Benzoylation of toluene with benzoyl chloride on Al-promoted sulfated solid superacids

Yongde Xia, Weiming Hua and Zi Gao *

Department of Chemistry, Fudan University, Shanghai 200433, PR China

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The catalytic performance of Al-promoted sulfated zirconia and sulfated titania for benzoylation of toluene with benzoyl chloride has been investigated. The incorporation of Al enhances the catalytic activity of the sulfated oxide catalysts prominently owing to an increase in superacidity of the catalysts. Al-promoted sulfated zirconia catalysts are more active than the analogous sulfated titania catalysts because of their higher superacidity. In particular, $SO_4^{2-}/3\%Al_2O_3–ZrO_2$ is a good clean catalyst for the benzoylation reaction, which gives 100% yield of methylbenzophenones after on stream for 12 h at 110 °C.

Keywords: sulfated zirconia, sulfated titania, promoting effect of Al, superacidity, benzoylation of toluene

1. Introduction

Friedel–Crafts acylation of aromatics is an important reaction producing valuable chemical intermediates. Lewis acids, such as $AlCl_3$ and BF_3, are often used as catalysts for the reaction, and the reaction is completed only when equimolar or an excess of the Friedel–Crafts catalysts is used [1]. For environmental concerns new clean solid acid catalysts, such as Nafion-H [2], $FeSO_4$ [3], SO_4^{2-}/γ-Al_2O_3 [4] and SO_4^{2-}/ZrO_2 [4,5], have been suggested to replace the conventional Friedel–Crafts catalysts. It has been reported in the literature [6–8] that the doping of sulfated zirconia with various transition metals, such as Fe, Mn, Ni, Cr and V, enhances its catalytic activity for n-butane isomerization reaction at low temperature in the absence of H_2, but the doped catalysts are not stable at high temperature in the presence of H_2. However, in our previous work [9], it has been found that Al promotes the catalytic activity and stability of SO_4^{2-}/ZrO_2 for n-butane isomerization more effectively than transition metals at high temperature in the presence of H_2 owing to a significant enhancement of the number of strong acid sites in the Al-promoted catalysts. The promoting effect of Al on sulfated zirconia and titania in the benzoylation of toluene with benzoyl chloride was further investigated in the present work. Benzoylation reaction was carried out on catalysts containing different amount of Al_2O_3, and optimum conditions for the catalytic reaction were explored. The activity of the Al-promoted catalysts was correlated with the data of catalyst characterization and the origin of the promoting effect was discussed.

2. Experimental

Aqueous ammonia was added dropwise to a solution of $ZrOCl_2$, $TiCl_4$ or $Al(NO_3)_3$ till pH = 9–10. The precipitate was washed, filtered, dried at 110 °C and then immersed in a 0.5 M H_2SO_4 solution for 30 min. The sulfated zirconia (SZ), sulfated titania (ST) and sulfated alumina (SA) were dried at 110 °C and then calcined at 650 and 500 °C for 3 h, respectively. Al-promoted catalysts were prepared in the same way from a mixed solution of $ZrOCl_2$ or $TiCl_4$ and $Al(NO_3)_3$, and they were labeled as SZA and STA, respectively.

X-ray powder diffraction measurements were carried out on a Rigaku D/MAX-IIA instrument with Cu Kα radiation at 40 kV and 20 mA. Infrared spectra of the samples were recorded on a Perkin–Elmer 983G spectrometer. The samples were pressed into self-supported disks with a density of 3–5 mg/cm^2 and placed in a quartz cell with CaF_2 windows. BET surface area of the samples was measured on a Micromeritics ASAP 2000 equipment using N_2 as the adsorbent. Sulfur content of the samples was detected by a chemical method. Dehydrated Na_2CO_3 and ZnO were used as fusing agents, and the sulfate was turned into $BaSO_4$ and determined by gravimetric method.

Isomerization of n-butane was performed at 35 °C in a closed reaction system. 0.5 g catalyst was placed in the reactor and 5 ml (STP) of n-butane was injected for each test. Benzoylation of toluene was carried out in a three-necked round bottom flask fitted with a reflux condenser. 1 ml benzoyl chloride, 20 ml toluene and 0.5 g catalyst were added into the flask and heated at 110 °C. The HCl effluent gas was absorbed by a NaOH solution. The products of these two reactions were analyzed by gas chromatography. The yield of methylbenzophenone was based on the amount of benzoyl chloride added into the reaction.

