Sulfated metal oxide catalysts

Superactivity through superacidity?

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Summary

Sulfated metal oxides are a useful group of strong acid catalysts. The nature of their acidity, the identities of the active sites and their use in hydrocarbon transformation reactions are discussed.

Introduction

Acid catalysis is of fundamental industrial importance. It plays a vital role in the petroleum industry where acid catalysts are employed in the various isomerisation, cracking and alkylation reactions used to upgrade oil. Acids are also employed as catalysts for large scale polymerisation processes and display activity for hydration/dehydration reactions such as the interconversion of ethanol and ethylene. In the following, we briefly describe the interest which one particular class of solid catalyst has attracted because of its extremely high efficacy for some such reactions.

Supported metal oxides and their preparation

Some metal oxides, when sulfated, develop the ability to catalyse reactions characteristic of very strong acid catalysts at low temperatures, although with limited lifetimes. This not only presents the opportunity of saving energy but also generates a thermodynamic advantage. Isomerisation of straight chain alkanes to more highly branched isomers, which not only have higher octane numbers but are more useful as intermediates for further synthesis, is more favourable at lower temperature. Arata has identified a range of active sulfated oxides including those based on SO_4^{2-}/ZrO_2, SO_4^{2-}/Fe_2O_3, SO_4^{2-}/SnO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/SiO_2, SO_4^{2-}/Al_2O_3 and SO_4^{2-}/HfO_2.[1,2] With the exception of Al_2O_3, sulfation must be performed on the amorphous precursors of the oxides such as hydroxides or oxyhydroxides in order to result in high activity. Although a variety of sulfation reagents can be used, most researchers have employed either dilute sulfuric acid (usually 0.5 mol dm^{-3}) or an aqueous solution of ammonium sulfate. The oxide precursor is generally immersed in the sulfating solution, left for a period of time, filtered, dried and calcined (heated in air or oxygen). Variation of any of these parameters can markedly affect the resultant catalytic activity. The temperature of calcination required to generate maximum performance depends upon both the oxide and the sulfation reagent. For example, in the case of sulfated iron oxide, maximum activity for *n*-butane isomerisation develops after calcination at 500–550 °C and for sulfated zirconia after 600–650 °C. Only a small uptake of sulfate is required, with optimum sulfur content being in the region of 1–2 wt%.

As well as promoting a variety of acid catalysed reactions, sulfation is also observed to affect physical properties, for example, it lowers crystallinity and increases surface area. The latter effect is always an important consideration in heterogeneously catalysed processes where reactions occur on surfaces. In the oxides where polymorphism (*i.e.* two or more crystal forms of the same chemical composition) occurs, sulfation has been observed to preferentially stabilise one form. Zirconia is an example of such a material. It can exist in the monoclinic, tetragonal, cubic and orthorhombic crystal forms depending upon the method of preparation and conditions. Sulfate is one of a range of dopants observed to favour the formation of the tetragonal phase over the more commonly encountered monoclinic form.[3]

The nature of their activity

It is always of interest to understand the mechanism of operation of a catalyst, since in some cases this can allow one to improve existing catalysts or develop new ones. *n*-Butane isomerisation to produce isobutane is probably the most well studied reaction catalysed by sulfated metal oxides. One mechanism of this reaction involves the generation of an intermediate substituted protonated cyclopropane cation (i) and primary carbenium ion (ii) which undergoes C–C and C–H bond fission and rearrangement (the unimolecular or intramolecular route—adapted from ref. 4); see Scheme 1.

This process is characteristic of strong acid catalysis—the intermediate carbenium ion can be produced by either a Lowry–Brønsted acid route (1) or a Lewis acid route (2) (Scheme 2). The observation that sulfated systems exhibit greater activity than concentrated sulfuric acid indicates that the oxides do not simply function as supports for H_2SO_4, although this is a point of debate.[5]

Many researchers have therefore concluded that these systems are 'superacidic'. Following Gillespie, a superacid is defined as a

Green Context

Of all the classes of industrial transformations, the conversion of hydrocarbon feedstocks into useful functional building blocks is arguably the most fundamental, since it provides all other processes with their raw materials. These reactions are typically catalysed by strong acids. It is therefore no surprise that there has been a great deal of work on solid acids, although the exact nature of their mode of action is not always clear. One particularly good example of this is given by the sulfated metal oxides. This review, intended for the non-specialist, provides an accessible description of the nature of these materials. While their activity is greater than that of sulfuric acid, their acidity is less clearly defined, with opinion moving away from the original position that these materials were superacids. This is based on the accumulation of reaction evidence as well as refinements in the physical techniques used to characterise the materials. DJM
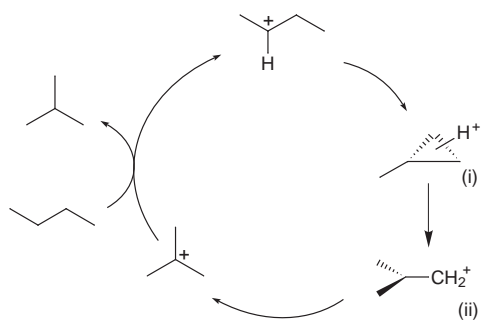
Scheme 1 Intramolecular butane isomerisation mechanism.
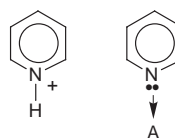

