Organic syntheses catalyzed by superacidic metal oxides: sulfated zirconia and related compounds

Kazushi Arata

Received 18th December 2008, Accepted 12th August 2009
First published as an Advance Article on the web 17th September 2009
DOI: 10.1039/b822795k

Recent studies on organic syntheses catalyzed by solid superacids, which are sulfate-supported metal oxides and tungsten- or molybdenum-supported metal oxides, are reviewed. The synthetic reactions are Friedel–Crafts acylations, reactions between amines and ketones, esterifications of acids with alcohols, and others. The catalysts are satisfactorily active in a heterogeneous liquid–solid system, recoverable, and reusable, and they offer new opportunities for developing environmentally benign and friendly processes in organic syntheses.

Introduction

An acid that is stronger than the acid strength of 100% sulfuric acid is known as a superacid.[1] Such superacidity is made up by mixing a fluorine containing Brønsted acid (HF, FSO_3H, CF_3SO_3H, *etc.*) and a fluorinated Lewis Acid (BF_3, SbF_5, TaF_5, *etc.*).[2,3] These liquid superacids have been developed since the 1960s and applied to various organic syntheses, especially in the field of hydrocarbon chemistry. The research articles were reviewed by Olah.[4]

In the 1980s we studied the synthesis of solid superacid catalysts on the surface of oxides of Fe, Ti, Zr, Sn, and others by strong co-ordination of sulfate materials.[5,6] The superacids were satisfactorily active in a heterogeneous system for reactions which are generally catalyzed by strong acids, especially liquid superacids. Following the same manner as those solid materials, we have also synthesized another type of superacid, consisting of metal oxides, which are tungsten oxide and molybdenum oxide supported on those metal oxides.[7]

Environmental concerns about the use of toxic liquid superacids and liquid inorganic acids in the transformation of hydrocarbons give an impetus to a search for stable and more environmentally friendly solid acid catalysts. This work has addressed an important opportunity related to green chemistry where solid superacids lead to new gas– and liquid–solid phase reactions which are environmentally benign processes in the chemical industry. We published our first paper on solid superacids in 1979.[8] Since then, numerous papers in addition to ours on these materials have been published, a review concerning sulfated zirconia being referenced.[9]

Solid acids have been extensively studied and used as catalysts or catalyst carriers in the chemical industry for many years. The preparation and use of strong solid acids and superacids are active areas of research for isomerization, cracking, and other reactions because of the reported advantages of solid catalysts, and recent research has focused on the preparation and characterization of stronger solid acids. Replacement of homogeneous liquid acids by heterogeneous solid acids as catalysts in the chemical industry is expected to bring about an ease of separation from the reaction mixture, which allows continuous operation, as well as regeneration and reutilization of the catalyst. Furthermore, heterogeneous solid catalysts can lead to other advantages, no corrosion of the reactor and no environmental problem for disposal of used catalyst.

In the field of catalysis chemistry, solid acid systems stronger than acidic oxides, such as silica-aluminas and zeolites, have been developed and are categorized as solid superacids. The search for solid superacids has become active since the early 1970s, and it is now the age of the superacid. This review summarizes recent studies on organic syntheses catalyzed by sulfate-supported metal oxides and tungsten- or molybdenum-supported metal oxides, mainly sulfated zirconia and related compounds.

Sulfated and tungstated/molybdated metal oxides

Table 1 summarizes the solid superacids, which we have prepared, together with their acid strengths.[10] The temperatures

Hokkaido University of Education, Department of Science, Hachiman-cho 1-2, Hakodate, 040-8567, Japan

Kazushi Arata

Kazushi Arata is Emeritus Professor of Chemistry at the Hokkaido University of Education (Hachiman-cho, Hakodate, Japan 040-8567). His B.S. and M.S. degrees and Ph.D. are from the Hokkaido University (Sapporo, Japan). He joined the Department of Science at the Hokkaido University of Education, Hakodate Branch, in 1971. For more than 30 years he has worked with heterogeneous catalysis, focusing on the synthesis, characterization, and application of solid acid catalysts. His current research is focussed on solid superacids and ceramic acids.

Table 1 Solid superacids and their acid strength

Catalyst (calcination $T/°C$)[a]	Highest acid strength (H_0 value)
SO_4^{2-}/SnO_2 (550)	−18.0
SO_4^{2-}/ZrO_2 (650)	−16.1
SO_4^{2-}/HfO_2 (700)	−16.0
SO_4^{2-}/TiO_2 (525)	−14.6
SO_4^{2-}/Al_2O_3 (650)	−14.6
SO_4^{2-}/Fe_2O_3 (500)	−13.0
WO_3/ZrO_2 (800)	−14.6
MoO_3/ZrO_2 (800)	−13.3
WO_3/SnO_2 (1000)	−13.3
WO_3/TiO_2 (700)	−13.1
WO_3/Fe_2O_3 (700)	−12.5

[a] Named sulfated stannia, zirconia, hafnia, titania, alumina, and ferria; Tungstated zirconia, stannia, titania, ferria; Molybdated zirconia.

shown in parentheses are the calcination temperatures required to generate the highest acidity or activity. The acid strengths were estimated by the color change of Hammett indicators, the temperature-programmed desorption of pyridine as a basic probe, the temperature programmed reaction of furan for its resinification, and the catalytic activities for various reactions.

Among the superacids listed in Table 1, sulfated zirconia (SO_4^{2-}/ZrO_2) has been most frequently investigated, modified, and applied to various reactions. The studies of the organic synthesis, thus, have been mainly limited to the sulfated zirconia. This may be because the sulfated zirconia possesses strong acid sites on the surface, is relatively easy to prepare, and was found to be superacidic at the very beginning of the history of the solid superacids. Sulfated zirconia is now commercially available from Wako Pure Chemical Industries, 7000 yen/25 g (8500 yen/25 g for tungstated zirconia), and used as a catalyst for organic synthesis in industry, is also available from MEL Chemicals and Süd Chemie.

The H_0 value in the table is described below. The equilibrium between an acid, BH⁺, and its conjugate base, B, can be written

$$BH^+ \rightleftharpoons B + H^+$$

The corresponding thermodynamic equilibrium constant, K_{BH^+}, gives the acid strength expressed by the Hammett acidity function, H_0,

$$H_0 = pK_{BH^+} + \log\frac{[B]}{[BH^+]}$$

The Hammett acidity function shows the ability of a solution to convert a neutral base (B) into its conjugate acid (BH^+). The experimental method indicates the determination of the BH^+ concentration converted from a very small amount of B (Hammett indicator) diluted in the solution. This concept estimates quantitatively the acidity of concentrated and non-aqueous acidic solutions. Lower values of H_0 correspond to greater acid strength. The acid strength of 100% H_2SO_4 is determined to be $H_0 = -11.93$.[11]

The Hammett acidity function is a logarithmic scale on which 100% H_2SO_4 has an H_0 of ~−12 and FSO_3H-SbF_5 has an H_0 of ~−19; thus, the acid strength of the latter is estimated from the difference in the H_0 scale to be seven orders of magnitude stronger than 100 percent sulfuric acid. This strength is termed *magic acid*.[4]

