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Synthesis of solid superacids and their activities for reactions of alkanes

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Abstract

Our recent works on synthesis of solid superacids are reviewed. For evaluation of the surface acidity, temperature-programmed desorption of argon is proposed. For elucidation of the preparative conditions determining the catalytic activity, sulfated zirconias were prepared under different preparative conditions. The conditions varied were type of hydrated zirconia gel, drying temperature before sulfation, calcination temperature after sulfation. Although the optimum drying temperature and calcination temperature were different depending on the type of zirconia gel, the attainable activities were independent of the type of zirconia gel. We also modified sulfated zirconia by addition of Pt, Ru, and Fe to see the effects of the modification on the catalytic activity. The addition of Pt to sulfated zirconia resulted in an increase of the catalytic activity. The optimum amount of Pt-added was 7.5 wt.%. The optimum amount of Pt could be reduced to 3 wt.% when the catalyst was prepared by the double calcination method in which calcination procedures were performed both before and after impregnation with platinate solution. The role of Pt in enhancement of the catalytic activity is suggested to be caused by enhancement of the acid strength due to the coordination of PtO to S=O groups. The catalytic activity of sulfated zirconia was also markedly enhanced by mechanically mixing with sulfated iron oxide. The enhancement was suggested to be caused by Fe^{3+} acting as a reservoir for H^- formed during the reaction.

Keywords: Solid superacids; Sulfated zirconia; Sulfated metal oxides; Alkanes; Platinum

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1. Introduction

We published our first paper on solid superacids in 1979 [1]. Since then, we have published the papers on solid superacids as two series: one is "Solid catalysts treated with anions", and the other is "Superacids by metal oxides". The first paper reported that large increases of both the surface acidity and the catalytic activity of Fe_2O_3 were caused by the sulfate ion adsorption followed by heat-treatment. In the early stage of the work on the superacids, we found that superacidity was generated on the oxides of Fe, Ti, and Zr by treatment with sulfate ion. Later, we also found that the superacidity was generated on the oxides of Hf, Sn, Si, and Al by treatment with sulfate ion. In the mean time, superacids were synthesized by supporting WO_3 or MoO_3 on the oxides of Zr, Ti, Sn, and Fe without treatment with sulfate ion [2].

Table 1 summarizes the superacids we prepared together with their acid strengths. The temperatures shown in parenthesis are the calcination temperatures to generate highest acidity or activity. Although the

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Table 1
Solid superacids and their acid strength

Catalyst (calcination temperature)	Highest acid strength[a] (Ho value)
SO_4/SnO_2 (550 °C)	−18.0
SO_4/ZrO_2 (650 °C)	−16.1
SO_4/HfO_2 (700 °C)	−16.0
SO_4/TiO_2 (525 °C)	−14.6
SO_4/Al_2O_3 (650 °C)	−14.6
SO_4/Fe_2O_3 (500 °C)	−13.0
SO_4/SiO_2 (400 °C)	−12.2
WO_3/ZrO_2 (800 °C)[a]	−14.6
MoO_3/ZrO_2 (800 °C)	−13.3
WO_3/SnO_2 (1000 °C)	−13.3
WO_3/TiO_2 (700 °C)	−13.1
WO_3/Fe_2O_3 (700 °C)	−12.5
B_2O_3/ZrO_2 (650 °C)	−12.5

[a] Acid strengths were estimated by color change of Hammett indicator, TPD of pyridine, TPR of furan, and catalytic activity for various reactions.

optimum calcination temperature varies with the type of vessel in which the catalyst was placed and calcined, the data shown in Table 1 were obtained for the catalysts calcined in a Pyrex glass tube below 700 °C and the catalysts calcined in a ceramic crucible above 700 °C for 3 h. The optimum calcination may change more than 50 °C depending on the type of calcination vessel, time, etc. The expression SO_4/MeO_x means sulfated metal oxide such as sulfated zirconia and sulfated alumina. The valence of S in the sulfated metal oxides is +6. Thus, this expression is not correct in the strict sense. This is based on the image of sulfation together with the neutral charge.

Among the superacids listed in Table 1, sulfated zirconia (SO_4/ZrO_2) has been most frequently investigated, modified, and applied to various reactions; this may be because the sulfated zirconia possesses strong acid sites, is relatively easy to prepare, and was found to be superacid in the very beginning of the history of the solid superacids. The sulfated zirconia is now commercially available and used as a catalyst for the organic synthesis in industry. In addition to the sulfated zirconia, we have a lot of materials with superacidity on their surfaces in our hand now.

In the present paper, we will focus on how the preparative conditions affect the acidity and catalytic activity of the sulfated zirconia, and how the modification of sulfated zirconia changes its catalytic activity.

2. Proposal of acidity measurement by TPD of argon

Although there are different methods to measure surface acidity, each method is not versatile for different types of solid acid. It is desirable to develop a new method to measure the surface acidity, especially very strong acidity. Acid strengths of solid acids with strong acidity on the surface are determined by means of temperature-programmed desorption (TPD) of Ar [3]. This method is especially useful for acidity measurement of superacids. Argon shows an acid–base-like interaction with acid sites at a low temperature. The acid strength can be evaluated as an activation energy of Ar desorption. The activation energy is calculated by the following equation:

$$2\ln T_{\mathrm{m}} - \ln\beta = \frac{E_{\mathrm{d}}}{RT_{\mathrm{m}}} + \text{const.}$$

Here T_{m} is the peak temperature of desorption, β the rate of temperature increase, and E_{d} the activation energy.

Fig. 1 shows a plot of $2\ln T_{\mathrm{m}} - \ln\beta$ vs. $1/T_{\mathrm{m}}$ for SiO_2–Al_2O_3, and E_{d} is calculated to be 5.5 kJ mol^{-1}. By this method, it was recently shown that the acid

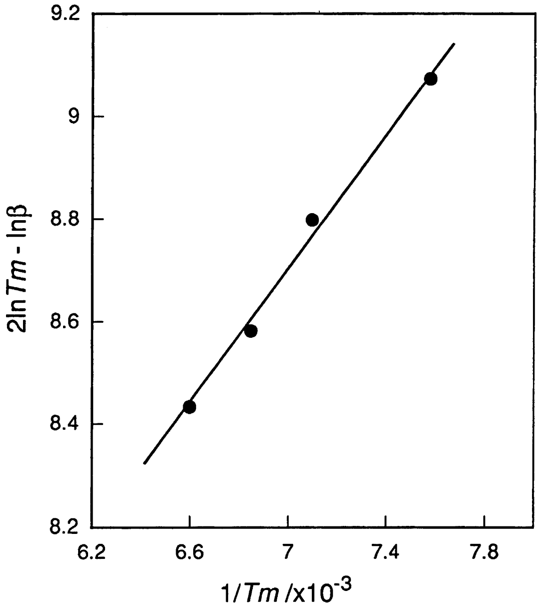


Fig. 1. A plot of $2\ln T_{\mathrm{m}} - \ln\beta$ vs. $1/T_{\mathrm{m}}$ on SiO_2–Al_2O_3 for calculation of the activation energy of Ar desorption.

