversible transformation between Bronsted and Lewis acidity upon hydration or dehydration [14,21,23]. Fraenkel suggested that sulfated zirconia with an effective superacid should contain a critical amount of moisture [51]. Several workers suggest that the strong acidity is originated from the presence of both Lewis and Bronsted sites.

4. Conclusion

Sulfated zirconia is analyzed by the thermal decomposition from room temperature to 1000 °C and by XPS, and calcination of the materials at 1000 °C generates a solid acid with acidity higher than that of silica–alumina.

1. The active species decompose at temperatures high than that of $Zr(SO_4)_2$ in the wide range from 700 to >1000 °C.
2. A structural model of the active surface is shown to be polysulfate species composing of mainly three or four olygomers with two ionic bonds of S–O–Zr in addition to coordination bonds of S=O with Zr.
3. The active site is Lewis acid on the S atoms.

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