A number of studies have attempted to determine the nature of acid sites in the catalyst of sulfated zirconia in order to know how the surface species enhances the surface acidity of zirconium oxide.[9] An example of the models is shown in Scheme 1, where two oxygens are bonded to Zr in addition to coordination of a S=O group with Zr, indicating three bonds in total. The active site is not on the metals, but on the S atoms. The addition of water causes the breaking of this coordination to bring about Brønsted acid sites which strengthen Lewis acid sites.[12]

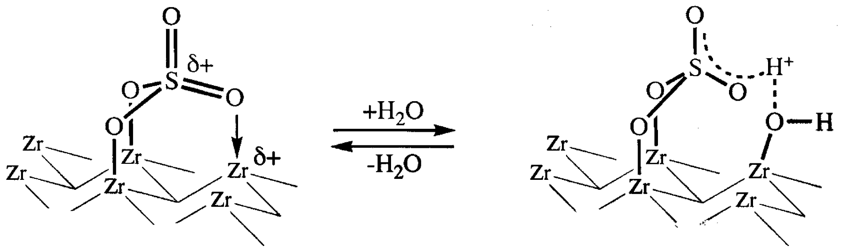
Preparation of sulfated and tungstated zirconias

Among the superacids of sulfate-supported and tungsten-/molybdenum-supported metal oxides, sulfated and tungstated zirconias have been most investigated and applied to various reactions. Those two materials are prepared as follows.

Zirconium hydroxide is obtained by hydrolyzing $ZrOCl_2\cdot 8H_2O$ with aqueous ammonia, washing, drying at 100 °C, and powdering the precipitate below a 100 mesh.[13] The prepared materials $[Zr(OH)_4]$ are treated with sulfate ion by exposing 2 g of the hydroxides in 30 ml of 0.5 M H_2SO_4, filtering, drying, and finally calcining in air at 600 °C for 3 h.[14]

For the preparation of tungstated zirconia, $Zr(OH)_4$ is heated at 300 °C, and the gels are impregnated with aqueous ammonium metatungstate $[(NH_4)_6(H_2W_{12}O_{40})\cdot nH_2O$, 50 wt% $WO_3]$ followed by evaporating water, drying, and calcining in air at 800 °C for 3 h. The concentration is 15 wt% W metal based on the hydroxide, 13 wt% W after calcination.[13]

A one-step synthesis of sulfated zirconia was investigated by the sol-gel method followed by supercritical drying. Zirconium *n*-propoxide is mixed with *n*-propanol, nitric acid, and sulfuric acid. This solution is then mixed with another solution containing *n*-propanol and water, and the mixture is vigorously stirred to form a zirconia-sulfate cogel; supercritical drying with carbon dioxide removes the alcohol solvent, forming a high surface area



Scheme 1

aerogel. Their properties and catalytic activities are similar to those of ours.[15]

Commercial Zr-gels are now supplied from chemical companies such as MEL, Nakarai, and Daiichi Kigenso; for instance, XZO631 and 632 are gels, and XZO682 is a sulfate-adsorbed gel from MEL.

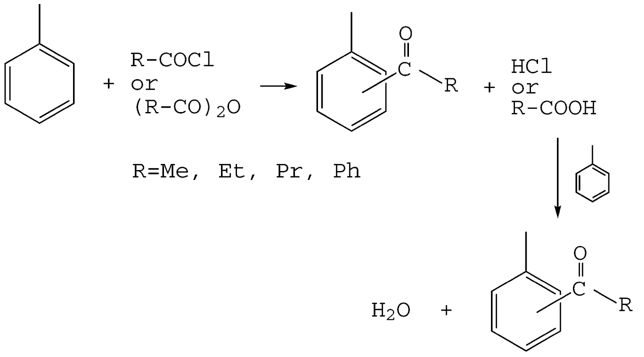
The preparation method of other metal oxides is described in a recent review.[16]

Organic reactions

1. The Friedel–Crafts reactions

The Friedel–Crafts reaction has been performed as a test reaction since these studies started;[6,17] our first study was the benzylation of toluene with benzyl chloride catalyzed by heat-treated iron sulfates. The benzylation over the present catalysts is also reported, with sulfated zirconia,[18,19] and with sulfated titania.[20,21]

In the two main reactions, alkylation and acylation, the latter has been predominantly selected; it is less reactive than the former. In addition, the catalytic acylation of aromatics *via* the Friedel–Crafts reaction is attractive for organic synthesis and a prerequisite challenge to green technology (Scheme 2). Traditional methods depend on the use of at least stoichiometric quantities of Lewis acids, such as aluminium trichloride and boron trifluoride, because the Lewis catalysts are consumed by coordination with the formed aromatic ketones.[22,23] The large amount of the acids and their waste matter after work-up procedures cause serious environmental problems. There have been several efforts to conduct the reaction using catalytic amounts of acidic promoters.



Scheme 2

A main test-reaction has been the benzoylation of toluene with benzoyl chloride or benzoyl anhydride as acylating reagent because of easy procedures operating in a batch mode at temperatures around 100 °C;[24,25] an example of a comparative study is shown in Table 2.[26] Both sulfated and tungstated zirconias along with stannias show satisfactory activities. The product distribution is 20–30% *o*-, 2–4% *m*-, and 70–80% *p*-methylbenzophenones, similar to that by the usual homogeneous reaction using $AlCl_3$. The well-known acid catalysts of aluminosilicates, silica-aluminas and zeolites are inactive under the conditions, though their acidic strength is in the range of superacid. Those materials are mainly composed of Brønsted acid sites on the surface, and this is the reason for their inactivity.

Table 2 Friedel–Crafts benzoylation of toluene with benzoyl chloride or benzoic anhydride at 100 °C[a]

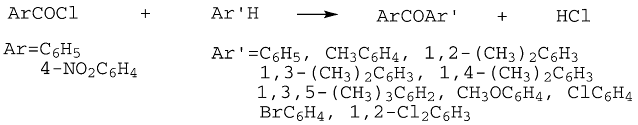
Catalyst	Yield/%	
	$(Ph–CO)_2O$	Ph–COCl
SO_4^{2-}/ZrO_2	92	22
SO_4^{2-}/SnO_2	48	52
SO_4^{2-}/TiO_2	28	17
SO_4^{2-}/Al_2O_3	27	18
WO_3/ZrO_2	55	19
WO_3/SnO_2	16	14
MoO_3/ZrO_2	15	18

[a] The reaction was carried out with a mixture of 141 mmol (15 ml) of toluene, 2 mmol of acylating reagent, and 0.5 g of catalyst.

Yields of the reactions with benzoyl chloride are lower than those with the anhydride, though the reactivity with acylating reagents is generally PhCOCl > $(PhCO)_2O$, strong acid sites being needed for the formation of acyl cation ($PhCO^+$) from the anhydride. However, the results are not coincident with the reactivity, in particular, with the case of SO_4^{2-}/ZrO_2.[27] The reason is based on strong interaction between oxygens of the anhydride and acid sites on the surface.