(A = Lewis acid)
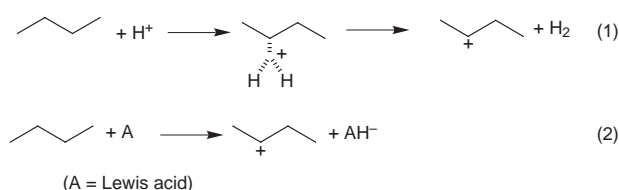
Scheme 2 Acidic activation routes of butane.

material which exhibits an acid strength greater than 100% H_2SO_4 (*i.e.* has a Hammett acidity function $\leqslant -12$).[6] This is, of course, a Lowry–Brønsted based definition. A definition of superacidity exists for Lewis acidity in that any material exhibiting an acid strength greater than anhydrous $AlCl_3$ is termed superacidic.[6] Initially attempts to measure the acid strengths of sulfated oxides centred around the use of Hammett acidity indicators. In this method, the acid strength of the material is determined by its ability to change an organic base adsorbed onto the solid into its conjugate acid form which is associated with a colour change. Therefore, if an indicator changes colour it is indicative that the material possesses a Hammett acidity value equal to or lower than its pK_a. A wide range of such indicators are available with different pK_a values. Samples of the material are suspended in an inert solvent (*e.g.* sulfuryl chloride) and tested with indicators of varying strength. Although application of this method indicates that the materials are strong acids, it is not without limitations: (i) equilibrium between the base and solid sample must be established which can take very long times; (ii) interaction with the solvent molecules or the adsorbate can generate misleading results, for example it has been reported that red shifts can occur which generate erroneous conclusions;[7] (iii) a colour change must be observed which can be difficult when the sample is coloured, *e.g.* SO_4^{2-}/Fe_2O_3; (iv) with most indicators it is not possible to distinguish between Lowry–Brønsted and Lewis acidity.

More favoured approaches to determining the acid site strengths and densities of solids involve studies of the adsorption of base probe molecules such as ammonia and pyridine, and also the use of test reactions such as the dehydration of isopropanol to produce propylene.[8] Microcalorimetry in conjunction with uptake measurements allows one to determine the heat of adsorption of a probe molecule which can be related to site strength and density. An example of the application of this method is provided in a study of sulfated zirconia by Dumesic and co-workers[9] who have studied the heat of adsorption of ammonia at 150 °C as a function of uptake—in this way, they determined a *differential* heat of adsorption which relates to the population of sites of various acid strength. By selective poisoning of the sets of these sites, it may be possible to determine the strength of sites responsible for a particular catalytic reaction. Thermal desorption meth-

ods determine site strength and density by measuring the loss of adsorbed probe molecules as a function of sample temperature. However, these approaches have been limited in their application due to adsorbate decomposition (*e.g.* ref. 10) which means that the true interaction of the probe molecule with the acid site is not being examined. Consequently, thermal desorption studies of adsorbed substituted benzenes (which are weaker bases than those generally used) was suggested as suitable. Subsequently, in some systems this method itself was shown to suffer the limitation of oxidation of benzene and even the evolution of SO_2 during heating.[11] So, in summary, many of the adsorption/desorption measurements have been limited by the intrinsic high reactivity of these materials. Therefore, spectroscopic studies of adsorbed molecules, which can also provide valuable information on acidic properties of solids, have been quite widely adopted in this field.

Following work by Parry in the 1960s, infra-red spectroscopic studies of the adsorption of pyridine have become routine for the discrimination of Lowry–Brønsted and Lewis acid sites on heterogeneous catalysts.[12] Pyridine interacts with the two types of site respectively in the manner shown in Scheme 3.


Scheme 3 Interaction of pyridine with Lowry–Brønsted (H^+) and Lewis acid (A) sites.

