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| Benzoylation of benzene and substituted benzenes catalyzed by superacid Zr02:H2S04 | Phản ứng benzoyl hóa của benzen và benzen thế được xúc tác bằng siêu axit Zr02:H2S04<br>Benzoylation: Phản ứng đưa nhóm benzoyl vào một phân tử. |
| Abstract Superacid Zr02:H2S04 showed high activity in Friedel-Crafts | Tóm tắt Siêu axit Zr02:H2S04 có hoạt tính cao trong phản ứng benzoyl hóa Friedel- |

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| benzoylation of benzene and substituted benzenes such as chlorobenzene, toluene and 1,3,5-trimethylbenzene. Benzophenones in 90-100% yields were obtained with catalytic amount of superacid Zr02:H2S04. The calcination temperature greatly influenced the acid strength and activity of the superacid Zr02:H2SC>4. The superacid has both Lewis and Bronsted acid sites. The reversibility of Priedel-Crafts benzoylation and transacylation were observed over the superacid. The used superacid could be readily regenerated and showed identical benzoylation activity to toluene. | Crafts của benzen và các benzen thế chẳng hạn như chlorobenzene, toluene và 1,3,5-trimethylbenzene.<br>Chúng tôi đã thu được benzophenone với hiệu suất 90-100% khi có một lượng chất xúc tác siêu axit Zr02: H2S04. Nhiệt độ nung ảnh hưởng rất lớn đến độ mạnh của axit và hoạt tính của siêu axit Zr02:H2SC>4. Siêu axit có cả vị trí axit Lewis và Bronsted. Khả năng đảo ngược phản ứng benzoyl hóa Priedel-Crafts và transacylation cũng xảy ra dưới tác dụng của siêu axit. Siêu axit đã qua sử dụng có thể tái tạo dễ dàng và cũng có hoạt tính benzoyl hóa tương tự đối với toluene.<br>Transacylation: một phản ứng hóa học liên quan đến việc chuyển gốc acyl.<br>Reversibility: phản ứng thuận nghịch |
| Introduction<br>Friedel-Crafts benzoylation of aromatics is of considerable value owing to the importance of aryl ketones and aldehydes as chemical intermediates. The reaction generally requires equimolar or even excess of the Friedel-Crafts catalysts such as AICI3. After the reaction, the catalysts were decomposed by water and impossible to be reused.1 It is, therefore, highly desirable to develop methods in which only catalytic amount of catalyst may be used for effective conversion.<br>Some sulfonated organic polymers have been reported as Friedel-Crafts acid catalysts,2,3 but polystyrene sulfonic acid shows low activity and lacks thermal and mechanical stability, and perfluorosulfonic acid polymers such as Nafion-H are very expensive and difficult to prepare. Recently, we have found that inorganic solid superacid Zr02:H2SC>4 could catalyze effectively the benzoylation of benzene and substituted benzenes. The reaction was | [redacted] |

very clean, with HC1 as the only by-product escaping during the reaction. The main advantages of the solid superacid are their high activity, high stability, easy preparation and regeneration.

## Experimental

### Materials and equipments

Chlorobenzene, benzene, toluene, 1,3,5-trimethylbenzene, benzoyl chloride, zirconyl chloride are commercial products, which were used without purification.

IR spectra were taken on a Perkin-Elemer 983 instrument. Benzoylation products were measured on a Beijing 2305E model gas chromatography instrument using a 2 m column of PEG on GDX-101 (150°C, N2 2.0 kg/cm2) and identified by comparison with authentic samples. The products were further confirmed by GC/MS (GC: HP-5890, MS: HP-5988).

### Preparation and regeneration of superacid Zr02:H2S04

Zr02:H2SC>4 was prepared according to reported method:4,5 Zr(OH)4 from hydrolyzing ZrOCl2 with 28% NH3 H2O was washed with deionized water, dried at 110°C, followed by milling and pre-calcination at 200°C for 2 h. Then it was treated with IN H2SO4 in a four folded filter paper on a funnel. After draining away, it was dried and calcined at certain temperature (400—800°C).

The acid strength was measured in a series of sulfuryl chloride solution of Hammett’s indicators.6 The colorless surface as basic state turns to yellow as acidic one.

The used superacid can be readily regenerated in the following way: After filtration, the catalyst was washed subsequently with acetone and

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| deionized water, and treated with IN H2SO4, then dried and calcined. | [redacted] |
| General procedure for preparation of benzophenones<br>A mixture of benzoyl chloride (1 mL), aromatics (4 mL) and Zr02:H2S04 (0.3 g) were heated in a three-necked round bottom flask (50 mL) fitted with a reflux condenser (connected through a drying tube to 4N NaOH as hydrogen chloride absorber) and a magnetic stirrer. The reaction flask was placed in a constant temprature bath (±0.5°C). The reaction was detected by GC through drawing a small amount of reaction liquid with a syringe at regular intervals. The yields of benzophenones were calculated based on benzoyl chloride. | [redacted] |
| Results and discussion<br>Zr(OH)4 treated with H2SO4 was calcined in the range of 400—800°C. Their acid strength is higher than 100% H2SO4 (H0 — —11.9), thus they are ail superacid (Table 1). The existence of both Bronsted and Lewis acid sites was shown by the IR spectra of pyridine absorbed on Zr02:H2S04 (600°C) (1610, 1540, 1450 cm-1), in accordance with the results in the literature.4 | [redacted] |
| The catalytic activity of Zr02:H2S04 was examined in the benzoylation of benzene and substituted benzenes:<br>The calcination temperature in the preparation of the superacid greatly influenced the acid strength, thus influenced the catalytic activity in the benzoylation of toluene and the isomer distribution of the methylbenzophenones obtained (Table 1). The maximum activity and acid strength were observed with calcination at 600—650°C. | [redacted] |