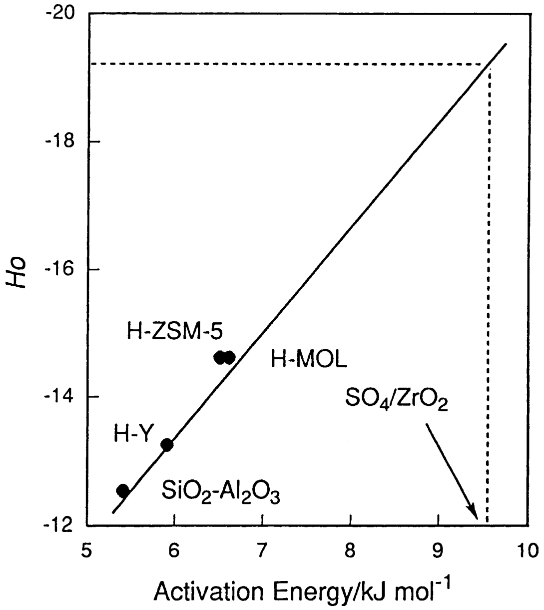


Fig. 2. Relation between the Ho function and the activation energy of Ar desorption.

strength of SO_4/SnO_2 is higher than that of SO_4/ZrO_2; E_d's were 10.6 and 9.6 kJ mol^{-1} for SO_4/SnO_2 and SO_4/ZrO_2, respectively [3–5].

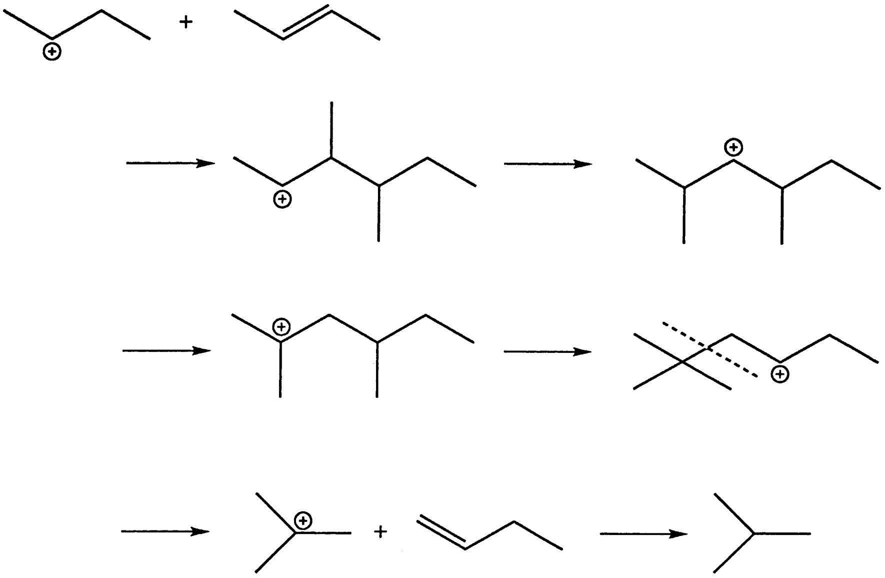
The adsorption heat of ammonia correlates with the Hammett acidity function, Ho [6]. Both the adsorption heat of ammonia and the activation energy of Ar desorption are measured by TPD of ammonia and Ar, respectively. The interaction with the surface acid sites is supposed to be similar to acid–base interaction. Therefore, the activation energy of Ar is considered to be correlated with the Hammett acidity function, Ho. Fig. 2 plots the Ho values against the activation energies of Ar desorption for SiO_2–Al_2O_3 and different types of zeolite. The Ho values were obtained by visual color change of the Hammett indicators. Therefore, the Ho values represent the highest acid strength of the surface. Since the plot is linear, Ho value could be estimated from the activation energy of Ar desorption. The Ho value for SO_4/ZrO_2 could be estimated to be −19 by extrapolation of the linear plot to the activation energy 9.6 kJ mol^{-1} which corresponds to the activation energy for SO_4/ZrO_2. The Ho value of −19 agrees with the reported value that was estimated by the adsorption heat of ammonia [6]. The Ho value −19 is close to the value −17.5 reported by Fraenkel on the basis of catalytic conversion of isobutane over SO_4/ZrO_2 [7].

3. Isomerization of alkanes catalyzed by sulfated zirconia

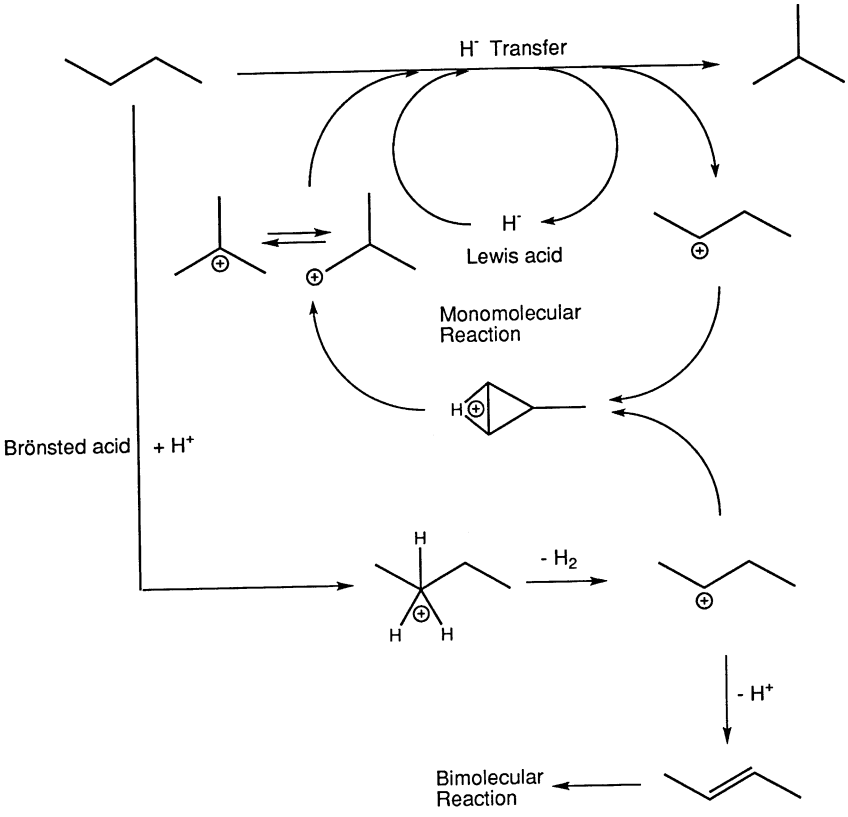
The skeletal isomerization of butane to isobutane is a typical reaction catalyzed by superacidity, and the sulfated oxides such as SO_4/Fe_2O_3 and SO_4/ZrO_2 are able to isomerize butane at room temperature or below [8,9]. Butane is converted into isobutane by a monomolecular mechanism through protonated methylcyclopropane with an activation energy of 8.4 kcal/mol followed by forming primary isobutyl cation with a high energy (20.6 kcal/mol) [10]. On the other hand, the reaction is also supposed to proceed via a bimolecular mechanism of oligomerization-cracking involving the formation of a C_8 intermediate by reaction of a C_4 carbenium ion with a butene followed by rearrangement and β-scission to yield isobutane finally as shown in Scheme 1 [11]. In this case the reaction is energetically lower than the monomolecular isomerization because of the formation of *secondary* and *tertiary* carbenium ions.