Infra-red bands unique to each form can be distinguished in the 1400 to 1700 cm^{-1} region of the spectrum. Furthermore, a knowledge of the absorption coefficient for each species makes quantification possible and acid site strength can be determined from the loss of band intensity as a function of temperature. However, it has been shown that application of some these methods to determine the acidic properties to sulfated metal oxides is severely limited due to oxidation and/or decomposition reactions which occur between adsorbent and adsorbate, *e.g.* ref. 13. Consequently, techniques such as FTIR studies of carbon monoxide adsorption have been applied. When CO interacts with Lewis acidic sites, the C=O stretching frequency increases *via* σ-bond donation. The shift in frequency can be directly related to Lewis acid strength.[14] Low temperature studies of the influence of CO adsorption on the OH groups of the oxides can be used to determine Lowry–Brønsted strength. As mentioned below, many of the studies currently published employing these techniques indicate that although sulfated metal oxides may be strong acids, they are not superacidic. Here we have only briefly touched on some of the measurements of acid site strength which have been reported, however, a more detailed description of various methods of acid site strength determination on solids along with their associated limitations is available elsewhere.[15]

## The nature of the active site

Many different proposals describing the nature of the active catalytic site have been made. Generally, these have been based around the symmetry of the co-ordinated sulfate ion. In principle a number of symmetries for SO_4^{2-} are possible (Scheme 4). It is possible to distinguish these forms by examination of the sample infra-red spectra in the 1200 to 900 cm^{-1} S=O stretching region.[16] As a consequence of the gross selection rule that a change in dipole moment must occur for a transition to be infra-red active, the different forms of sulfate give different numbers of bands. The T_d form of SO_4^{2-} (*i.e.* tetrahedral symmetry like the

CH_4 molecule) gives two infra-red active transitions in this region, the C_{3v} form (*i.e.* pyramidal symmetry like the NH_3 molecule) three and the C_{2v} form (*i.e.* symmetry like the H_2O molecule) four. An additional consideration is that the C_{2v} form of sulfate can occur in bridging or chelating configuration. Both C_{2v} and C_{3v} forms have been commonly reported by different researchers in the literature and therefore different models of the active site have been made.[17]
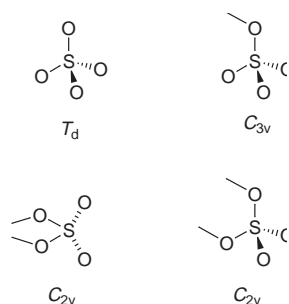
Scheme 4   Different SO_4^{2-} symmetries.

One such proposal from Arata for SO_4^{2-}/ZrO_2 is shown in Scheme 5, in which sulfate adopts a bridging C_{2v} symmetry. It is argued that the sulfate group enhances the Lewis acidity of the Zr cations by an inductive effect (Lowry–Brønsted acidity can be generated from this form as described below).
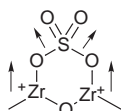
Scheme 5   Proposed active site in SO_4^{2-}/ZrO_2.

## Alternative proposals for catalytic activity

Increasingly, based on spectroscopic and calorimetric studies, the consensus is emerging that sulfated metal oxides do not possess the superacidity originally postulated. A number of recent studies have demonstrated that the acid strength is similar to that encountered for transitional aluminas or protonic zeolites. An example of this is provided in a study by Drago and Kob[18] in which they have applied the 'cal-ad' method to the determination of acidity of sulfated zirconia and related systems. In this method a calorimetric titration of a basic probe is carried out in a hydrocarbon solvent of similar molecular mass. It is claimed that this technique allows the determination of the number, equilibrium constant and site strengths of different acid sites on solids. The results for the highest enthalpies of pyridine adsorption in cyclohexane for various SO_4^{2-}/ZrO_2 samples along with silica and the zeolites HZSM-5 and HY are given in Table 1.

Table 1   Results of 'cal-ad' measurements of pyridine adsorption on various solids—adapted from ref. 18

Material	$-\Delta H_{ads}$(pyridine)/ kJ mol^{-1}
SiO_2	50 ± 4
H-ZSM-5	171 ± 4
HY	142 ± 4
SO_4^{2-}/ZrO_2 calcined at 600 °C	130 ± 8
SO_4^{2-}/ZrO_2 calcined at 300 °C	63 ± 4
Pt/SO_4^{2-}/ZrO_2	125 ± 4
Fe/Mn/SO_4^{2-}/ZrO_2	109 ± 4

Along with many other studies, the data in Table 1 certainly suggest that SO_4^{2-}/ZrO_2 based systems are not superacidic. However, this view is still contentious. Amongst those who believe that superacidic sites are present, there continues to be disagreement as to whether these are Lowry–Brønsted or Lewis in nature. A possible explanation for the division of opinion on all these matters relates to the observation that the catalytic activity of these materials is strongly dependent upon storage/pre-treatment conditions.

Inter-conversion of Lewis and Lowry–Brønsted sites can occur by hydration/dehydration processes—
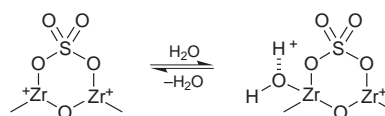
Scheme 6   Proposed interconversion of Lewis and Lowry–Brønsted acidic sites in SO_4^{2-}/ZrO_2.

see Scheme 6. An important question, therefore, is if not superacidity, what is the origin of the exceptional behaviour of these catalysts?

