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Preparation of SO_4^{2-}/ TiO_2-La_2O_3 solid superacid and its catalytic activities in acetalation and ketalation[*]

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Abstract: SO_4^{2-} / TiO_2-La_2O_3, a novel solid superacid, was prepared and its catalytic activities at different synthetic conditions are discussed with esterification of *n*-butanoic acid and *n*-butyl alcohol as probing reaction. The optimum conditions have also been found, mole ratio of $n(La^{3+})$:$n(Ti^{4+})$ is 1:34, the soaked consistency of H_2SO_4 is 0.8 mol/L, the soaked time of H_2SO_4 is 24 h, the calcining temperature is 480 °C, the calcining time is 3 h. Then it was applied in the catalytic synthesis of ten important ketals and acetals as catalyst and revealed high catalytic activity. Under these conditions on which the molar ratio of aldehyde/ketone to glycol is 1:1.5, the mass ratio of the catalyst used in the reactants is 0.5%, and the reaction time is 1.0 h, the yields of ketals and acetals can reach 41.4%~95.8%.

Key words: SO_4^{2-} / TiO_2-La_2O_3, Rare earth, Solid superacid, Catalysis
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INTRODUCTION

There is considerable interest in synthesizing acetals and ketals as important perfume substances and industrial raw materials of organic synthesis (Loader and Anderson, 1978; Dhrubojyoti *et al*., 1999; Wang *et al*., 1992b). Concentrated sulfuric acid and other analogous Brönsted acids used as catalysts in industrial processes for many years, exposed their defects, such as the corrosion of the reactors, difficulties in product separation and catalyst recovery, pollution by acidic waste water, poor quality of the products, etc. The alternative catalysts, for example, transition metal salt (Dhrubojyoti *et al*., 1999; Li and Cheng, 2001), $TiSiW_{12}O_{40}/TiO_2$ (Yang *et al*., 2003), tungstosilicic acid supported on active carbon (Yang *et al*., 2005a), montmorillonite K 10 (Li *et al*., 1996), solid superacid (Wang *et al*., 1992b), have been developed for environmental protection and techno-economical profit. Among substitutes, much attention has been paid to solid superacids in various industrial processes due to their successful application in several important acid-catalyzed reactions (esterification, acelation) (Wang *et al*., 1992b; Kirbaslar *et al*., 2001; Hess and Kemnitz, 1997). Lu and Zu (2002) reported that the SO_4^{2-}-M_xO_y-type solid superacid has excellent catalytic activity for esterification due to its super acidity in heterogeneous systems. However, the structural stability and the catalytic activity should be further improved. It was suggested that intermingling SO_4^{2-}-M_xO_y with transition metal oxides was a possible method for solving the above problems (Ma and Li, 2002; Yang *et al*., 2005b). We found it had better catalytic activity when La_2O_3 was selected.

In this paper, we report the compositing method

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for a new kind of solid superacid-SO_4^{2-}/TiO_2-La_2O_3 and discuss its catalytic activity under different synthetic conditions, esterification of *n*-butanoic acid and *n*-butyl alcohol as probing reaction. Solid superacid-SO_4^{2-}/TiO_2-La_2O_3 was used as catalyst to synthesize acetals and ketals for the first time and the corresponding catalytic activity was investigated.

EXPERIMENTAL DETAILS

Materials and measurements

All chemicals were commercial products of reagent grade. The X-ray powder diffraction pattern of the powder samples was measured by a Rigaku model XRD-6000 X-ray diffractometer employing Cu K_α radiation with the accelerating voltage 40 kV and applied current of 30 mA, respectively in scanning range of 2θ of 10°~70°. The infrared spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer with liquid membrane in the 400~4000 cm^{-1} region. ^1H NMR spectra were determined on a MERCURY-VX 300 MHz spectrometer with tetramethylsilane (TMS) as internal standard in $CDCl_3$. The SO_4^{2-} and La_2O_3 content in the SO_4^{2-}/TiO_2-La_2O_3 were determined by chemical analysis.