Although the acid anhydride has been predominantly used in place of the acid chloride for a genuinely environmental trend, the successive acylation with the carboxylic acid produced could be more advantageous; the carbon materials would be used most efficiently. In this case, the reaction is equivalent to a dehydrated acylation that needs strong acidity. In fact, the benzoylation of toluene with benzoic anhydride was carried out at 180 °C, a temperature above reflux, using an autoclave, and marked conversion with benzoic acid produced was observed.[24]

Several papers concerning the benzoylation of toluene (Scheme 3) catalyzed by sulfated zirconia have been published: with benzoyl chloride as acylating reagent[28,29] and with benzoic anhydride.[30] The reaction with the chloride catalyzed by SO_4^{2-}/SnO_2 is also reported.[31] The following results are the acylations of a variety of aromatic compounds to afford the corresponding diaryl ketones in good yields 75–93%.[32]

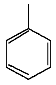
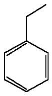
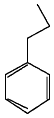
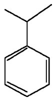
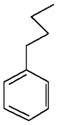
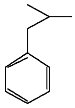
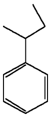
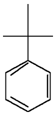


Scheme 3

Similarly, the above aromatic compounds are sulfonylated with arylsulfonyl chlorides ($ArSO_2Cl$, Ar=C_6H_5 or $CH_3C_6H_4$) in 78–93% yields.[33]

In the study of the benzoylation, an unexpected result was found.[34] As shown in Table 3, the benzoylation of alkyl-activated benzenes with benzoic anhydride shows that propyl and butylbenzenes, including their isomers, are exceedingly inactive in spite of the high reactivities of toluene and ethylbenzene, whether the reaction condition is homogeneous or heterogeneous using $AlCl_3$ or sulfated zirconia as a catalyst. The result can not interpret the activity of the benzene ring by the electron-releasing effect of the alkyl groups.

Table 3 Friedel–Crafts benzoylation of alkylbenzenes with benzoic anhydride

Catalyst	Yield/%							
								
SO_4^{2-}/ZrO_2[a]	92	97	5	2	0	14	0	0
$AlCl_3$[b]	37	21	6	1	0	—	3	2

[a] Reaction at 110 °C. [b] Reaction at 0 °C.

Table 4 Acylations of toluene and anisole with alkyl anhydrides catalyzed by sulfated zirconia[a]

Substrate	Reaction	T/°C	Time/h	Yield/%
Toluene	Acetylation	110	4	8
Toluene	Propionylation	110	2	31
Toluene	Butyrylation	110	2	46
Anisole	Acetylation	110	1	100
Anisole	Acetylation	25	1	60
Anisole	Acetylation	50	1	61[b]

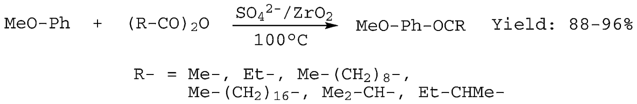
[a] The reaction was carried out with a mixture of 15 ml of toluene, 2 mmol of the anhydride, and 0.5 g of the catalyat with stirring. [b] Reaction with tungstated zirconia.

The catalysts were examined for the acetylation of toluene, one of the difficult acylations because of the difficulty in the formation of an intermediate acetyl cation ($MeCO^+$) from alkyl chain acid anhydrides [$(RCO)_2O$] and hydrides (RCOCl). As a function of the number of carbon atoms, R, of the acylating reagents, the reactivities increase as the hydrocarbon chain is lengthened;[35] this phenomenon shows the acetylation to be the most difficult acylation. In fact, the acetylation with the anhydride is quite difficult to complete the reaction under the reflux conditions, as shown in Table 4.[36]

More reactive acylations by using acylating reagents with longer hydrocarbon chains, propionylation and butyrylation, were examined. The SO_4^{2-}/ZrO_2 catalyst gave yields higher than that of the acetylation for the propionylation as well as the butyrylation; the latter was higher than the former. The reactivity with acylating reagents is $(PrCO)_2O > (EtCO)_2O > (MeCO)_2O$, which agrees with their intermediate stability of $PrCO^+ > EtCO^+ > MeCO^+$.

The present catalyst was examined in a more reactive acetylation, the acetylation of anisole with acetic anhydride. A quantitative yield of methoxyacetophenone was obtained under the conditions (Table 4), showing how reactive anisole is, in comparison with toluene; in other words, an oxygen is exceedingly effective for reactivity. The difference in reactivity between anisole and toluene is close to 100 °C on the reaction temperature as shown in Table 4.[37] Deutsch and co-workers studied the rate of benzoylation of various aromatics catalyzed by sulfated zirconia and found the reactivity decreases in the following order: anisole > mesitylene > 3-chloroanisole ~ *m*-xylene ~ 2-chloroanisole > toluene.[27] Sunajadevi and Sugunan conducted the nitration of phenol with HNO_3 at 0–5 °C, catalyzed by sulfated tinatia (SO_4^{2-}/TiO_2), showing 90% yield with a remarkable *ortho* selectivity, 98%.[38]

Several papers concerning the Friedel–Crafts acylation of anisole catalyzed by sulfated zirconia have been published; the benzoylation with benzoyl chloride[39,40] and with benzoic anhydride:[41–44] the benzoylation together with the acetylation and propionylation with the corresponding carboxylic anhydrides.[45] The following results are the acylations of anisole with different types of aliphatic carboxylic anhydrides (Scheme 4).[46]

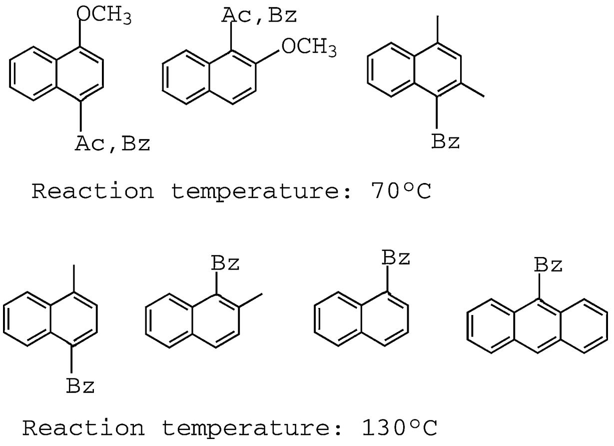


$$\text{MeO-Ph} + (\text{R-CO})_2\text{O} \xrightarrow[100\,°\text{C}]{SO_4^{2-}/ZrO_2} \text{MeO-Ph-OCR} \quad \text{Yield: 88-96\%}$$

$$\text{R- = Me-, Et-, Me-(CH}_2)_8\text{-, Me-(CH}_2)_{16}\text{-, Me}_2\text{-CH-, Et-CHMe-}$$

Scheme 4

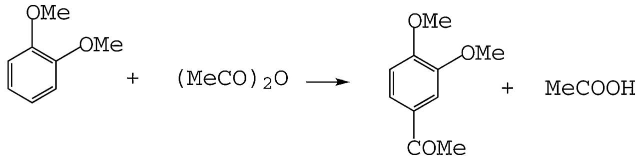
Acetylates and benzoylates of substituted naphthalenes along with anthracene have been synthesized by the acylations of the corresponding aromatics in yields 53–98% (Scheme 5).[47]



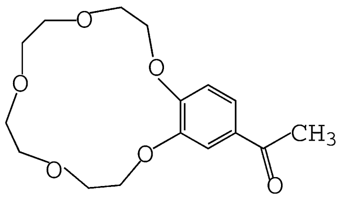
Scheme 5

Acetoveratrole, which is a precursor for the syntheses of an insecticide and an opium-alkaloid antispasmodic, was obtained by the acetylation of veratrole (1,2-dimethoxybenzene) with acetic anhydride over sulfated and tungstated zirconias at 70–80 °C (Scheme 6).[48,49]