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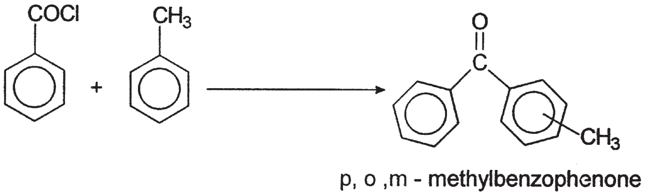
[*] To whom correspondence should be addressed.

3. Results and discussion

The product of the heterogeneous benzoylation of toluene with benzoyl chloride on our catalysts is a mixture of p-, o- and m-methylbenzophenone, and the proportions of the isomers are in the range of p-methylbenzophenone 62–71%, o-methylbenzophenone 28–35% and m-methylbenzophenone 1–3% (scheme 1).

The yields of methylbenzophenones on SZA and STA series catalysts containing different amount of Al_2O_3 at 110 °C are compared in table 1. The yield of methylbenzophenones increases with reaction time. The catalytic activity of the sulfated oxide catalysts is in the order of SZ $>$ ST $>$ SA. For the SZA series of catalysts the catalytic activity increases with Al_2O_3 content up to 3.0 mol% and then decreases as the Al_2O_3 content is further increased. The variation of catalytic activity with Al_2O_3 content for the STA series of catalysts displays the same feature, but the maximum shifts to 1.5 mol% Al_2O_3. The yield of methylbenzophenones for SZA-2 after on stream for 10 h is 93.2%, which is 1.3 times higher than that for SZ, and the yield of methylbenzophenones for STA-2 is also 1.3 times higher than that for ST. Thus, the addition of an appropriate amount of alumina to ZrO_2 or TiO_2 promotes the catalytic activity of the sulfated catalysts for benzoylation of toluene with benzoyl chloride as effectively as what we have observed in n-butane isomerization [9].



Scheme 1.

Table 1
Yields for benzoylation of toluene on different catalysts.[a]

Catalyst	Al_2O_3 (mol%)	Calcination temp. (°C)	Yield (%) 2 h	6 h	10 h
SZ	0	650	32.8	59.5	70.9
SZA-1	1.5	650	38.4	73.1	88.6
SZA-2	3.0	650	58.7	84.3	93.2
SZA-3	6.0	650	37.1	61.3	79.2
SZA-4	10.0	650	29.5	50.3	72.4
SZA-5[b]	15.0	750	25.0	39.0	48.5
ST	0	500	24.4	34.8	41.7
STA-1	0.5	500	24.6	39.6	48.5
STA-2	1.5	500	30.6	45.6	55.3
STA-3	3.0	500	25.0	37.5	44.7
STA-4	6.0	500	23.7	35.4	42.6
STA-5	10.0	500	21.4	30.9	39.5
SA	100	500	5.6	13.4	18.3

[a] Reaction conditions: reaction temperature 110 °C, catalyst amount 0.5 g, benzoyl chloride 1 ml, toluene 20 ml.

[b] Calcination temperature for this catalyst is 750 °C, because ZrO_2 in the catalyst crystallizes at this temperature.

The optimization of reaction conditions was studied using STA-2 as a representative of the sulfated catalysts. Figure 1 shows the effect of reaction temperature on the yield of methylbenzophenones. As the temperature is raised from 70 to 110 °C, the yield of methylbenzophenones increases significantly. The effect of catalyst amount on product yield is shown in figure 2. The yields after on stream for 8 h lie close to each other when the catalyst loads are in the range of 0.25–0.5 g, but the yield is much lower at a catalyst load of 0.125 g. Changing the volume ratio of benzoyl chloride to toluene from 1 : 5 to 1 : 20 has little effect on the product yield, as shown in figure 3.

The activities of SZ, ST, SZA-2 and STA-2 catalysts were compared under optimum reaction conditions and shown in figure 4. The benzoylation of toluene is completed on SZ and SZA-2 at 110 °C. 100% yield of methylbenzophenones is obtained on SZ and SZA-2 at 18 and 12 h, respectively. The reaction rates on ST and STA-2 catalysts are slower. After on stream for 28 h, the product yields on ST and STA-2 are 66.6 and 91.3%, respectively.