Preparation of SO_4^{2-}/TiO_2-La_2O_3

SO_4^{2-}/TiO_2-La_2O_3 was prepared as follows. Hydroxides or oxides of Ti and La were obtained by dissolving chloride of Ti and La in water, hydrolyzing with aqueous ammonia to pH=8~9 in solution, washing the precipitate, drying at 110 °C, and powdering it. The precipitates were treated with sulfate ion by immersing the dried Ti-La-O substrate in 0.8 mol/L H_2SO_4 solution for 24 h, then filtered, dried, and calcinated in furnace at 480 °C for 3 h. Finally the catalysts were stored in a desiccator until use. The microstructure of SO_4^{2-}/TiO_2-La_2O_3 was identified by means of FT-IR and XRD.

Determination of sulphate content

Sulphate-modified TiO_2-La_2O_3 samples calcined at different temperatures were fused by $m(ZnO)$:$m(Na_2CO_3)=4:1$, and extracted with water. The filtrate was titrated for sulphate estimation by the standard procedure (Gao *et al.*, 1994).

Acid strength measurement of catalysts

The acid strengths of the catalysts were examined by the colour change method using the Hammett indicator (Gao *et al.*, 1992), when a powdered sample was added to an indicator dissolved in dry benzene.

Synthesis of acetals and ketals

The reaction was carried out in a three-neck flask equipped with a stirrer, a reflux condenser and a thermometer. Certain amounts of ethyl acetoacetate, cyclohexanone, butanone, butyraldehyde, benzaldehyde were added separately with alcohol (ethylene glycol or 1,2-propylene glycol) and the catalyst. The solution was heated to boiling and refluxed until no water flowed off, then distilled after ridding the water anhydrous magnesium sulfate to obtain the desired product.

RESULTS AND DISCUSSION

Solid-state structure of the complexes

1. Infrared spectra of SO_4^{2-}/TiO_2-La_2O_3

Fig.1 shows the IR spectra of SO_4^{2-}/TiO_2-La_2O_3. Infrared spectrum of solid samples (Fig.1) showed that the characteristic peaks of SO_4^{2-}/TiO_2-La_2O_3 are at 1379 cm^{-1}, 1132 cm^{-1} and 1043 cm^{-1}, indicating sulphurous species on the catalyst surface (Gao *et al.*, 1996) and provide the corner of strong acid by induction, with the result according with reports of SO_4^{2-}-M_xO_y-type solid superacid in (Yin *et al.*, 1994).

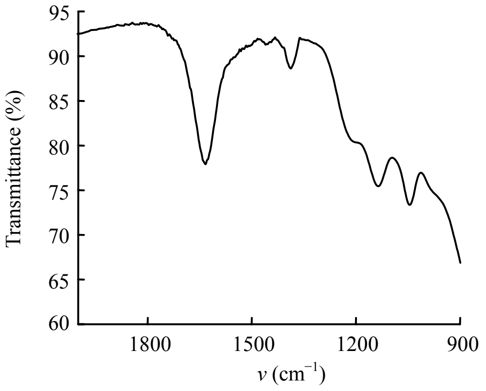


Fig.1 IR spectra of SO_4^{2-}/TiO_2-La_2O_3

Generally, there are two absorption bands in the infrared spectrum of SO_4^{2-}-M_xO_y-type solid super acid at 900~1300 cm^{-1} and 1300~1400 cm^{-1}, which can be attributable to the vibration of S=O being similar to that of sulfate and sulfuric ester, respectively. The absorption peaks at low frequency partly show double bond in the former and fully show double bond at high frequency in the latter. And we can surmise that adsorbed water exists in the catalyst compound as shown by the strong and broad peaks at 1636 cm^{-1} and 3415 cm^{-1} attributable to the bending vibrations of H-O-H bond and the stretching vibrations of O-H. The peak at 1383 cm^{-1} is distinguished from the 1630~1620 cm^{-1} sulphate pears for the double coordination between metal ions and SO_4^{2-}.