A similar acetylation to the above is performed with benzo-15-crown-5 crown ether to yield 4′-acetyl-benzo-15-crown-5 which is an intermediate for products of ionophore antibiotics and phase transfer catalysts (Scheme 7).[50,51]



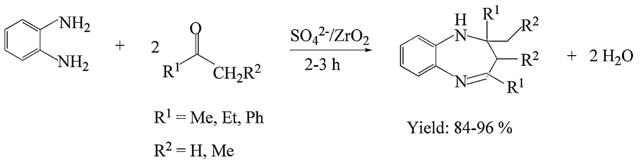
Scheme 6



Scheme 7

2. Reactions of amines and ketones

Amines and related compounds are basic materials. Ammonia is a well-known poison for acid sites on the solid surface; temperature-programmed desorption using base adsorbents such as ammonia and pyridine is one of the common techniques to evaluate the amount and strength of acid sites on solid acids. An organic reaction using the amines catalyzed by the present solid superacids was reported in 2003 by Reddy and Sreekanth.[52] 1,5-Benzodiazepine derivatives were synthesized by the condensation of *o*-phenylenediamine and various ketones in the presence of sulfated zirconia under solvent free conditions, the synthesized materials being valuable intermediates for the synthesis of bioactive compounds (Scheme 8).



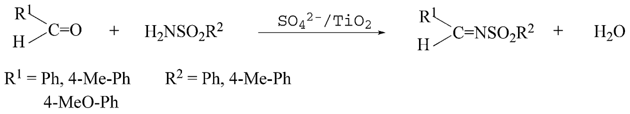
Scheme 8

The benzodiazepines were obtained by taking a 1 : 2.5 mole ratio mixture of *o*-phenylenediamine and the ketones along with a catalytic amount of sulfated zirconia with stirring at ambient conditions. The wet catalyst was filtered after the reaction was recycled, and no appreciable change in activity was noticed.

Several reactions of amines and the related compounds are summarized in Table 5. Those are syntheses of diphenylureas (Entry 1),[53] bis(indolyl)methane derivatives (Entry 2),[54] β-aminoalcohols (Entry 3),[55,56] β-amino-α,β-unsaturated ketones (Entry 4),[57] and new heterocyclic compounds (Entry 5),[58] in addition to aza-Michael addition (Entry 6),[59] one-pot and three-component condensation (Entry 7),[54,60,61] and three-component Mannich type reactions (Entry 8).[62,63] The products are synthetic intermediates and key intermediates for anticancer drugs, and some products are present in a large family of natural products with biological activities. As for the catalysts used, the wet materials were reused for their reactions and there were no big changes in the catalytic activity.

The reactions of the related compounds are Knoevenagel condensation of aldehydes with malononitrile (Entry 9) and ring-opening of aziridines with potassium thiocyanate and thiols (Entry 10–13),[64,65] giving the corresponding β-aminothiocyanates and β-aminosulfides, respectively, for the latter.

Jin and co-workers found that sulfated titania catalyzes well the reaction of aldehydes with sulfonamides to afford N-sulfonylimines, which are valuable synthetic intermediates (Scheme 9).[66]

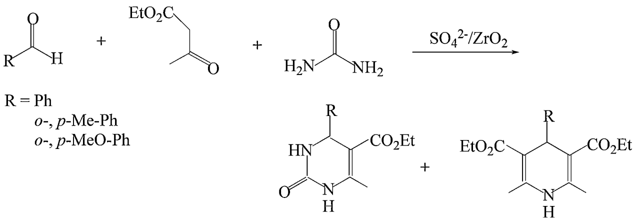


Scheme 9

Lin and co-workers showed that sulfated zirconia effectively catalyzes the reaction between aniline and trimethyl orthoformate to form formamidine with a yield of 97% at 40 °C;[67] formamidine and its derivatives are ligands for coordination compounds.

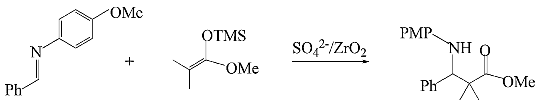
$$2\ \mathrm{Ph{-}NH_2} + \mathrm{HC(OMe)_3} \rightarrow \mathrm{Ph{-}N{=}CHNH{-}Ph} + 3\ \mathrm{MeOH}$$

Beltran and co-workers showed the synthesis of 1,4-dihydropyridines (Hantzsch products) and/or Biginelli products [3,4-dihydropyrimidin-2(1H)-ones] depending on the reaction temperature, an increase of the latter at elevated temperatures (Scheme 10).[68]



Scheme 10

The Mannich-type reaction of ketene silyl acetals and aldimines catalyzed by sulfated zirconia proceeded smoothly to afford β-amino esters (Scheme 11).[69]



Scheme 11

3. Miscellaneous reactions

Toshima and co-workers showed that the stereoselective and direct construction of both the α- and β-manno- and 2-deoxyglucopyranosides is conducted with manno- and 2-deoxyglucopyranosyl fluorides and alcohols in MeCN or in the presence of Molecular sieve 5A in Et_2O when catalyzed by sulfated zirconia (Scheme 12).[70–72]

Their other related work is glycosidations of glucopyranosyl diethyl phosphate,[73] mannopyranosyl sulfoxides,[74] and 2-iodo-olivosyl fluoride.[75]

Benzal chloride, which is one of *gem*-dihalides, was synthesized for the first time from the reaction of benzaldehyde with benzoyl chloride in the presence of solid acids; *gem*-dihalides