Detailed studies of the skeletal isomerizations of butane and *n*-pentane over SO_4/ZrO_2 showed that changes in the apparent activation energy and product selectivity are observed during the reactions. As shown in Scheme 2 the isomerization of butane proceeds by a monomolecular mechanism through a protonated cyclopropane intermediate on superacidic Lewis sites in the initial period. Then the reaction changes to a bimolecular mechanism on Bronsted sites by forming surface alkenes, intermediates, giving additional products of C_3, C_5, and C_6. In the isomerization of *n*-pentane with reactivity higher than that of butane, *n*-pentane is converted into isobutane after a short induction period; this period disappears by the addition of isobutane, a supplier of H^- to an isopentyl carbenium ion formed on the Lewis site, giving isopentane with very high selectivity [12].

Cyclohexane is known to be isomerized to methylcyclopentane when catalyzed by strong acids. In fact, the SO_4/ZrO_2 catalyst converted cyclohexane into methylcyclopentane and methylcyclopentane into cyclohexane as shown in Fig. 3. The reactions proceed



Scheme 1. Isomerization of butane via bimolecular intermediate.



Scheme 2. Mechanism for the reaction of butane over SO_4/ZrO_2.

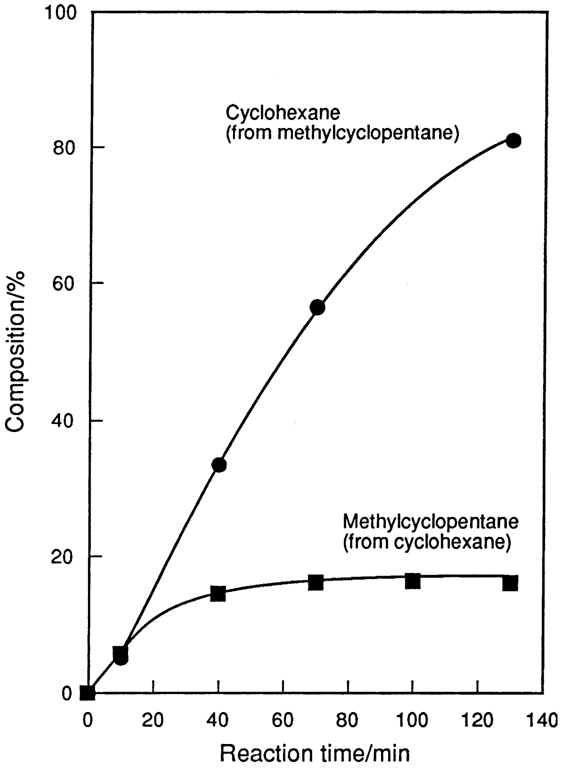


Fig. 3. Conversions of cyclohexane and methylcyclopentane over SO_4/ZrO_2, pretreated in a vacuum at 150 °C, at room temperature. Conditions: closed recirculation reactor (291 cm^3), catalyst 0.8 g, reactant 50 Torr.

by the monomolecular mechanism via the intermediates of *secondary* and *tertiary* carbenium ions followed by protonated cyclopropanes.

Reactions of cycloheptane and cyclooctane were performed over SO_4/ZrO_2 at 50 °C, the reactants being in the state of liquid [13]. The major products were methylcyclohexane from cycloheptane and ethylcyclohexane from cyclooctane through the intermediates of a protonated cyclopropane [4.0.1] and a protonated cyclobutane [4.0.2], respectively, which were formed from the *secondary* carbenium ions. Cyclodecane was dehydrogenated into *cis*- or *trans*-decaline with an evolution of dihydrogen. The reaction schemes for the cyclic hydrocarbons of heptane, octane, and decane are summarized in Scheme 3.

Cyclododecane was, however, converted into lots of products, more than 30 species.

4. Effects of preparation method on the catalytic activities of sulfated zirconia

The catalytic activity of SO_4/ZrO_2 varied with the type of zirconia gel, drying and calcination conditions, and the type of additives. In this section, the effects of preparative conditions on the catalytic activity are summarized.

4.1. Effect of drying temperature and calcination temperature on the catalytic activity of sulfated zirconia

Sulfated zirconia 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 [14].

The activity also depends on the drying temperature of the gel before sulfation. Fig. 4 shows the effect of the drying temperature of the zirconia gel on the butane isomerization activity [15]. The gel was obtained by hydrolyzing $ZrO(NO_3)_2$ with aqueous ammonia at pH

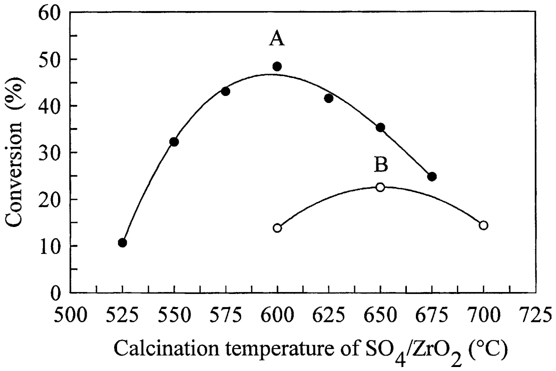
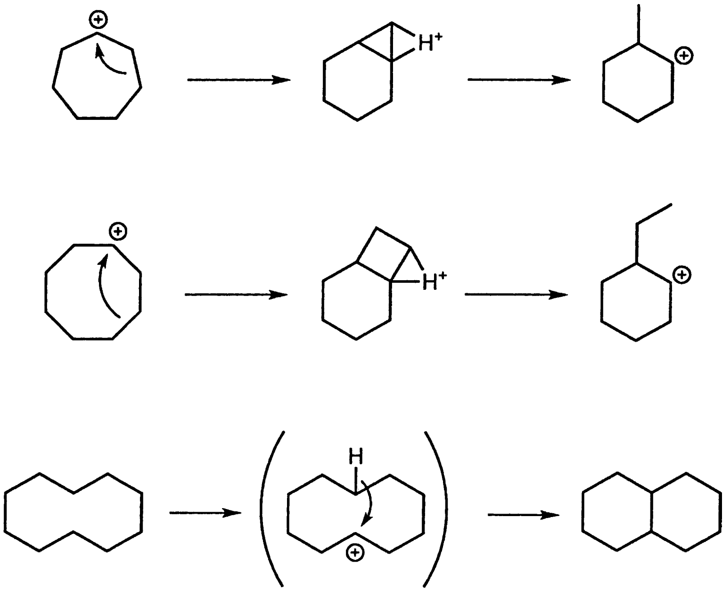


Fig. 4. Activities for reaction of butane at 180 °C over the SO_4/ZrO_2 catalysts prepared from the Zr gels dried at 100 °C for 24 h (○) and 300 °C for 1.5 h (●). Pulse reaction conditions: He carrier 20 ml/min, pulse size 0.05 ml (gas), catalyst 0.1 g. Yields: (A) 7.7% C_3, 39.2% *i*-C_4, 1.5% C_5; (B) 1.4% C_3, 20.5% *i*-C_4, 0.6% C_5.