2. X-ray structure of SO_4^{2-}/TiO_2-La_2O_3

The X-ray powder diffraction spectrum of solid samples (Fig.2) suggests anatase crystalline phase in both SO_4^{2-}/TiO_2 and SO_4^{2-}/TiO_2-La_2O_3 having the same value of diffraction peaks. We did not find the diffraction peaks that La_2O_3 should display, indicating that no sole crystalline phase caused by La_2O_3 and La is dispersed on the catalyst surface in case the amount of La is below a threshold value (Pan and Xie, 2001). The mass fraction of SO_4^{2-} and La_2O_3 in the SO_4^{2-}/TiO_2-La_2O_3 are about 9.48% and 0.70%, respectively.

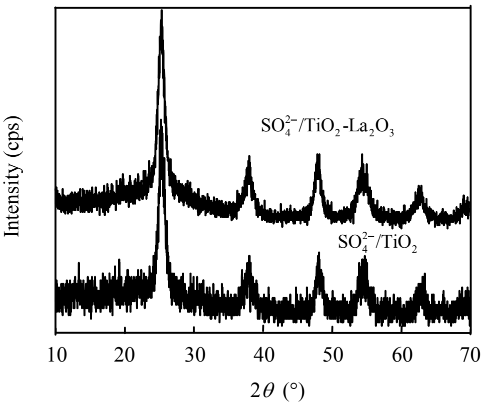


Fig.2 X-ray powder diffraction spectra of SO_4^{2-}/TiO_2-La_2O_3 and SO_4^{2-}/TiO_2

3. Acid strengths of the catalysts

The acid strengths of the catalysts were examined by the colour change method using the Hammett indicator (2,4-dinitroluene (H_o=−14.52), 1,3,5-trinitrotoluene (H_o=−16.04)). It was seen that the Hammett acidity function of SO_4^{2-}/TiO_2-La_2O_3 is $-16.04<H_o<-14.52$.

Effect of preparation conditions on the activity of SO_4^{2-}/TiO_2-La_2O_3 catalysts

The reaction was carried out in a three-neck flask equipped with a stirrer, a reflux condenser and a thermometer. Certain amounts of *n*-butanoic acid and *n*-butyl alcohol were added with molar ratio of acid to alcohol being 1.3:1 separately, mass ratio of the catalyst used in the reactants being 1.5%. The solution was heated to boiling in the range of 94 °C to 112 °C and refluxed for 1 h. To find the optimum reaction factors affecting activities of SO_4^{2-}/TiO_2-La_2O_3, we studied the effects of mole ratio of $n(La^{3+}):n(Ti^{4+})$ included in compound, soaked consistency of H_2SO_4, impregnation time of H_2SO_4, calcination temperature and burnt time on the results shown in Fig.3.

The preparation conditions are important factors affecting the SO_4^{2-}/TiO_2-La_2O_3 properties. The results in Fig.3a show influences of the mole ratio of $n(La^{3+}):n(Ti^{4+})$ on the catalytic activity of SO_4^{2-}/TiO_2-La_2O_3 prepared under the following conditions: impregnation time in 0.8 mol/L H_2SO_4, 24 h; calcinations temperature of SO_4^{2-}/TiO_2-La_2O_3, 480 °C; burnt time, 3 h. The results showed that the SO_4^{2-}/TiO_2-La_2O_3 catalytic activity under mole ratio of $n(La^{3+}):n(Ti^{4+})$=1:34 is relatively higher.