Table 5 Reactions of amines and the related compounds

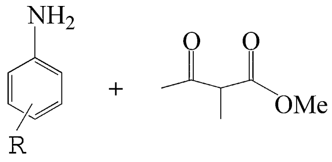
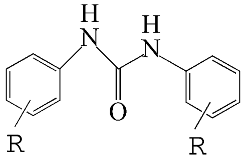
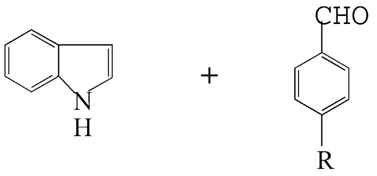
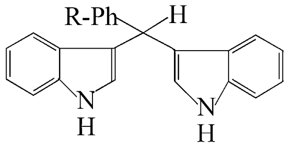
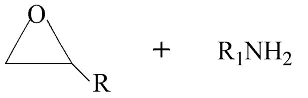
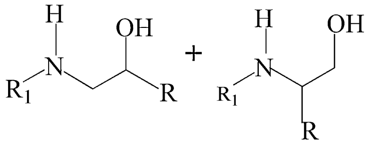
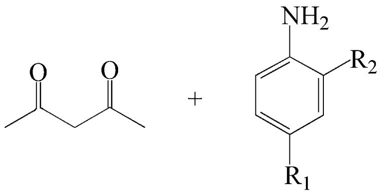
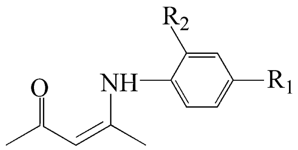
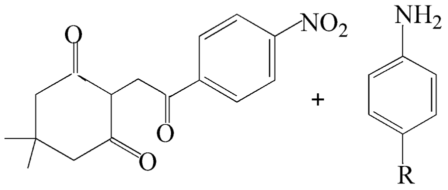
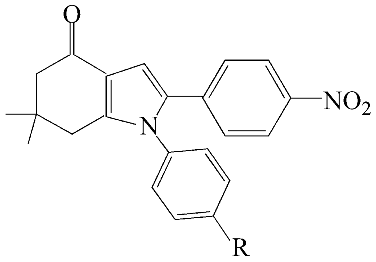
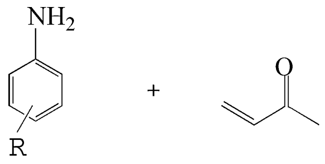
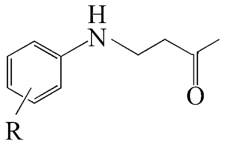
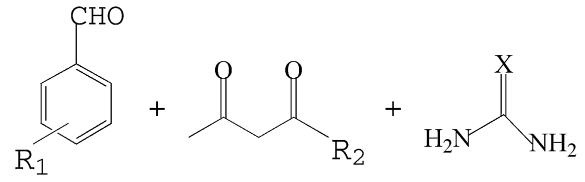
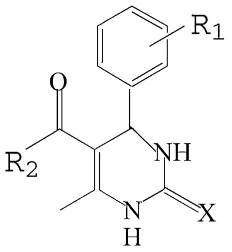
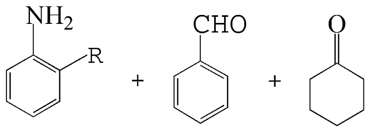
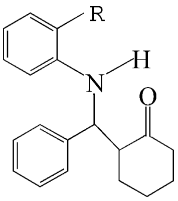
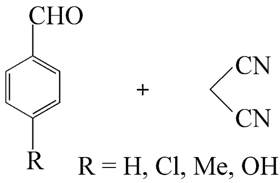
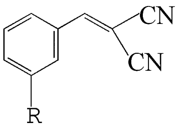
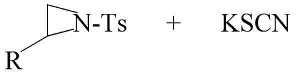
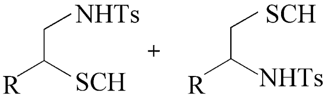
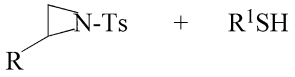
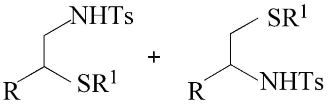
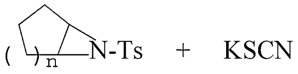
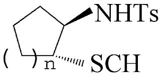
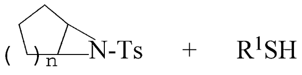
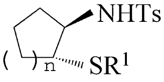
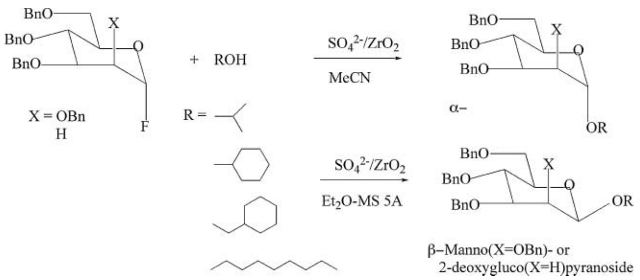
Entry	Reaction	Products	Catalyst
1	 R = H, Me, OMe, OH, Cl, F		MoO_3/ZrO_2
2	 R = H, OMe, NO_2		SO_4^{2-}/ZrO_2
3	 R_1=Ph, $PhCH_2$		SO_4^{2-}/ZrO_2
4	 R_1 = H, Me, Cl R_2 = H, Me, Br		SO_4^{2-}/ZrO_2
5	 R = H, Me, OMe, F, Cl, Br, I, NO_2		SO_4^{2-}/ZrO_2
6	 R = Me, Cl		SO_4^{2-}/ZrO_2
7	 R_1 = H, *p*-Cl *p*-OMe *m*-, *p*-NO_2 R_2 = Me, Ph OEt		SO_4^{2-}/ZrO_2, SO_4^{2-}/SnO_2

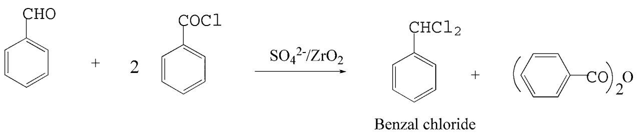
Table 5 *(Contd.)*

Entry	Reaction	Products	Catalyst
8	 R = H, Cl, OMe		WO_3/ZrO_2, $SO_4^{2-}/CeO_2–ZrO_2$
9	 R = H, Cl, Me, OH, OMe, CN, NO_2		SO_4^{2-}/ZrO_2
10	 R=aryl,alkyl		SO_4^{2-}/ZrO_2
11	 R=aryl,alkyl R^1=aryl		SO_4^{2-}/ZrO_2
12	 n=1,2	 n=1,2	SO_4^{2-}/ZrO_2
13	 n=1,2 R^1=aryl	 n=1,2	SO_4^{2-}/ZrO_2



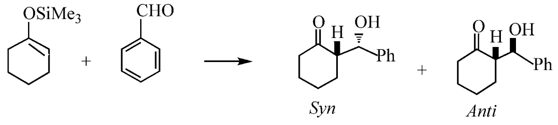
Scheme 12

are important intermediates in the pharmaceutical, agricultural and dye industries (Scheme 13).[76]



Scheme 13

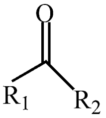
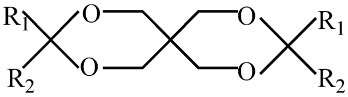
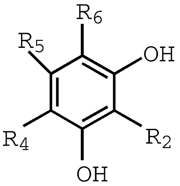
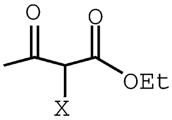
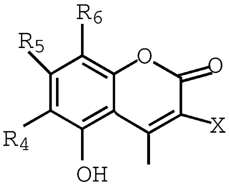
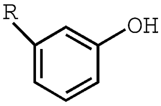
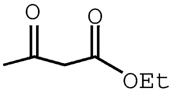
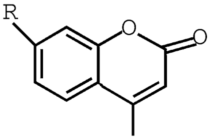
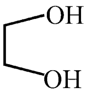
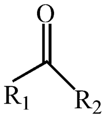
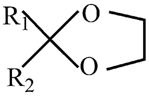
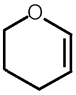
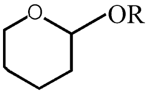
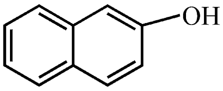
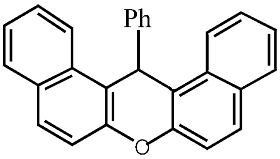
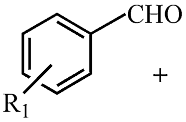
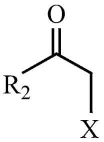
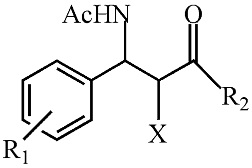
The cross aldol reaction of 1-trimethylsilyloxy-1-cyclohexene with benzaldehyde afforded diastereoselectively aldols with preferential *syn* selectivity over SO_4^{2-}/TiO_2, WO_3/ZrO_2, and WO_3/TiO_2, and *anti* selectivity over SO_4^{2-}/ZrO_2; SO_4^{2-}/SnO_2, SO_4^{2-}/Al_2O_3, and MoO_3/ZrO_2 gave both products (Scheme 14).[77]