Scheme 3. Carbenium ion intermediate.

8.0 followed by washing with water. The gel was dried at different temperatures: 100 °C for 24 h and 300 °C for 1.5 h. Then the dried samples were powdered to below 100 mesh, exposed to 1 N H_2SO_4, and finally calcined for 3 h in the temperature range 525–700 °C. The reaction of butane was carried out in a microcatalytic pulse reactor as described elsewhere [16]. The figure shows that different drying temperature causes a large difference in activity, and the calcination temperature showing the maximum activity is dependent on the drying temperature. The difference in the calcination temperature showing the maximum activity is 50 °C, and the difference in the maximum activity is twice for the catalysts dried at different temperature.

In order to clarify the relation between the drying temperature of the zirconia gel and the calcination temperature, several sulfated zirconia catalysts were prepared from a commercial gel, XZO 631/01 of MEL Chemicals, by changing the drying temperature in the range 100–400 °C, and calcination temperature in the range 475–700 °C. The catalytic activity for butane isomerization was measured. The results are shown in Fig. 5 [15]. The differences both in the calcination temperature showing maximum activity and in the maximum activity for the gels dried at different temperatures are large. Among the catalysts prepared under different drying and calcination temperatures, the catalyst dried at 300 °C and calcined at 550 °C exhibits the highest activity. The low activity of the catalyst calcined at 400 °C is caused by the crystallization of ZrO_2 (crystallization temperature of ZrO_2: ~400 °C). The crystallized zirconia is difficult to react with sulfate ion to form catalytically active species on the surface [2].

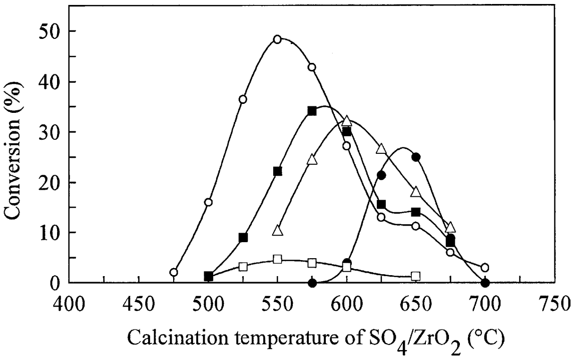


Fig. 5. Activities for reaction of butane at 180 °C over the SO_4/ZrO_2 catalysts prepared from the Zr gels of MEL 631/01 with treatment of drying at 100 °C for 24 h (△), 200 °C for 1.5 h (■), 300 °C for 1.5 h (○), 400 °C for 1.5 h (□), and without any treatment (●). Pulse reaction conditions in Fig. 1.

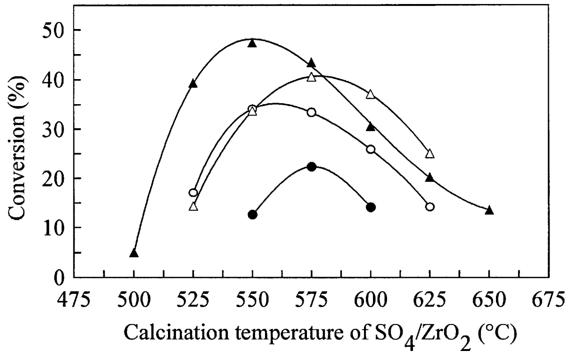


Fig. 6. Activities for reaction of butane at 180 °C over the SO_4/ZrO_2 catalysts prepared from the Zr gels of MEL 632 with treatment of drying at 100 °C for 24 h (△), 200 °C for 1.5 h (▲), 300 °C for 1.5 h (○), and without any treatment (●). Pulse reaction conditions in Fig. 1.

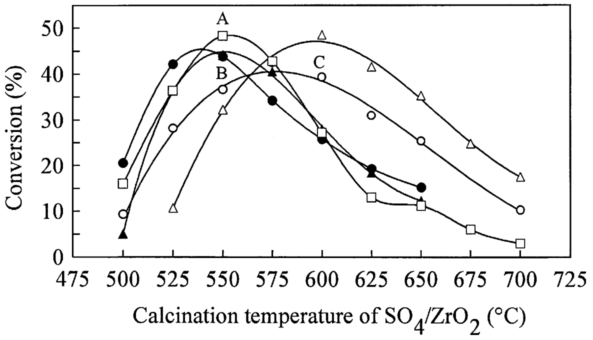


Fig. 7. Activities for reaction of butane at 180 °C over the SO_4/ZrO_2 catalysts prepared from various Zr gels: MEL 631 dried at 300 °C (□), MEL 632 dried at 200 °C (▲), Nakarai dried at 300 °C (●), and the gels prepared by hydrolysis of $ZrO(NO_3)_2$ (△) and $ZrOCl_2$ (○) followed by drying at 300 and 200 °C, respectively. Yields: (A) 8.1% C_3, 38.4% i-C_4, 1.8% C_5; (B) 5.1% C_3, 37.4% i-C_4, 1.4% C_5; (C) 4.0% C_3, 34.2% i-C_4, 1.2% C_5.

Although the optimum drying temperature and calcination temperature were shown to be 300 and 550 °C, respectively, for the gel, XZO 631/01, these temperatures are not always fixed. The optimum drying and calcination temperatures are dependent on the type of the zirconia gel. We used the other type of gel, XZO 632 of MEL Chemicals, and dried at 100–300 °C and calcined at 500–600 °C. The activities for the reaction of butane are shown in Fig. 6 [15]. The highest activity was obtained for the catalyst dried at 200 °C and calcined at 550 °C. Thus, the type of gel has a large effect on the subsequent procedures for obtaining high activity.