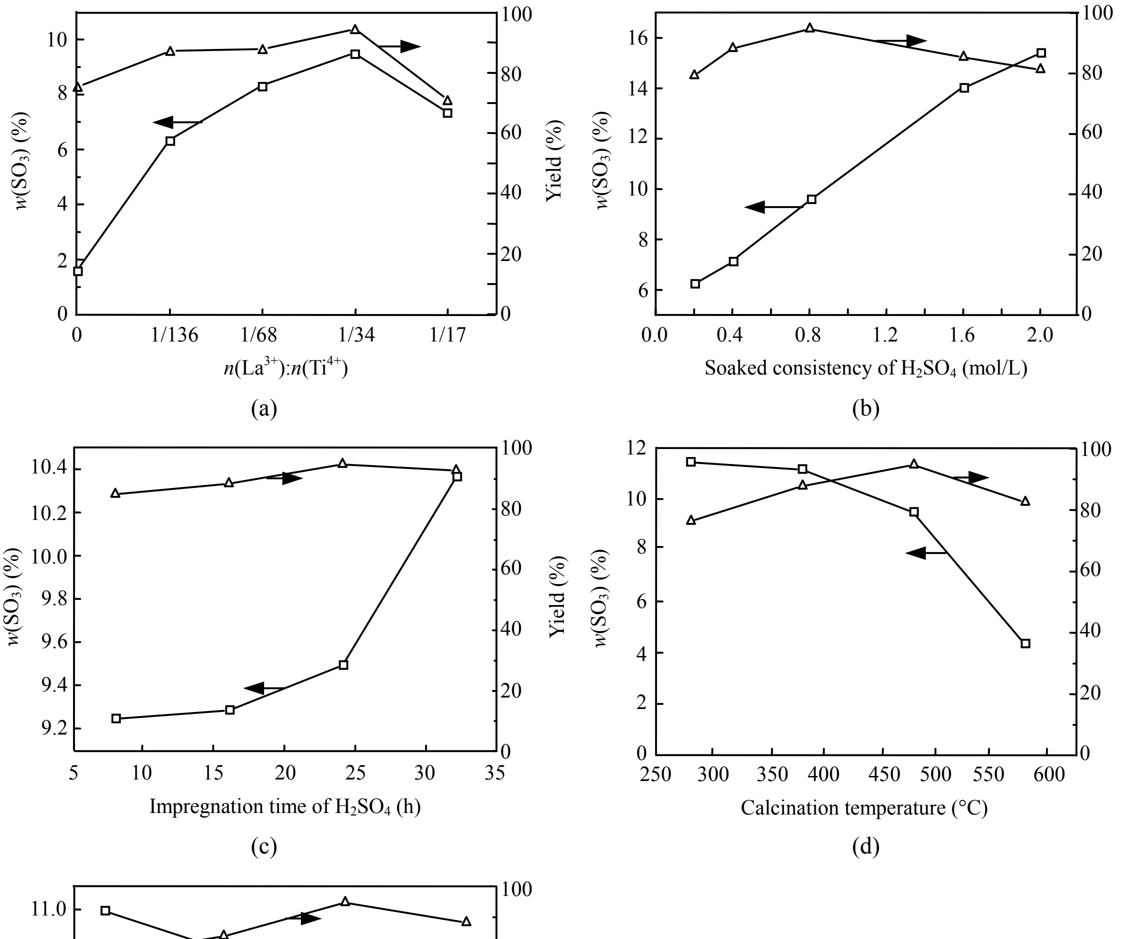
The results in Fig.3b and Fig.3c show the influences of the H_2SO_4 solution concentration used and the impregnation time on the SO_4^{2-}/TiO_2-La_2O_3 activities, showing that immersion of TiO_2-La_2O_3 in 0.8 mol/L H_2SO_4 for 24 h is appropriate for the preparation of SO_4^{2-}/TiO_2-La_2O_3 catalyst, which show higher esterification activity, indicating that a proper amount of SO_4^{2-} on TiO_2-La_2O_3 is necessary to achieve high activity. If the SO_4^{2-} amount added to the catalyst surface is more or less than the proper amount, high SO_4^{2-}/TiO_2-La_2O_3 activity cannot be achieved.

The results in Fig.3d and Fig.3e show influences of calcination temperature and the burnt time on the SO_4^{2-}/TiO_2-La_2O_3 activities. It is known that the calcination temperature in the preparation of a catalyst and the burnt time are key factors, which not only can affect the SO_4^{2-} amount added to the catalyst surface but the activity of the catalysts as well. The results showed that the catalytic activity of $SO_4^{2-}/TiO_2\text{-}La_2O_3$ calcined at about 480 °C for 3 h is higher than that calcined at other temperatures, and that above 480 °C this sulphureous complex gradually decomposes.