Scheme 14

The following is several reactions of alcohols, well used for the acid-catalyzed reaction, as summarized in Table 6 together with reactions of aldehydes. Those are the synthesis of diacetals from 2,2-bis(hydroxymethyl)-1,3-propanediol with aldehydes and ketones (Entry 1),[78] the synthesis of coumarins

Table 6 Reactions of alcohols and ketones

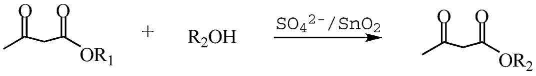
Entry	Reaction	Products	Catalyst
1	 + $C(CH_2OH)_4$		SO_4^{2-}/ZrO_2
2	 + 		SO_4^{2-}/SnO_2, WO_3/ZrO_2
3	 + 		SO_4^{2-}/ZrO_2
4	 + 		Pt–MoO_3/ZrO_2
5	R-OH + 		SO_4^{2-}/ZrO_2
6	Ph-CHO + 2 		WO_3/ZrO_2
7	 +  + CH_3COCl CH_3CN		SO_4^{2-}/ZrO_2
8	Ph-CHO + Ac_2O	Ph-CH$(OAc)_2$	SO_4^{2-}/SnO_2

(Entry 2),[53,61] the coumarin synthesis by Pechmann reaction using *m*-aminophenol (Entry 3),[79,80] protection of carbonyl compounds (Entry 4),[53] tetrahydropyranylation of alcohols (Entry 5),[53] and the synthesis of benzoxanthenes with biological and therapeutic properties (Entry 6).[81] The synthesis of β-acetamido carbonyl compounds and the synthesis and protection of 1,1-diacetates are reported (Entry 7,8).[82,83]

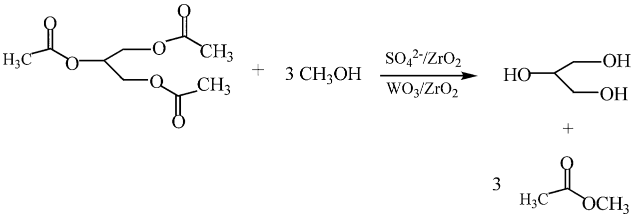
The synthesis of esters is one of the typical reactions catalyzed by acids. Table 7 summarizes the syntheses performed with the present catalysts.

Transesterifications are also reported as follows,

1. β-Ketoesters with alcohols,[100]



2. Triacetin with methanol,[101]



3. Methyl salicylate with phenol.[102]

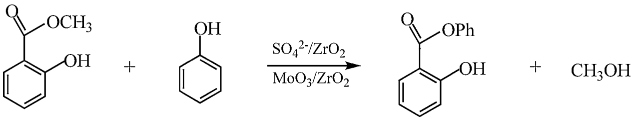


Table 7 The syntheses of esters from acids and alcohols over superacidic metal oxides

Acid	Alcohol	Catalyst	Reference
Acetic acid	Methyl ~ Butyl alcohol	SO_4^{2-}/ZrO_2	84
Acrylic, Salicylic acid	Methyl, Ethyl alcohol	SO_4^{2-}/TiO_2, SO_4^{2-}/ZrO_2	85
Phthalic, Terephthalic acid	*n*-Octyl, 2-Ethylhexyl alcohol	SO_4^{2-}/TiO_2, SO_4^{2-}/ZrO_2	85
Phthalic anhydride	2-Ethylhexyl alcohol	SO_4^{2-}/ZrO_2	86
Phthalic anhydride	2-Ethylhexyl alcohol	SO_4^{2-}/TiO_2, SO_4^{2-}/Al_2O_3, SO_4^{2-}/SnO_2	87
Mandelic acid	Methyl ~ Octyl, Benzyl alcohol	SO_4^{2-}/TiO_2	88
Acetic anhydride	Alcohols	WO_3/ZrO_2	89
Acetic acid	Cyclohexanol	SO_4^{2-}/TiO_2	90
Acetic acid	Butyl alcohol	$SO_4^{2-}/ZrO_2–Fe_2O_3\text{-}SiO_2$	91
Palmitic acid	Methyl alcohol	WO_3/ZrO_2	92
Sebacic, Adipic, Caproic acid	2-Ethylhexanol, Diethyleneglycol, Pentaerythritol	SO_4^{2-}/ZrO_2	93
Acetic, Benzoic, Oxalic, Malonic acid	Methyl, Butyl, Benzyl alcohol, Ethylene glycol	WO_3/ZrO_2	53
Dodecanoic acid	Methyl, Propyl, 2-Ethylhexyl alcohol	SO_4^{2-}/ZrO_2	94
Acetic acid	Butyl alcohol	SO_4^{2-}/ZrO_2	95
Sebacic acid, Phthalic anhydride	Ethyl, 2-Octyl alcohol	SO_4^{2-}/TiO_2	96
n-Octanoic acid	Methyl alcohol	SO_4^{2-}/SnO_2, WO_3/SnO_2	97–99

Furuta and coworkers studied the *trans*-esterification of soybean oil with methanol and found $WO_3/ZrO_2–Al_2O_3$ to be a promising catalyst for the production of biodiesel fuels from soybean oil.[103] Several papers on this study were also published very recently, the catalysts being WO_3/ZrO_2,[104] SO_4^{2-}/ZrO_2,[105] SO_4^{2-}/TiO_2,[106] and $SO_4^{2-}/ZrO_2–SiO_2$.[107]

Conclusion

Liquid superacids are not recognized as environmentally friendly at the present time. Solid superacids of sulfated and supported metal oxides offer new opportunities for developing environmentally benign and friendly processes in organic syntheses.

I have attempted to present the recent studies on syntheses of organic compounds catalyzed by solid superacids of sulfated and supported metal oxides. The acid strength of sulfated zirconia, however, has been a subject of debate; several workers came to the conclusion that it is not a superacid, but a strong acid with an acid strength similar to 100% H_2SO_4 or the acidic zeolites. For the answer to this question, we tried the use of Ar as a probe atom for the evaluation of the acid strength of solid superacids, and it was shown that the acid strength of the present catalysts is higher than that of any zeolites, determined by new methods of temperature-programmed desorption of Ar and of the heat of adsorption of Ar.[108–112]

The studies of organic synthesis have been limited to a few of the catalytic materials, mainly sulfated zirconia. All the materials prepared show their own catalytic properties; it is advisable that other superacidic substances should be extensively studied.

