

Fries Rearrangement of Phenyl Acetate over Solid Acid Catalyst

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Abstract: A silica-supported zirconium based solid acid (ZS) has been used as catalyst for the Fries rearrangement of phenyl acetate (PA). The catalyst showed a higher PA conversion activity and a much higher selectivity for *o*-hydroxyacetophenone (*o*-HAP) than for strongly acidic zeolite catalysts. The supported catalyst was characterized by XRD, IR, XPS, pyridine-TPD and the surface area measurements. The catalytic properties were influenced significantly by pretreatment temperature.

Keywords: Supported catalyst, solid acid, Fries rearrangement, zirconium.

The Fries rearrangement of phenyl acetate leads to hydroxyacetophenone (HAP), which is very valuable precursors in the pharmaceutical industry¹. In the conventional process, Friedel-Crafts catalysts are employed. Replacement of these catalysts by reusable solid acid catalysts would make the process much more environmentally friendly. The heterogeneous catalysts such as zeolites are not successful in use due to low selectivities and rapid catalyst deactivation²⁻⁴. We have previously reported the preparation of a new kind of supported solid acid catalyst, a well-dispersed supported zirconium based solid acid which shows excellent catalytic properties in esterification reactions⁵. In this work, the same catalyst has been applied in the Fries rearrangement.

The silica gel supported zirconium based catalyst was prepared by following literature procedures⁵. The loading of zirconium sulfate tetrahydrate was 16.7%(wt). It was pretreated at 110°C in air for 2 h before reaction. Zeolites (HZSM-5, H β and HY, with Si/Al ratios 25, 50 and 3.5 respectively) used for comparison were pretreated at 500°C for 4 h in air before reaction. The Fries rearrangement reaction were performed in a batch reactor at an ambient pressure (under N₂ protection) and 196°C for 4 h. The catalyst (1.0 g) was introduced to the reactor containing 23.8 g (175 mmol) of PA. The reaction mixtures were periodically collected and off-line analyzed by GC (FID detector) using a capillary column (ϕ 0.25 mm \times 20 m) coated with SE-30.

The surface area of the supported ZS catalyst was found to be 381 m² g⁻¹ which is almost the same as that of the SiO₂ support alone. The surface area of the active component is only about 10 m² g⁻¹. The supported catalyst showed no obvious X-ray diffraction peaks. The morphology from scanning electronic micrographs and the IR spectra showed no noticeable difference between the supported catalyst and the silica

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support alone. However, an XPS study showed that the ratio of Zr/Si at the surface is higher than the total loading ratio. These results indicate that the active component is well dispersed over the surface of the silica gel. The TPD curve for pyridine adsorbed catalyst showed two desorption peaks at Tm values of approximately 130°C and 255°C. This indicates that two kinds of acid site with different strength exist on the catalyst.

Table 1 Reaction results over different catalysts

Catalyst	PA Conv. (%)	S _{<i>o</i>-HAP} (%)	S _{<i>p</i>-HAP} (%)
HZSM-5	16.6	6.0	10.0
HB	17.9	8.6	10.8
HY	11.0	11.4	1.7
ZS-110	18.6	16.3	1.0
ZS-170	11.4	15.7	0.9
ZS-340	7.8	22.8	1.1

Table 1 shows the results obtained over different catalysts. The main side product was phenol in each case. It is note worthy that ZS showed the highest conversion of PA. When the same amount of unsupported zirconium sulfate tetrahydrate was used for comparison, the conversion of PA was lower than 5%. The high activity for PA conversion with the supported catalyst may be attributed to the high degree of dispersion of the catalytically active component over the surface of the support. In addition, the *o*-HAP selectivity over the ZS catalyst is much higher than that over any of the zeolites. The zeolites, HZSM-5 showed the highest activity and HY showed the lowest activity. It can be seen that the selectivity for *o*-HAP increases with increasing pore size of the zeolites. The ratio of *o*-/*p*-HAP increases in the same manner. *o*-HAP may be produced *via* an intramolecular rearrangement reaction. However, the *p*-HAP is mainly formed from intermolecular reaction, if the intramolecular rearrangement is sterically hindered³. The pore size distribution analysis suggested that mesopores are predominant in the ZS catalyst. The average diameter of these pores is about 7.2 nm which is much larger than that of zeolites.

Table 1 also shows the reaction results over ZS pretreated at different temperatures. The activity for PA conversion over the ZS catalyst decreased dramatically with the increase in pretreatment temperature. If the catalyst was treated at 340°C, the PA conversion activity decreased to about 7.8%. The deactivation of the catalyst may result from the decomposition of the active component on the surface of support.

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