We changed only one of the five reaction factors and kept the others constant in the experimental runs, then the optimum conditions were selected. That is, the mole ratio of $n(La^{3+}):n(Ti^{4+})$ is 1:34, the soaked consistency of H_2SO_4 is 0.8 mol/L, impregnation time of H_2SO_4 is 24 h, the calcination temperature is 480 °C, the burnt time is 3 h.

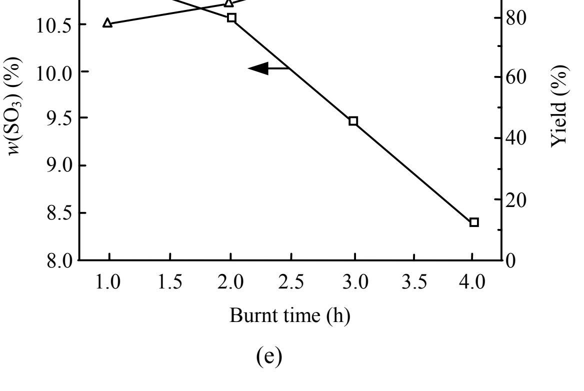
Comparsion of catalytic activity of different catalysts

Table 1 summarizes the activities of $SO_4^{2-}/TiO_2\text{-}La_2O_3$ and H_2SO_4, $H_3PW_{12}O_{40}$ (Zhang *et al.*, 1993) for



(a) (b)

(c) (d)



(e)

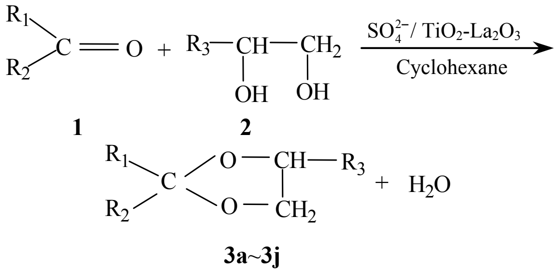
Fig.3 Effects of (a) mole ratio of $n(La^{3+}):n(Ti^{4+})$, (b) soaked consistency of H_2SO_4, (c) impregnation time of H_2SO_4, (d) calcination temperature and (e) burnt time on catalytic activity

esterification of *n*-butanoic acid and *n*-butyl alcohol. The activity of catalysts and other data were obtained at the temperature of the reactant solution reflux.

SO_4^{2-}/TiO_2-La_2O_3 has the most intense catalytic activity among these H_2SO_4 and $H_3PW_{12}O_{40}$ acid catalysts, even if compared on the basis of the catalyst weight and reaction time.

Acetals and ketals

Some equations and experiment results on the synthetic acetals and ketals are listed:



The yield of ten classes of acetals and ketals under typical reaction conditions (molar ratio of aldehyde/ketone to glycol is 1:1.5, the quantity of catalyst is equal to 0.5% of feed stocks, the reaction time is 1.0 h) can reach 41.4%~95.8%. The amount of reactant of aldehyde/ketone was fixed in 0.2 mol with cyclohexane as water-removed reagent. Results of these synthesis reactions are summarized in Table 2.

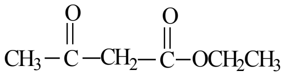
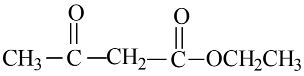
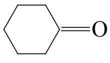
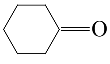
From the data listed in the table, we can find that SO_4^{2-}/TiO_2-La_2O_3 was highly active, leading to yields of ten ketals and acetals up to 95.8% and no less than 41.4% after 1.0 h. Moreover, the reaction temperature was controlled at the reflux temperature and the amount of SO_4^{2-}/TiO_2-La_2O_3 was much lower than that of other catalyst used in these reactions (Wang *et al.*, 1992a; Zhang *et al.*, 1995). All these helped to solve the technical problems of industrial processes.