References

1 N. F. Hall and J. B. Conant, *J. Am. Chem. Soc.*, 1927, **49**, 3047.
2 R. J. Gillespie and T. E. Peel, *J. Am. Chem. Soc.*, 1973, **95**, 5173.
3 G. A. Olah, G. K. S. Prakash and J. Sommer, *Science*, 1979, **206**, 13.
4 G. A. Olah, G. K. S. Prakash and J. Sommer, *Superacids*, 1985, Wiley, New York.
5 K. Arata, *Adv. Catal.*, 1990, **37**, 165.
6 K. Arata and M. Hino, *Mater. Chem. Phys.*, 1990, **26**, 213 and references cited therein.
7 K. Arata, *Appl. Catal., A*, 1996, **146**, 3 and references cited therein.
8 M. Hino and K. Arata, *Chem. Lett.*, 1979, 1259.
9 X. Song and A. Sayari, *Catal. Rev. Sci. Eng.*, 1996, **38**, 329.
10 K. Arata, H. Matsuhashi, M. Hino and H. Nakamura, *Catal. Today*, 2003, **81**, 17 and references cited therein.
11 R. J. Gillespie, T. E. Peel and E. A. Robinson, *J. Am. Chem. Soc.*, 1971, **93**, 5083.
12 M. Hino, M. Kurashige, H. Matsuhashi and K. Arata, *Thermochim. Acta*, 2006, **441**, 35.
13 K. Arata, *J. Jpn. Pet. Inst.*, 1996, **39**, 185.
14 M. Hino and K. Arata, *Chem. Lett.*, 1979, 477.
15 D. A. Ward and E. I. Ko, *J. Catal.*, 1994, **150**, 18; 1995, **157**, 321.
16 K. Arata, Preparation of Superacidic Metal Oxides and Their Catalytic Actionin *Metal Oxide Catalysis*, ed. S. D. Jackson and J. S. J. Hargreaves, 2008, Wiley-VCH, Weinheim, Germany.
17 K. Arata, *Trends Phys. Chem.*, 1991, **2**, 1 and references cited therein.
18 H. Suja, C. S. Deepa, K. Sreejarani and S. Sugunan, *React. Kinet. Catal. Lett.*, 2003, **79**, 373.
19 G. D. Yadav and A. D. Murkute, *J. Catal.*, 2004, **224**, 218.
20 K. R. Sunajadevi and S. Sugunan, *React. Kinet. Catal. Lett.*, 2004, **82**, 11.
21 K. R. Sunajadevi and S. Sugunan, *Catal. Commun.*, 2004, **5**, 575.
22 G. A. Olah, *Friedel–Crafts and Related Reactions* 1963-1964, Wiley-Interscience, New York-London, Vol. I-IV.
23 G. A. Olah, *Friedel–Crafts Chemistry*, Wiley-Interscience, New York-London-Sydney-Toronto, 1973.
24 M. Hino and K. Arata, *J. Chem. Soc., Chem. Commun.*, 1985, 112.
25 K. Arata and M. Hino, *Appl. Catal.*, 1990, **59**, 197.
26 K. Arata, H. Nakamura and M. Shouji, *Appl. Catal., A*, 2000, **197**, 213.
27 J. Deutsch, A. Trunschke, D. Muller, V. Quaschning, E. Kemnitz and H. Lieske, *J. Mol. Catal. A: Chem.*, 2004, **207**, 51.
28 Y. Xia, W. Hua and Z. Goa, *Catal. Lett.*, 1998, **55**, 101.
29 H. Suja, C. S. Deepa, K. SreejaRani and S. Sugunan, *Appl. Catal., A*, 2002, **230**, 233.
30 S. Goto, M. Goto and Y. Kimura, *React. Kinet. Catal. Lett.*, 1990, **41**, 27.
31 Y. Du, S. Liu, Y. Zhang, C. Yin, Y. Di and F.-S. Xiao, *Catal. Lett.*, 2006, **108**, 155.
32 T.-S. Jin, M.-N. Yang, G.-L. Feng and T.-S. Li, *Synth. Commun.*, 2004, **34**, 479.
33 T.-S. Jin, M.-N. Yang, G.-L. Feng and T.-S. Li, *J. Chem. Res. (S)*, 2003, 721.
34 H. Nakamura and K. Arata, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1893.
35 B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Graille and D. Pioch, *J. Org. Chem.*, 1986, **51**, 2128.
36 H. Nakamura, Y. Kashiwara and K. Arata, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1071.
37 C. Nakagawa and H. Nakamura, unpublished data.