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| Table 1 Effect of the calcination temperature on the catalytic activity in the benzoylation of toluene and acid strength | [redacted] |
| a, Yields of methyl benzophenones, reaction conditions: benzoyl chloride 1 mL, toluene 4 mL, Zr02:H2S04 0.3 g, 110°C, 12 h.<br>b, Acidic colour of the indicator was obseved (+) distinctly, (±) slightly and (—) hardly. | [redacted] |
| With increase of calcination temperature at the range of 400—650°C, the acid strength and the yields of methylbenzophenones were increased, at the same time, the percentage of par a-methylbenzophenone was decreasing accompanied with increase of ortho- and meia-methylbenzophenone. In all cases, the para- and orf/io-product were main products, in accordance with typical electrophilic aromatic substitution pathway. The increase of the highest acid strength enhanced the electrophilicity of attaching benzoyl cation, and resulted in the decrease of regional selectivity. Therefore, it is reasonable that the increase of benzophenones’yields was accompanied by the decrease of the percentage of para-methylbenzophenone. | [redacted]<br>[redacted] |
| Table 2 Effect of the calcination temperature on the yield of methyl benzophenones in benzoylation of toluene | [redacted] |
| The effect of reaction temperature and time on the yield of methylbenzophenones in benzoylation of toluene has been investigated and the results are given in Table 2 and Table 3 respectively. The yield increased with both time and the rise of temperature, and 1009c yield was obtained at 110°C | [redacted] |

for 3.6 h. The isomer distribution of methylbenzopheiicne was influenced by reaction temperature and time. In all cases, the main products were para- and ortho-methylbenzophenone. and the para : ortho ratio was generally lower than those obtained with AICI3 as catalyst under usual solution Priedel-Crafts conditions.1 Therefore, benzoylcation over the present superacid catalyst was considered to act as relatively stronger electrophile in the reaction. As temperature increased, the reactivity of benzoyl cation increased, and consequently the regional selectivity decreased. So the ortho- and meta-products, relatively increased (Table 2).

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Table 3 Time dependence of the yield of methylbenzophenones in the benzoylation of toluene

Conditions: benzoyl chloride 1 mL, toluene 4 mL, 110°C, ZrC>2:H2S04 (650°C), 0.3 g.‘

When we elongated the reaction time after 100% yield was obtained, the isomer dis-tribution of methylbenzophenones changed (Table 3). This can be explained only by the reversibility of Friedel-Crafts reaction and transacylation of methylbenzophenones over the superacid. In a separate run, upon heating under reflux a mixture of para-methylbenzophenone (2.0 g), ZrC)2:H2S04 (650°C) (0.3 g) and 1,4-dimethyIbenzene (4 mL) for 15 h, 0.3% meta-, 0.1% ortftomethylbenzophenone and 0.03% 2,5-dimethylbenzophenone, 0.03% 2,5,4,-trimethylbenzophenone were detected by GC besides 95.1% para-methylbenzophenone:

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This result confirmed the above

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| explanation. Simimiar phenomena were occasionally observed by other authors.7,8 | [redacted] |
| The benzoylation reaction was further studied by reacting various substituted benzenes with benzoyl chloride. The results are showed in Table 4. | [redacted] |
| Table 4 Reaction of various aromatics with benzoyl chloride catalyzed by ZrOjiHaSO* (650°C)<br>Conditions: benzoyl chloride 1 mL, aromatics 4 mL, Zr02:H2SC>4 (650°C) 0.3 g.<br>The yields of benzophenones for toluene and 1,3,5-trimethylbenzene were compara-ble, and higher yields of benzophenones for benzene and chlorobenzene required long time. Para-chlorobenzene was predominant product (95.1%) for chlorobenzene. Isomer distribution also changed with the reaction time. | [redacted] |
| The used superacid catalyst ZrC>2:H2S04 (650°C) showed low activity in the ben-zoylation of toluene, only 30% yield of methylbenzophenones was obtained, but it can be readily regenerated and showed identical activity to the freshly prepared one (Table 5). | [redacted] |
| Table 5 Recyling the superacid in the benzoylation of toluene<br>Conclusion<br>The superacid Zr02:H2S04 is an efficient catalyst in the benzoylation of benzene and substituted benzenes. Calcination temperature greatly influenced activity of the superacid and the highest acid strength. The reversibility of Friedel-Crafts benzoylation and transacylation occurred over the present superacid | [redacted] |

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| catalyst. | |