When the temperature rose, we observed the solution of reagents became dark in color because

Table 1 Comparison of catalytic activities of different catalysts

Catalyst	Molar ratio of alcohol to acid	Reaction time (min)	The highest reaction temperature (°C)	Yield (%)
SO_4^{2-}/TiO_2-La_2O_3	1.3:1	60	114	94.7
H_2SO_4	1.0:1	120	158	72.1
$H_3PW_{12}O_{40}$	1.0:1	113	140	62.5

Table 2 Synthetic results of 10 classes of acetals and ketals

Product	Aldehyde/ketone **1**	Glycol **2**	Range of boiling point (°C)	Refractive index	Yield (%)	IR (cm^{-1})
3a	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_3$	$HO(CH_2)_2OH$	126~128 (6.7 kPa)	1.4325	84.7	1738, 1375, 1244, 1188, 1047
3b	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_3$	$CH_3CH(OH)CH_2OH$	150~154 (6.7 kPa)	1.4275	88.6	1740, 1377, 1244, 1188, 1043
3c		$HO(CH_2)_2OH$	174~180	1.4580	84.3	2937, 2863, 1163, 1104
3d		$CH_3CH(OH)CH_2OH$	172~176	1.4493	84.6	2937, 2864, 1163, 1103
3e	$CH_3CH_2COCH_3$	$HO(CH_2)_2OH$	116~119	1.4105	41.4	1254, 1215, 1194, 1130
3f	$CH_3CH_2COCH_3$	$CH_3CH(OH)CH_2OH$	126~130	1.4102	64.6	1250, 1218, 1194, 1157
3g	$CH_3CH_2CH_2CHO$	$HO(CH_2)_2OH$	130~134	1.4190	95.3	1146, 1123, 1023, 946
3h	$CH_3CH_2CH_2CHO$	$CH_3CH(OH)CH_2OH$	139~144	1.4150	95.8	1150, 1123, 1024, 970
3i	C_6H_5CHO	$HO(CH_2)_2OH$	226~230	1.5264	80.0	1096, 1071, 1028, 947
3j	C_6H_5CHO	$CH_3CH(OH)CH_2OH$	218~222	1.5094	80.8	1097, 1067, 1011, 976

temperature above the optimum condition would decrease the activity of catalyst. More reaction time was needed to keep the yield but the activity began to decrease after two hours. Comparing the 2 alcoholic reactants, the special steric hindrance and the density of electron atmosphere on oxygen atoms exerted opposite effects on yield. The former kept oxygen atoms from approaching carbonium ions and the C-O binding was difficult to form. But the latter decreased the density of electron atmosphere on oxygen atoms bonded with carbonium ions so as to alleviate the rejection of the electron atmosphere of two oxygen atoms. To reactions **3a** and **3j**, the special steric hindrance disadvantageous effect and took the leading role. For the rest, the density of electron atmosphere on oxygen atom predominated.

CONCLUSION

The following conclusions can be drawn from this study: (1) The optimum synthetic conditions of $SO_4^{2-}/TiO_2\text{-}La_2O_3$ are: mole ratio of $n(La^{3+})$:$n(Ti^{4+})$ is 1:34, the soaked consistency of H_2SO_4 is 0.8 mol/L, impregnation time of H_2SO_4 is 24 h, the calcination temperature is 480 °C, the calcining time is 3 h. (2) The molar ratio of aldehyde/ketone to glycol is 1:1.5, the mass ratio of the catalyst used in the reactants is 0.5%, and the reaction time is 1.0 h, the yields of ketals and acetals can reach 41.4%~95.8%. (3) The esterification of *n*-butanoic acid and *n*-butyl alcohol as probing reaction showed efficiently highly catalytic activity of $SO_4^{2-}/TiO_2\text{-}La_2O_3$ at its optimum conditions as catalyst. At the same time, it also shows much higher catalytic activity than other solid acid catalysts, such as H_2SO_4, $H_3PW_{12}O_{40}$, and so on. Valuable products, ten important ketals and acetals have been obtained at high yield.

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