Fig. 7 summarizes the effect of the calcination temperature on the catalytic activity for butane isomerization over the sulfated zirconia catalysts prepared from different zirconia gels dried at the optimum temperatures. Fig. 7 includes the data taken from Figs. 4–6 and those for two more gels, a commercial gel, Nakarai Chemicals, dried at 300 °C, and the gel prepared by hydrolysis of $ZrOCl_2$, in the same manner as the case of $ZrO(NO_3)_2$, followed by drying at 200 °C [15]. The figure indicates that the maximum activities are approximately the same for different catalysts even though the temperatures to give maximum activity are different. The calcination temperatures to give maximum activity for different catalysts fall within the temperature range <50 °C. It seems that residual species such as Cl^- and $NO_3{}^-$ in the gel result in difference in the optimum drying and calcination temperatures owing to discrepancy in a state of dehydration of the zirconia gel or to reactivity of the zirconia support with the sulfate species. However, selection of the optimum drying and calcination temperature leads the catalytic activity to the same level. The present results point out that the optimum temperature for drying the Zr gel and the final calcination should be found depending on the type of zirconia gel.

4.2. Effect of addition of Pt, Ru, and Fe to sulfated zirconia on the catalytic activity

A large number of metal-promoted superacids which are highly active for the butane conversion have been prepared by the addition of salts of Pt, Fe, Mn, V, Cr, Ni, and others to SO_4/ZrO_2 [11,17–24].

A highly active catalyst for the conversion of butane is obtained by adding a large quantity (7–8 wt.%) of Pt to SO_4/ZrO_2 as shown in Fig. 8 [25], though an active component such as platinum has been usually present in low percentages, 0.1–0.5. The most active catalyst is prepared by impregnation of Zr gel with an aqueous sulfuric acid followed by impregnation of the sulfated gel with a solution of H_2PtCl_6 and calcination [26]. When the order of the addition of metal component and the addition of sulfate ion is reversed, the activity of the resulting catalyst changes. The addition of 2–4 wt.% Ru to SO_4/ZrO_2 gave a catalyst whose activity was comparable to that of the Pt-added

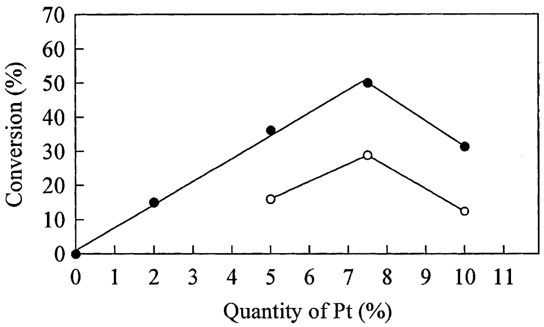


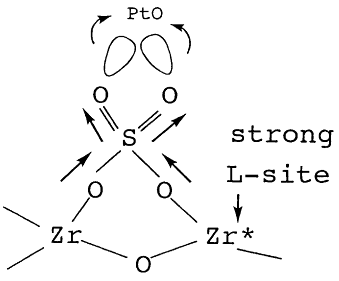
Fig. 8. Activities of Pt–SO_4/ZrO_2 catalysts with various amounts of Pt for the reaction of butane at 100 °C (●) or 80 °C (○).

SO_4/ZrO_2 [27]. An active catalyst was obtained by the addition of 2 wt.% Fe before sulfation followed by calcining in air for more than 24 h [28].

The XPS analysis of the 7.5% Pt-added SO_4/ZrO_2 shows the binding energy of Pt $4f_{7/2}$ to be 72.3 eV, which is assigned to Pt^{2+}. Aubke and co-workers reported the existence of a molecular cation $[Pt(CO)_4]^{2+}$ from the following synthesis:

$$2Pt(SO_3F)_4 + 5CO \xrightarrow{HSO_3F} [Pt(SO_3F)_6] \cdot [Pt(CO)_4]$$

where Pt^{2+} is a coordinating species [29]. Therefore, it is proposed that the Pt-added sulfated zirconia is SO_4/ZrO_2 coordinated with PtO as illustrated in Scheme 4, though several structures of the sulfated zirconia have been proposed. The PtO coordinated to the S=O groups acts as electron withdrawing species followed by the inductive effect illustrated by the arrows; thus, the Lewis acid strength of Zr^{4+} becomes stronger. Pt^{2+} is known to form sulfoxide complexes which are S-bonded, O-bonded, or a mixture of S- and O-bonded ligands [30].



Scheme 4. Structure of Pt-added SO_4/ZrO_2.

The SO_4/ZrO_2 catalyst with the highest activity usually contains approximately 2 wt.% S. This value is equivalent to 12 wt.% Pt. Thus, 60% of sulfate species in the present 7.5 wt.% Pt-added sulfated zirconia are coordinated with PtO as shown in Scheme 4.

4.3. Effect of double calcination on the catalytic activity of Pt-added sulfated zirconia

Platinum-added sulfated zirconia was usually prepared by impregnating zirconia gel with sulfuric acid followed by impregnating the sulfated gel with a solution of H_2PtCl_6 and finally calcining in air at 600 °C [26]. If one more procedure of calcination is done before impregnation with a solution of H_2PtCl_6, the optimum quantity of Pt is reduced. The zirconia gel prepared by hydrolysis of $ZrOCl_2$ was exposed to 1 N H_2SO_4 followed by the first calcination at 600 °C to obtain SO_4/ZrO_2, then the SO_4/ZrO_2 was impregnated with the platinate and calcined for the second time at 500 °C. This procedure is termed as “double calcination” to distinguish from the usual method “single calcination”. The thus-prepared catalysts with various quantities of Pt were examined in the reaction of butane; the results are shown in Fig. 9 together with those by the single calcination for comparison [31].

The highest activity was observed with 3 wt.% of Pt for the catalyst prepared by “double calcination”, while the highest activity was observed with 7.5 wt.%

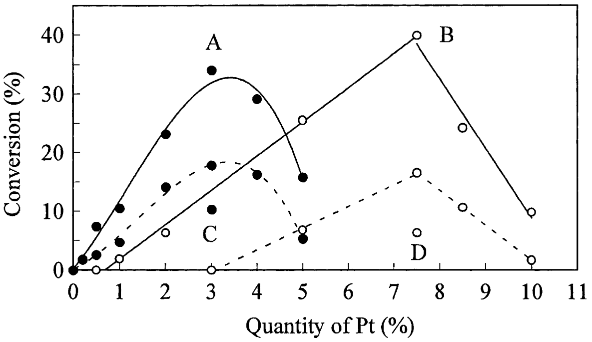


Fig. 9. Activities of Pt–SO_4/ZrO_2 catalysts with various amounts of Pt for the reaction of butane at 60 °C (—) and 40 °C (- - -). Pulse reaction conditions: He carrier 20 ml/min, pulse size 0.05 ml (gas), catalyst 0.05 g. First pulse data. Prepared by the double calcination (●) and the single calcination (○). Yields: (A) 2.4% C_3, 30.7% i-C_4, 0.9% C_5; (B) 5.2% C_3, 33.8% i-C_4, 0.9% C_5; (C) and (D) reactions at 30 °C; yield: (C) 10.3% i-C_4; (D) 6.3% i-C_4.

of Pt in the case of the single calcination. The highest activity for both catalysts being approximately the same. A large quantity of Pt seems to be wasted when prepared by the single calcination. The structure of Pt–SO_4/ZrO_2 shown in Scheme 4 also shows that the double calcination operates efficient use of Pt species in enhancing the activity. The calcination temperatures for showing the maximum activity were 600 °C for the first calcination, and 500 °C for the second calcination. This preparation method was satisfactorily applied to Ru-added SO_4/ZrO_2 for which the optimum temperatures were 550 °C for the first calcination and 400 °C for the second one.