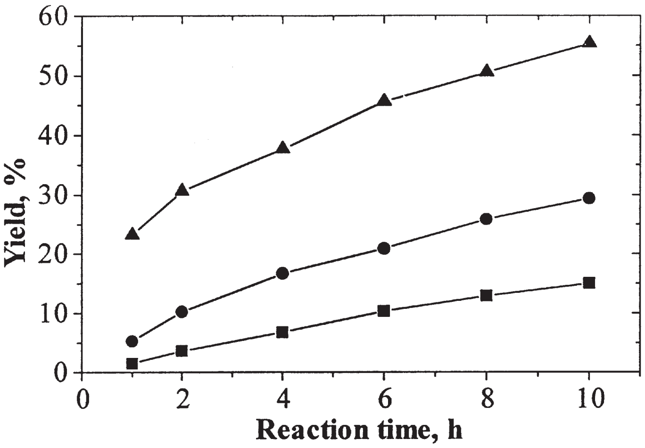


Figure 1. Effect of reaction temperature on product yield: (▲) 110 °C, (●) 90 °C, (■) 70 °C. Reaction conditions: catalyst amount 0.5 g, benzoyl chloride 1 ml, toluene 20 ml.

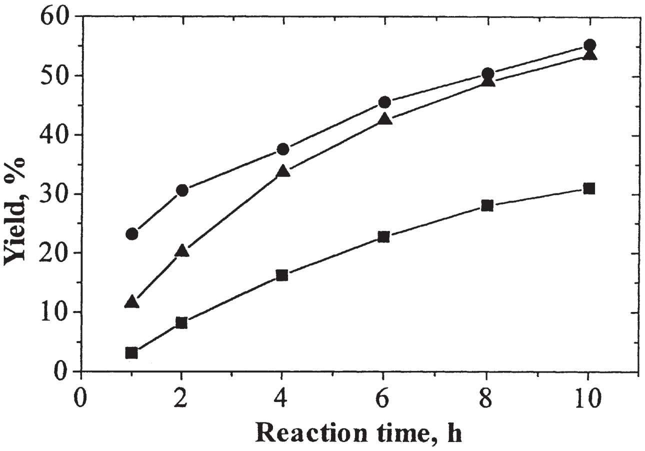


Figure 2. Effect of catalyst amount on product yield: (●) 0.5 g, (▲) 0.250 g, (■) 0.125 g. Reaction conditions: reaction temperature 110 °C, benzoyl chloride 1 ml, toluene 20 ml.

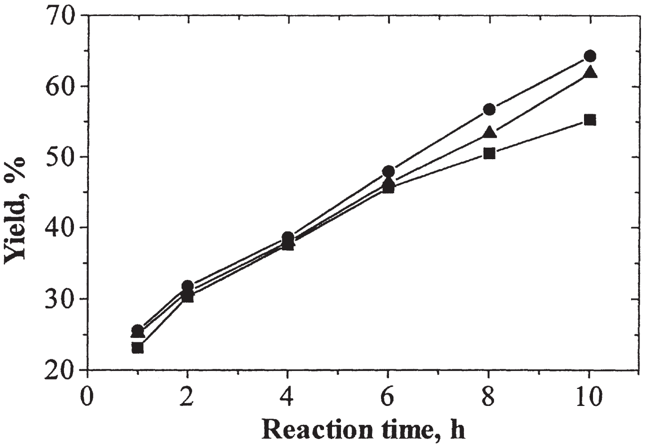


Figure 3. Effect of benzoyl chloride/toluene volume ratio on product yield: (■) 1 : 20, (●) 1 : 10, (▲) 1 : 5. Reaction conditions: reaction temperature 110 °C, catalyst amount 0.5 g, benzoyl chloride 1 ml.

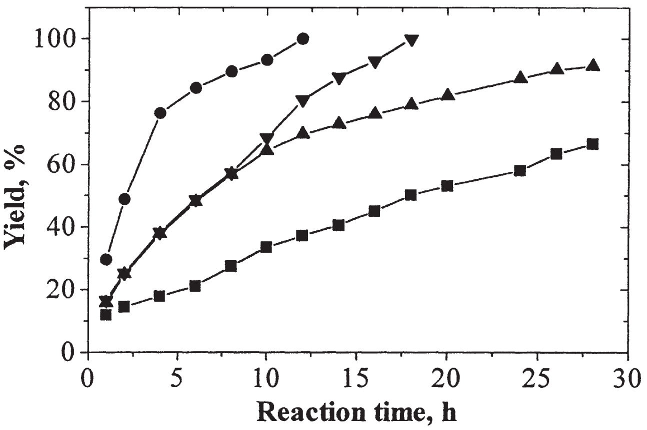


Figure 4. Comparison of activity of the catalysts: (●) SZA-2, (▼) SZ, (▲) STA-2, (■) ST. Reaction conditions: reaction temperature 110 °C, catalyst amount 0.5 g, benzoyl chloride 1 ml, toluene 10 ml.