38 K. R. Sunajadevi and S. Sugunan, *Catal. Commun.*, 2005, **6**, 611.
39 K. Parida, V. Quaschning, E. Lieske and E. Kemnitz, *J. Mater. Chem.*, 2001, **11**, 1903.
40 P. T. Patil, K. M. Malshe, P. Kumar, M. K. Dongare and E. Kemnitz, *Catal. Commun.*, 2002, **3**, 411.
41 V. Quaschning, J. Deutsch, P. Druska, H.-J. Niclas and E. Kemnitz, *J. Catal.*, 1998, **177**, 164.
42 V. Quaschning, A. Auroux, J. Deutsch, H. Lieske and E. Kemnitz, *J. Catal.*, 2001, **203**, 426.
43 A. Trunschke, J. Deutsch, D. Muller, H. Lieske, V. Quaschning and E. Kemnitz, *Catal. Lett.*, 2002, **83**, 271.
44 E. Ghedini, M. Signoretto, F. Pinna, G. Cerrato and C. Morterra, *Appl. Catal., B*, 2006, **67**, 24.
45 J. Deutsch, V. Quaschning, E. Kemnitz, A. Auroux, H. Ehwald and H. Lieske, *Top. Catal.*, 2000, **13**, 281.
46 J. Deutsch, A. Trunschke, D. Muller, V. Quaschning, E. Kemnitz and H. Lieske, *Catal. Lett.*, 2003, **88**, 9.
47 J. Deutsch, H. A. Prescott, D. Muller, E. Kemnitz and H. Lieske, *J. Catal.*, 2005, **231**, 269.
48 A. Breda, M. Signoretto, E. Ghedini, F. Pinna and G. Cruciani, *Appl. Catal., A*, 2006, **308**, 216.
49 A. Bordoloi, N. T. Mathew, B. M. Devassy, S. P. Mirajkar and S. B. Halligudi, *J. Mol. Catal. A: Chem.*, 2006, **247**, 58.
50 K. Biro, S. Bekassy, B. Agai and F. Figueras, *J. Mol. Catal. A: Chem.*, 2000, **151**, 179.
51 K. Biro, F. Figueras and S. Bekassy, *Appl. Catal., A*, 2002, **229**, 235.
52 B. M. Reddy and P. M. Sreekanth, *Tetrahedron Lett.*, 2003, **44**, 4447.
53 B. M. Reddy, P. M. Sreekanth and V. R. Reddy, *J. Mol. Catal. A: Chem.*, 2005, **225**, 71.
54 B. M. Reddy, P. M. Sreekanth and P. Lakshmanan, *J. Mol. Catal. A: Chem.*, 2005, **237**, 93.
55 B. M. Reddy, M. K. Patil, B. T. Reddy and S.-E. Park, *Catal. Commun.*, 2008, **9**, 950.
56 G. Negron-Silva, C. X. Hernandez-Reyes, D. Angeles-Beltran, L. Lomas-Romero, E. Gonzalez-Zamora and J. Mendez-Vivar, *Molecules*, 2007, **12**, 2515.
57 Z.-H. Zhang and L.-M. Song, *J. Chem. Research*, 2005, 817.
58 G. Negron, D. Angeles, L. Lomas, A. Martinez, M. Ramirez and R. Martinez, *Heterocycles*, 2004, **63**, 367.
59 B. M. Reddy, M. K. Patil and B. T. Reddy, *Catal. Lett.*, 2008, **126**, 413.
60 D. Kumar, M. S. Sundaree and B. G. Mishra, *Chem. Lett.*, 2006, **35**, 1074.
61 M. Sowmiya, A. Sharma, S. Parsodkar, B. G. Mishra and A. Dubey, *Appl. Catal., A*, 2007, **333**, 272.
62 B. M. Reddy, P. M. Sreekanth, P. Lakshmanan and A. Khan, *J. Mol. Catal. A: Chem.*, 2006, **244**, 1.
63 B. M. Reddy, M. K. Patil and B. T. Reddy, *Catal. Lett.*, 2008, **125**, 97.
64 B. M. Reddy, M. K. Patil, K. N. Rao and G. K. Reddy, *J. Mol. Catal. A: Chem.*, 2006, **258**, 302.
65 B. Das, R. Ramu, B. Ravikanth and K. R. Reddy, *Tetrahedron Lett.*, 2006, **47**, 779.
66 T.-S. Jin, G.-L. Feng, M. N. Yang and T.-S. Li, *J. Chem. Research (S)*, 2003, 591.
67 C.-H. Lin, C.-H. Tsai and H.-C. Chang, *Catal. Lett.*, 2005, **104**, 135.
68 D. Angeles-Beltran, L. Lomas-Romero, V. H. Lara-Corona, E. Gonzalez-Zamora and G. Negron-Silva, *Molecules*, 2006, **11**, 731.
69 S. Wang, S. Matsumura and K. Toshima, *Tetrahedron Lett.*, 2007, **48**, 6449.
70 K. Toshima, H. Nagai, K. Kasumi, K. Kawahara and S. Matsumura, *Tetrahedron*, 2004, **60**, 5331.
71 K. Toshima, K. Kasumi and S. Matsumura, *Synlett*, 1998, 643.
72 K. Toshima, K. Kasumi and S. Matsumura, *Synlett*, 1999, 813.
73 H. Nagai, S. Matsumura and K. Toshima, *Tetrahedron Lett.*, 2002, **43**, 847.
74 H. Nagai, K. Kawahara, S. Matsumura and K. Toshima, *Tetrahedron Lett.*, 2001, **42**, 4159.
75 K. Toshima, K. Uehara, H. Nagai and S. Matsumura, *Green Chem.*, 2002, **4**, 27.
76 A. Wolfson, O. Shokin and D. Tavor, *J. Mol. Catal. A: Chem.*, 2005, **226**, 69.
77 H. Nakamura, H. Matsuhashi and K. Arata, *Synlett*, 2000, 668.
78 T. Jin, M. Yang, X. Wang, G. Feng and T. Li, *J. Chem. Res.*, 2004, 203.
79 B. Tyagi, M. K. Mishra and R. V. Jasra, *J. Mol. Catal. A: Chem.*, 2007, **276**, 47.
80 B. Tyagi, M. K. Mishra and R. V. Jasra, *J. Mol. Catal. A: Chem.*, 2008, **286**, 41.
81 L. Nagarapu, M. Baseeruddin, N. V. Kumari, S. Kantevari and A. P. Rudradas, *Synth. Commun.*, 2007, **37**, 2519.
82 B. Das, M. Krishnaiah, K. Laxminarayana and K. R. Reddy, *J. Mol. Catal. A: Chem.*, 2007, **270**, 284.
83 J. R. Satam and R. V. Jayaram, *Catal. Commun.*, 2007, **8**, 1414.
84 M. Hino and K. Arata, *Chem. Lett.*, 1981, 1671.
85 M. Hino and K. Arata, *Appl. Catal.*, 1985, **18**, 401.
86 T. S. Thorat, V. M. Yadav and G. D. Yadav, *Appl. Catal. A*, 1992, **90**, 73.
87 G. Lu, *Appl. Catal., A*, 1995, **133**, 11.
88 T.-S. Jin, Y.-R. Ma, Y. Li, X. Sun and T.-S. Li, *Synth. Commun.*, 2001, **31**, 2051.
89 B. M. Reddy and P. M. Sreekanth, *Synth. Commun.*, 2002, **32**, 2815.
90 C.-H. Lin, S.-H. Chien, J.-H. Chao, C.-Y. Sheu, Y.-C. Cheng, Y.-J. Huang and C.-H. Tsai, *Catal. Lett.*, 2002, **80**, 153.
91 W. Chu, J. Hu, Z. Xie and Q. Chen, *Catal. Today*, 2004, **90**, 349.
92 S. Ramu, N. Lingaiah, B. L. A. P. Davi, R. B. N. Prasad, I. Suryanarayana and P. S. S. Prasad, *Appl. Catal., A*, 2004, **276**, 163.
93 F. T. Sejidov, Y. Mansoori and N. Goodarzi, *J. Mol. Catal. A: Chem.*, 2005, **240**, 186.
94 A. A. Kiss, A. C. Dimian and G. Rothenberg, *Adv. Synth. Catal.*, 2006, **348**, 75.
95 T. A. Peters, N. E. Benes, A. Holmen and Jos T. F. Keurentjes, *Appl. Catal., A*, 2006, **297**, 182.
96 M. K. Moghaddam and M. R. Gholami, *Mater. Lett.*, 2006, **60**, 715.
97 S. Furuta, H. Matsuhashi and K. Arata, *Appl. Catal., A*, 2004, **269**, 187.
98 M. Hino, S. Takasaki, S. Furuta, H. Matsuhashi and K. Arata, *Catal. Commun.*, 2006, **7**, 162.
99 M. Hino, S. Takasaki, S. Furuta, H. Matsuhashi and K. Arata, *Appl. Catal., A*, 2007, **321**, 147.
100 S. P. Chavan, P. K. Zubaidha, S. W. Dantale, A. Keshavaraja, A. V. Ramaswamy and T. Ravindranathan, *Tetrahedron Lett.*, 1996, **37**, 233.
101 D. E. Lopez, J. G. Goodwin Jr., D. A. Bruce and E. Lotero, *Appl. Catal., A*, 2005, **295**, 97.
102 S. Z. M. Shamshuddin and N. Nagaraju, *Catal. Commun.*, 2006, **7**, 593.
103 S. Furuta, H. Matsuhashi and K. Arata, *Catal. Commun.*, 2004, **5**, 721.
104 Y.-M. Park, D.-W. Lee, D.-K. Kim, J.-S. Lee and K. Y. Lee, *Catal. Today*, 2008, **131**, 238.
105 A. S. Dias, S. Lima, M. Pillinger and A. A. Valente, *Catal. Lett.*, 2007, **114**, 151.
106 R. M. de Almeida, L. K. Noda, N. S. Goncalves, S. M. P. Meneghetti and M. R. Meneghetti, *Appl. Catal., A*, 2008, **347**, 100.
107 X.-R. Chen, Y.-H. Ju and C.-Y. Mou, *J. Phys. Chem. C*, 2007, **111**, 18731.
108 H. Matsuhashi and K. Arata, *Chem. Commun.*, 2000, 387.
109 H. Matsuhashi and K. Arata, *Catal. Surv. Asia*, 2006, **10**, 1.
110 H. Matsuhashi, T. Tanaka and K. Arata, *J. Phys. Chem. B*, 2001, **105**, 9669.
111 H. Matsuhashi and K. Arata, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2529.
112 H. Matsuhashi and A. Futamura, *Catal. Today*, 2006, **111**, 338.