The binding energies of Pt $4f_{7/2}$ in XPS for the catalysts prepared by double calcination and single calcination were almost the same. The binding energy for the catalyst prepared by double calcination with 3% Pt was 72.2 eV and that for the catalyst prepared by single calcination with 7.5% Pt was 72.3 eV. These values were essentially the same, and the platinum species on both catalyst are in the state of Pt^{2+} [32]. The acid strength of solid acids with high acidity on the surface can be estimated by the adsorption heat of Ar, calculated from the TPD of Ar [33]. The data by this measurement were also almost the same. The adsorption heats were 24.2 and 24.6 kJ mol^{-1} for the catalysts with 3 and 7.5 wt.% of Pt, respectively [34].

5. Effects of mechanical mixing of Pt-added zirconia and iron compounds on the catalytic activity

5.1. Mechanical mixture of Pt/ZrO_2 and superacids

An active catalyst for the conversion of butane to isobutane was obtained by mechanical mixing of WO_3/ZrO_2 and Pt/ZrO_2 (0.5 wt.% Pt) as shown in Table 2. The activity of Pt–WO_3/ZrO_2 prepared by co-impregnation of zirconia with W and Pt materials was lower than that of the mechanical mixture of WO_3/ZrO_2 and Pt/ZrO_2 [35]. The reaction was carried out with a reactor in which two catalysts were placed separately and successively. In both arrangements where Pt/ZrO_2 was placed ahead of WO_3/ZrO_2 and WO_3/ZrO_2 was placed ahead of Pt/ZrO_2, the conversions of *n*-butane were far less than that of the mechanical mixture, and methane and ethane were produced to a considerable extent.

Table 2
Physical mixture of WO_3/ZrO_2 and Pt/ZrO_2 for the reaction of butane into isobutane

Catalyst	Products (%)[a]				
	$C_1 + C_2$	C_3	i-C_4	i-C_4'	C_5
WO_3/ZrO_2	0	0	0	0	0
Pt–WO_3/ZrO_2	0	0.1	1.0	Trace	0
$WO_3/ZrO_2 + Pt/ZrO_2$	0	2.9	7.8	0.6	0.2
$Pt/ZrO_2 \rightarrow WO_3/ZrO_2$	1.3	2.3	2.2	0.2	0
$WO_3/ZrO_2 \rightarrow Pt/ZrO_2$	1.4	2.6	1.5	1.2	0

[a] Products: C_1, methane; C_2, ethane; C_3, propane; i-C_4, isobutane; i-C_4', isobutene; C_5, pentane.

The catalytic activities of several sulfated metal oxides, zeolites, and silica–aluminas were enhanced by addition of Pt/ZrO_2 as shown in Table 3: the activity order of SO_4/MeO_x being $TiO_2 > Al_2O_3 > Fe_2O_3$ [36]. The mixture of SO_4/Al_2O_3 and Pt/ZrO_2 gave the highest selectivity for the skeletal isomerization. The mechanical mixtures of Pt/ZrO_2 with zeolites and silica–aluminas showed satisfactory conversions of butane, but their selectivities for isobutane were low. As for Ru, a mixture of SO_4/ZrO_2 and Ru/SnO_2 was highly effective [37].

Although the effect of mixing of Pt/ZrO_2 with SO_4/ZrO_2 on the enhancement of the activity of SO_4/ZrO_2 for the skeletal isomerization of butane was not appreciable, the positive effect was observed for the conversion of propane into butanes as shown in Table 4 [38]. The catalysts which are effective for

Table 3
Reaction of butane over solid acids mixed with Pt/ZrO_2

Catalyst	Reaction temperature (°C)	Products (%)	
		C_3	i-C_4
SO_4/TiO_2	300	0.3	1
$SO_4/TiO_2 + Pt/ZrO_2$	200	6	13
SO_4/Al_2O_3	300	0	0.2
$SO_4/AlO_2O_3 + Pt/ZrO_2$	200	4	19
$SO_4/FeO_2O_3 + Pt/ZrO_2$	220	3	7
Mordenite	300	1	2
Mordenite + Pt/ZrO_2	200	22	17
ZSM-5	300	0	0.1
ZSM-5 + Pt/ZrO_2	200	10	3
SiO_2–$Al_2O_3 + Pt/ZrO_2$	240	6	13

Table 4
Conversion of propane into butane

Catalyst	Temperature (°C)	Conversion (%)	Products (%)			
			C_1	C_2	C_4[a]	C_5
SO_4/ZrO_2	200	0.1			0.1	
$Pt–SO_4/ZrO_2$	200	0.2			0.2	
$Pt–SO_4/ZrO_2$	250	0.3	Trace	0.2	0.1	
$SO_4/ZrO_2 + Pt/ZrO_2$	200	3.2	Trace	0.2	3.0	Trace
$SO_4/ZrO_2 + Pt/ZrO_2$	225	6.1	0.3	1.6	4.1	0.1

[a] Butanes.

the butane conversion are not always efficient for the propane conversion. As the acidic sites on SO_4/ZrO_2 are stronger than those on SO_4/TiO_2, SO_4/Al_2O_3, and SO_4/Fe_2O_3, it is suggested that a high superacidity is needed to become active for the propane conversion to butanes by mixing with Pt/ZrO_2.

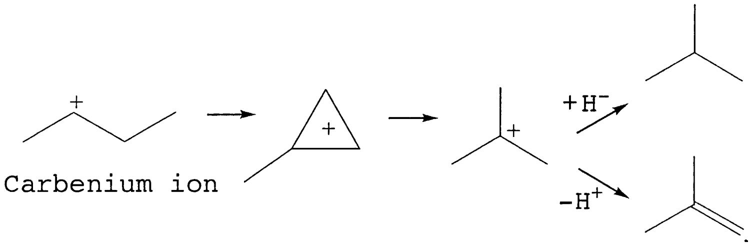
The effect of mixing was specific to Pt/ZrO_2, because no positive effect was observed with Pt/other metal oxides such as Pt/TiO_2 and Pt/SiO_2. The XPS analysis of Pt/ZrO_2 showed the binding energy of Pt $4f_{7/2}$ to be 72.6 eV, close to that of the Pt^{2+} species. On the other hand, the binding energies, 70.5–71.2 eV, for $Pt–WO_3/ZrO_2$, Pt/TiO_2, and Pt/SiO_2 were close to 71.7 eV, the binding energy for Pt^0. The results indicate that affinity of Pt to ZrO_2 is quite specific.