It is obvious that both Al-promoted catalysts are more active than the respective unpromoted catalysts.

In order to elucidate the nature of the promoting effect of aluminum, the surface area, sulfate content and superacidity of the catalysts in table 1 were characterized and summarized in table 2. The surface area of SZA catalysts is slightly higher than that of SZ, whereas the surface area of STA catalysts increases more markedly with Al_2O_3 content. The SO_3 content of both SZA and STA catalysts increases significantly with Al_2O_3 content, showing that the incorporation of Al may help to stabilize the surface sulfate species during calcination of the catalysts at 650 °C for SZA series and 500 °C for STA series. The surface area and SO_3 content of SZA-5 are evidently lower than for all the other SZA catalysts, since its calcination temperature has been raised to 750 °C which is needed for ZrO_2 in the catalyst to crystallize.

Table 2

Properties of the catalysts.

Catalyst	Surface area (m^2/g)	SO_3 content (wt%)	n-C_4 isomerization ($k_1 \times 10^3$/h^{-1})	SO frequency shift (cm^{-1})
SZ	113	3.3	40.1	40
SZA-1	126	4.9	57.2	41
SZA-2	140	6.4	55.3	42
SZA-3	135	7.0	45.2	41
SZA-4	133	7.8	14.8	–
SZA-5	104	3.9	9.4	–
ST	114	5.1	10.7	22
STA-1	121	5.2	12.8	22
STA-2	135	6.0	16.1	24
STA-3	147	8.1	15.6	24
STA-4	193	9.5	8.75	–
STA-5	192	9.6	7.07	–
SA	316	9.5	0.27[a]	–

[a] The isomerization rate content for this sample was tested at 75 °C.

The acid strengths of the catalysts were identified by the method of infrared spectroscopic study of water adsorption [10]. Infrared spectra of the catalysts after evacuation at 350 °C for 3 h display a strong absorption band at 1369–1392 cm^{-1}, characteristic of the surface sulfate species with covalent S=O bonds [11]. As water is adsorbed on the surface sulfate, a red shift of this IR band indicating a strong interaction between water and the surface sulfate is observed. The magnitude of this frequency shift is associated with the acid strength of the catalyst [10]. The S=O frequency shifts of SZ and SZA catalysts are greater in table 2, indicating that the acid strengths of these catalysts are higher than those of ST and STA catalysts. On the other hand, the frequency shifts of the Al-promoted catalysts are almost identical with those of the unpromoted catalysts, implying that the incorporation of aluminum has little effect on the enhancement of acid strength of the catalysts.

The superacidity of the catalysts was tested by n-butane isomerization [12]. The isomerization of n-butane at 35 °C follows the rate law of a first-order reversible reaction. The activity of a catalyst for the reaction expressed in terms of the forward rate constant k_1 is associated with its superacidity, comprising the effect of strength and density of acid sites. In table 2, the isomerization activities of SZ and SZA series catalysts except SZA-5 are much higher than those of the SA, ST and STA series, and for both series of Al-promoted catalysts the isomerization activity increases with Al_2O_3 content up to a maximum and then decreases as the Al_2O_3 content is further increased. Clearly, the superacidity of the catalysts is out of proportion to the SO_3 content of the catalysts, which implies that not all the surface sulfate species on the catalysts are superacidic sites. Microcalorimetric measurements of NH_3 adsorption on SZ and SZA-2 in our previous work [9] have shown that the incorporation of Al helps to stabilize the surface sulfate complex on the oxide and increases the number of superacidic sites. The total numbers of acid sites with differential heat of adsorption above 40 kJ/mol for SZ and SZA-2 are 328 and 510 μmol/g, which amount to 80 and 64% of the surface sulfate in the catalysts, respectively. In addition, the acid strengths of the acid sites on SZ are more evenly distributed, whereas SZA-2 possesses a greater number of superacidic

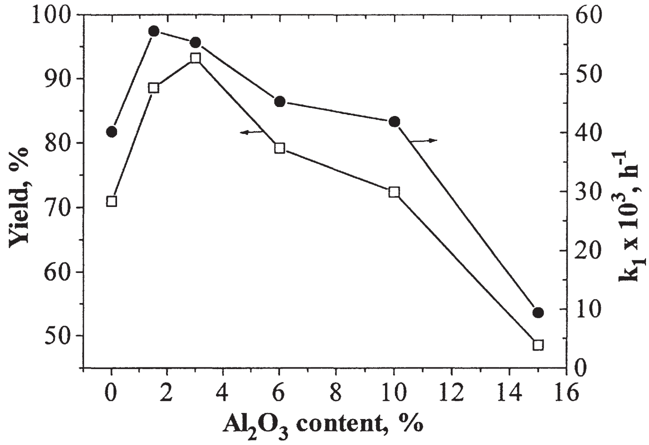


Figure 5. Variation of superacidity and product yield with Al_2O_3 content for SZA series.