Sachtler and coworkers have performed experiments which aim to address this problem.[19] They noted that although Fe/Mn/SO_4^{2-}/ZrO_2 (reputedly the strongest 'superacidic' sulfated metal oxide known to date) had acid sites of similar strength to SO_4^{2-}/ZrO_2 in their measurements, its butane isomerisation activity was much greater. Furthermore, they pointed out that the occurrence of the unimolecular isomerisation mechanism described above is not expected at the low temperatures of activity for these catalysts because of the primary carbenium ion intermediate. By analysing the product distributions in reactions using doubly isotopically labelled butane, $^{13}CH_3CH_2CH_2^{13}CH_3$, they have shown that the reaction occurs by formation of a bimolecular (intermolecular) intermediate which isomerises to give the 2,4,4-trimethylpentyl carbenium ion, followed by β-fission to yield an isobutene molecule and the isobutyl carbenium ion (Scheme 7). The catalytic cycle then progresses by the loss of a hydride species from the *n*-butane reactant to the isobutyl carbenium ion to generate the isobutane product and the C_8 intermediate *via* reaction with the isobutene. Unlike the intramolecular process, this pathway does not involve the intermediacy of the unfavourable primary carbenium ion.
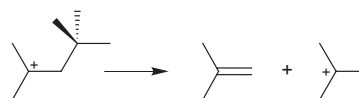
Scheme 7   Decomposition route of C_8 intermediate.

They proposed that the activity of sulfated metal oxides arises from their ability to stabilise reaction intermediates possibly by the formation of C–O–S bonds such as sulfate esters. Farcasiu and colleagues have made a comprehensive study of the pathways involved in the reaction of adamantane over SO_4^{2-}/ZrO_2.[20] They have proposed that rather than behaving as a superacid, this system operates *via* a one electron oxidation mechanism in which an electron is transferred between the substrate and the sulfate group. A sulfite ester is proposed to be an intermediate in the reaction, as shown in Scheme 8.
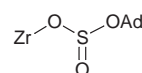
Scheme 8   Adamantyl sulfite ester. Ad = adamantyl radical.

Limitations to application

Despite the current controversy over the mechanism of operation of sulfated metal oxides, it is obvious that they possess extraordinary catalytic behaviour. However, to our knowledge, they have not yet found commercial application. They deactivate quickly on use due to poisoning of active sites by the deposition of coke (carbonaceous residues). This can be overcome to some extent by including hydrogen in the feed, which hydrogenates the coke as it is formed, or by the inclusion of additional catalyst components, *e.g.* Pt, which retard coke deposition. Such deactivation is not necessarily a limitation to industrial application. Fluidised catalytic cracking is a large scale catalytic process in which zeolites are used to convert long chain hydrocarbons into more useful shorter chain forms. In operation the catalyst becomes rapidly deactivated by coking, its lifetime is usually about 3 seconds! However, the process has been engineered such that regeneration, which involves the exothermic combustion of coke by air, supplies the heat necessary to conduct the reaction. A major limitation for the application of sulfated metal oxides relates to preparation. It is difficult to prepare separate batches of catalyst which exhibit reproducible catalytic performance. This problem, which may relate to inhomogeneous sulfation, needs to be addressed and has already been the subject of some research attention.[21]

Summary

In this short article, we have attempted to briefly describe some of the current interest in sulfated metal oxide catalysts. Due to limitations of space, we have not been able to fully describe some of the emerging areas of interest. We have only briefly mentioned the inclusion of additional metallic components. In some cases these may have proved beneficial by suppressing deactivation (*e.g.* Pt/SO$_4^{2-}$/ZrO$_2$) whereas in others they enhance the intrinsic catalytic activity (*e.g.* Fe/Mn/SO$_4^{2-}$/ZrO$_2$).[22] The range of reactions to which these materials are being applied is also broadening. In our own work, we are investigating the effect of combining the unique activity of sulfated systems with the underlying catalytic activity of the base oxides for methane oxidation (see for example refs. 23, 24). In experiments performed at elevated pressure using iron oxide based catalysts, we have observed that the sulfation procedure suppresses the low temperature (*i.e.* <400 °C) total oxidation activity of these materials, (presumably by a site blocking mechanism) whilst enhancing activity at higher temperature (*i.e.* >500 °C) leading to some production of selective oxidation products (methanol and higher hydrocarbons) probably as a consequence of the stabilisation of higher surface areas and the formation of new types of active site. In the case of iron oxide systems prepared from goethite, the sulfation procedure also generates interesting structural effects which are currently the subject of further study.

Although much remains to be explained about sulfated metal oxides in general, their remarkable catalytic activity is clear.

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