As described before, it is proposed that the Pt^{2+} species on ZrO_2 act as coordinate sites for H^- formed during reaction or reservoirs for the coordination of H^-. A stable Pt^{2+} complex with an hydride ion is also known [39]. The reaction mechanisms for the conversions of butane and propane are illustrated in Schemes 5 and 6, respectively, where the H^- intermediates are important for completion of the reactions.

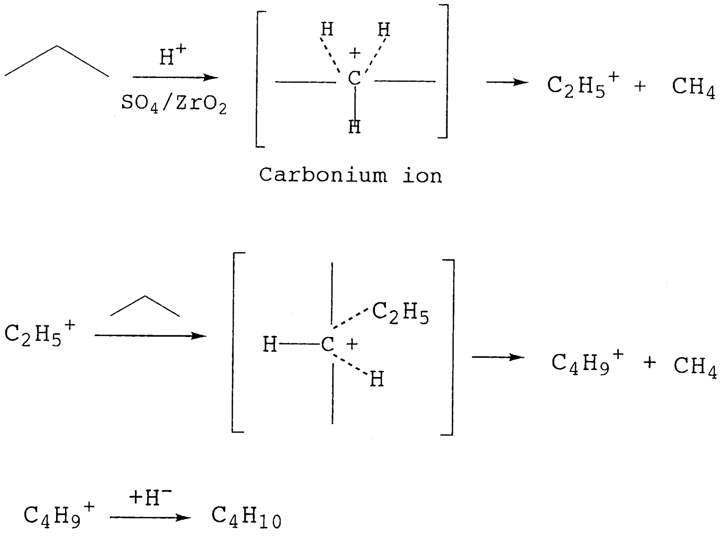
5.2. Mechanical mixture of sulfated zirconia and iron compounds

The catalytic activity of SO_4/ZrO_2 was enhanced by mechanical mixing with iron compounds. The catalytic activities of the mixtures for *n*-butane conversion are given in Table 5 [31]. The activity of the SO_4/ZrO_2 mixed with $FeSO_4$ heat-treated at 600 °C is six times higher than that of the SO_4/ZrO_2 without mixing. $FeSO_4$ transforms to $Fe_2(SO_4)_3$ by calcination at 600 °C in air [40]. Thus, sulfated iron oxide, a superacid, was examined for the effect of mixing; the same effect to the case of the iron sulfate was observed. A remarkable enhancement of the conversion was also obtained by mixing sulfate free Fe_2O_3 with SO_4/ZrO_2. The maximum activity was observed with calcination at 600 °C for $FeSO_4$ and at 400 °C for SO_4/Fe_2O_3. As for the ratio of the mixtures, 1:1 mixture was satisfactory. The catalytic activity increased with the amount of the additives up to the equal ratio.

Fig. 10 shows the variations of the conversion in *n*-butane isomerization as a function of the reaction temperature for the mixtures containing SO_4/ZrO_2 and iron compounds. The variation for SO_4/ZrO_2 without mixing iron compounds is also included for



Scheme 5. Reaction of butane.



Scheme 6. Conversion of propane into butane.

comparison. The figure shows how the effect of mixing with the sulfate or the sulfated oxide is large, the temperature difference to show the same conversion between A and B being close to 60 °C. However, it is noted that the effect of mixing is observed only above a reaction temperature of 140 °C.

In the case of mixing Pt/ZrO_2, the species of Pt^{2+} were proposed to be coordinate sites or reservoirs for the intermediate H^- ions. Similarly, Fe^{3+} ions are able to act as the same sites. The temperatures above 140 °C must be the indispensable energies for transfer of the H^- species in macroscopic space. The catalytic activity of Fe- and Mn-added SO_4/ZrO_2 for butane is three orders of magnitude higher than that of SO_4/ZrO_2 around room temperature [41]. The function of Fe to play an important role for the alkane conversion has not been elucidated, and the Fe in the catalyst is characterized as Fe^{3+} species by several

Table 5
Physical mixture of SO_4/ZrO_2 and $FeSO_4$, SO_4/Fe_2O_3, or Fe_2O_3 for the reaction of butane into isobutane at 150 °C

Catalyst[a]	Conversion (%)	Products (%)		
		C_3	i-C_4	C_5
SO_4/ZrO_2	8.6	0.1	8.5	Trace
SO_4/ZrO_2 + $FeSO_4$ (600 °C)[b]	48.8	9.3	37.7	1.5
SO_4/ZrO_2 + SO_4/Fe_2O_3 (400 °C)[b]	51.1	11.6	38.1	1.4
SO_4/ZrO_2 + Fe_2O_3 (450 °C)[b]	17.1	0.5	16.3	0.3

[a] Calcination temperature.

[b] Mixture of 0.1 g of SO_4/ZrO_2 and 0.1 g of the iron compound. Pulse reaction conditions: He carrier 20 ml/min, pulse size 0.05 ml (gas). Pulse data showing the highest conversion. SO_4/ZrO_2: prepared by impregnation of the gel of MEL 632/01 with 0.5 M H_2SO_4 followed by calcination at 600 °C. Fe_2O_3: prepared by hydrolysis of $FeCl_3$ to $Fe(OH)_3$ followed by calcination. SO_4/Fe_2O_3: prepared by impregnation of $Fe(OH)_3$ with 0.25 M H_2SO_4 followed by calcination.

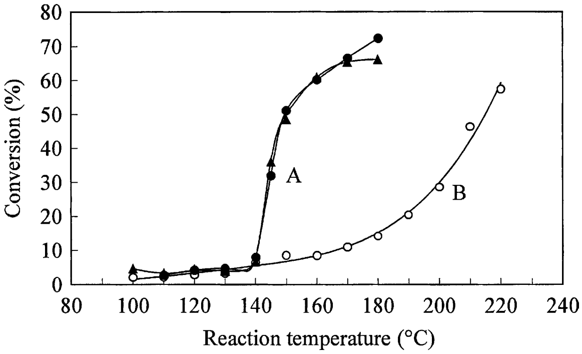


Fig. 10. Activities of catalysts for the reaction of butane: (●) a mixture of 0.1 g of SO_4/Fe_2O_3 (400 °C) and 0.1 g of SO_4/ZrO_2; (▲) a mixture of 0.1 g of $FeSO_4$ (600 °C) and 0.1 g of SO_4/ZrO_2; (○) 0.1 g of SO_4/ZrO_2. Yields: (A) 4.7% C_3, 26.7% i-C_4, 0.6% C_5; (B) 2.7% C_3, 24.7% i-C_4, 1.2% C_5.

workers [28,42–47]. The Fe species must act partly as the coordinating sites for transfer of H^- in the microscopic space.