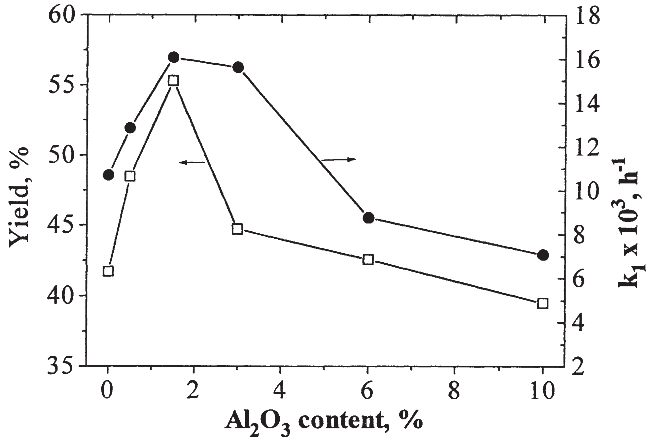
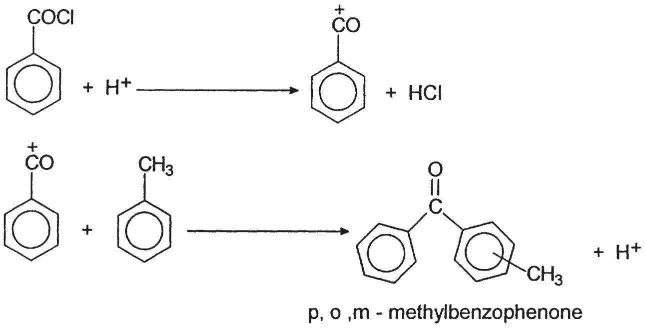


Figure 6. Variation of superacidity and product yield with Al_2O_3 content for STA series.

sites with differential heats between 125 and 140 kJ/mol. The number of superacidic sites with differential heats in the range of 125–140 kJ/mol for SZA-2 is 4.3 times greater than that for SZ. This enhancement in the number of superacidic sites could be explained by an interaction of Zr with Al atoms due to the formation of a Zr–O–Al bond in the binary oxide [13,14]. Since the electronegativity of Al^{3+} is larger than that of Zr^{4+}, the partial charge on Zr is increased after the formation of the Zr–O–Al bond, which may help to stabilize the surface surfur complex and to increase the number of strong acid sites. The acid strength distribution of the acid sites on other catalysts and the structure aspects of the Al-promoted catalysts will be further explored. The trends of the variation of superacidity of the catalysts with Al_2O_3 content and the variation of the yield of methylbenzophenones in table 1 with Al_2O_3 content coincide quite well, as shown in figures 5 and 6, demonstrating that the benzoylation reaction probably only proceeds on the superacidic sites of the catalysts. The above results are consistent with observations in the literature [15], i.e., acid sites with acid strengths in the superacidic range are needed for the formation of the reaction intermediate, $PhCO^+$ cation, as shown in scheme 2, and the stronger the acid sites the higher the activity of the catalyst for the benzoylation reaction.



Scheme 2.

4. Conclusions

Benzoylation of toluene with benzoyl chloride on SO_4^{2-}/ZrO_2 and SO_4^{2-}/TiO_2 catalysts gives good yields of methylbenzophenones. The reaction needs superacidic sites for the formation of $PhCO^+$ cation intermediate. The incorporation of an appropriate amount of Al_2O_3 into ZrO_2 and TiO_2 promotes the activity of SO_4^{2-}/ZrO_2 and SO_4^{2-}/TiO_2 catalysts effectively owing to an increase in superacidity of the catalysts. $SO_4^{2-}/3\%Al_2O_3–ZrO_2$ is a good clean catalyst for the benzoylation reaction, which gives 100% yield of methylbenzophenones at 110 °C within 12 h.

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