6. Miscellaneous reactions catalyzed by sulfated metal oxide-based catalysts

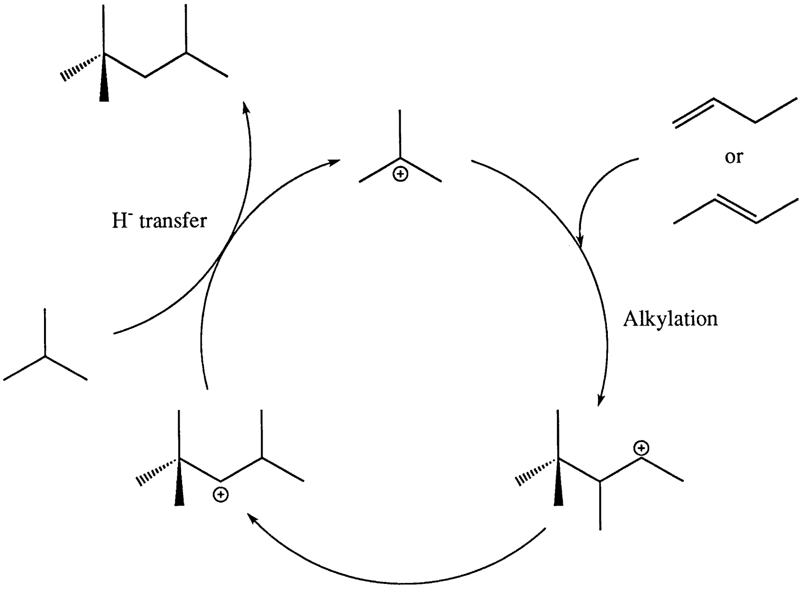
The alkylation of isobutane with 1-butene is an important process in industry for the production of high octane gasoline. The reaction was studied in the gas-phase system over various sulfated metal oxides [48,49]. The highest acid strength of the catalysts was related to the total yield of C_8 paraffins, SO_4/SnO_2 giving the highest yield of trimethylpentanes (TMP). An additional relationship between the acidities of variously prepared SO_4/ZrO_2 catalysts and the yields of C_8 paraffins indicated that the alkylation to form C_8 paraffins is based on the catalytic action by highly superacidic sites.

It was proved that the first intermediate species is a *t*-butyl cation formed on the superacidic Lewis site by abstraction of a H^- from isobutane, followed by the alkylation with butenes to form TMP as shown in Scheme 7. Accordingly, the reaction is alkylation of alkenes with isobutane via the *t*-butyl cation formed on highly superacidic sites to result in the formation of TMP. The reaction has so far been considered to be the alkylation of isobutane with alkenes via the protonated alkenes as an intermediate.

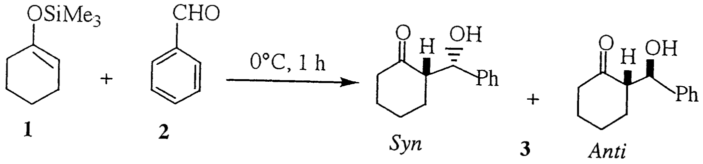
Table 6
Reaction of silyl enol ether (**1**) with benzaldehyde (**2**)

Catalyst	Yield of aldol (**3**) (%)	Yield of syn:anti of **3** (%)
SO_4/ZrO_2	53	28:72
SO_4/SnO_2	27	46:54
SO_4/Al_2O_3	15	58:42
SO_4/TiO_2	38	72:28
WO_3/ZrO_2	64	80:20
WO_3/TiO_2	48	61:39
MoO_3/ZrO_2	50	41:59

Yields of the TMP products have not been satisfactory when catalyzed by solid acids such as zeolites and silica–aluminas in the heterogeneous system [50–54]. Table 6 shows the results of cross aldol reaction of 1-trimethylsilyloxy-1-cyclohexene with benzaldehyde [55] (Scheme 8). The table shows how the catalyst species control the stereo chemistry. The syn selectivity was given by SO_4/TiO_2, WO_3/ZrO_2, and



Scheme 7. Mechanism of the alkylation of 1-butene with isobutane.



Scheme 8. Aldol reaction of 1-trimethylsilyloxy-1-cyclohexene and benzaldehyde.

WO_3/TiO_2, in particular 80% selectivity was given by WO_3/ZrO_2 with high yields. The anti selectivity was given by SO_4/ZrO_2; SO_4/SnO_2, SO_4/Al_2O_3, and MoO_3/ZrO_2 were not selective, nearly equal amounts of syn and anti products being produced. SO_4/Fe_2O_3 and SO_4/SiO_2 were low in activity because of their weak acidity.

In the Friedel–Crafts benzoylation of toluene with benzoic anhydride, SO_4/ZrO_2, WO_3/ZrO_2, and SO_4/SnO_2 yielded methylbenzophenone isomers in 92, 55, and 48%, respectively. WO_3/TiO_2, SO_4/HfO_2, SO_4/Al_2O_3, and SO_4/TiO_2 yielded methylbenzophenone isomers in 26–28%. Distribution of methylbenzophenone isomers was almost the same for all catalysts: 20–30% *o*-isomer, 2–4% *m*-isomer, and 70–80% *p*-isomer. WO_3/Fe_2O_3 and B_2O_3/ZrO_2 were inactive [56].

When benzoyl chloride was used as the acylating reagent, the reactions over SO_4/Fe_2O_3 and WO_3/Fe_2O_3 were homogeneously catalyzed by $FeCl_3$ produced during the reaction, but the reactions over the other catalysts were heterogeneously catalytic. The yields of methylbenzophenones were lower with benzoyl chloride than with benzoic anhydride over these catalysts. This is in contrast to the general recognition that benzoyl chloride is more reactive than benzoic anhydride as an acylation reagent.

The catalyst prepared by calcination of iron sulfates in air at 500–800 °C were examined in hydrocracking of the model compounds of coal, diphenyl ether, benzyl phenyl ether, and diphenylmethane under pressurized hydrogen; highly active and stable catalysts were obtained by calcination at 800 °C, while the catalyst prepared by calcination of iron sulfates below 700 °C was inactive for the hydrocracking of the model compounds [40].

An active and stable catalyst of 3 wt.% $Pt–SO_4/ZrO_2$ for the dehydrogenative coupling of methane without oxidant was obtained by reducing in H_2 at 500 °C; the active site was shown to be $Pt^0–SO_4/ZrO_2$ surrounded by 10 times platinate–SO_4/ZrO_2 with various oxidation numbers of Pt except 0, whose species protecting the active one from aggregation [57,58].

A mesoporous solid acid with ordered mesopores was prepared by modification of FSM-16 with SO_4/ZrO_2; the acid sites were formed inside the ordered pores, and the catalyst was active for the reactions producing large molecules [59].

7. Conclusions

We have attempted to present the recent works on syntheses of solid superacids for transformation of alkanes. It is hoped to synthesize superacids by the system of metal oxides, but WO_3 supported on ZrO_2 (WO_3/ZrO_2), which is most active among the synthesized superacids by metal oxides, is not satisfactorily high in acidity as well as activity compared with SO_4/ZrO_2. It is also advisable to prepare a superacid with acidity higher than that of the SO_4/ZrO_2 catalyst. Therefore, we hope that new substances other than the tungstated and sulfated zirconias will be extensively studied.

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