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Benzylation of benzene by benzyl chloride over silica-supported iron sulfate catalysts

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The silica-supported Fe-containing catalysts prepared using $FeSO_4$ as a precursor exhibit high activity toward the reaction of benzene with benzyl chloride.

The Friedel–Crafts alkylation comprises an important class of reactions commonly used in organic chemistry.[1] Among these reactions, the liquid-phase benzylation of benzene and other aromatic compounds by benzyl chloride is used to produce diphenylmethane and substituted diphenylmethanes, which are key intermediates for pharmaceutical and fine chemicals.[2] Generally, such reactions are carried out using strong homogeneous acid, such as $AlCl_3$, $FeCl_3$, $TiCl_4$, H_2SO_4 and $GaCl_3$,[1,3,4] which induce problems associated with high corrosion, toxicity and separating of homogeneous catalysts.

Efforts to develop more eco benign heterogeneous catalysts instead of the traditionally used homogeneous acids have revealed the promising features of iron oxide or sulfate.[2,5–14] Nanosized Fe_2O_3 clusters with a high degree of coordinative unsaturation are responsible for high catalytic activity.[9,10] Arata and co-workers found that bulk iron-containing materials, such as iron sulfate and iron oxide, are also effective catalysts for the Friedel–Crafts benzylation of toluene with benzyl chlorides.[13,14] Previously, we found that the impregnation of silica with iron(II) sulfate led to the formation of sulfate-containing iron compounds after thermal treatment at 110–500 °C, which transformed into nanosized ε-Fe_2O_3 particles after calcination at higher temperatures.[15–17] The aim of this work was to study iron-containing silica-supported catalysts prepared using iron(II) sulfate as a precursor in the Friedel–Crafts benzylation of benzene.[†]

Three sets of samples containing approximately 2, 4 and 6 wt% iron were prepared by the impregnation of silica with aqueous $FeSO_4$ solution and subsequent drying and calcination. The samples were denoted as *n*FS300, *n*FS400, *etc*., where 300, 400, *etc*. denotes the calcination temperature and *n* corresponds roughly to the iron concentration (wt%).

The calcination temperature strongly affects the catalytic properties of the catalysts containing 4 wt% iron in the benzylation reaction at 60 °C: the sample 4FS400 provides the reaction, whereas neither the samples FS110, FS300, FS500, FS600, FS700 and FS900 nor the silica support induce the benzylation of benzene even after 24 h. The effect of calcination temperature on the transformation of iron species in a $FeSO_4/SiO_2$ catalyst was studied using Mössbauer spectroscopy, XRD, TGA, TEM and XPS.[15–17] The complex compounds containing randomly distributed oxide, hydroxide and sulfate groups as anions surrounding iron atoms are formed on the catalyst surface after calcination at 400 °C. An increase in calcination temperature is accompanied by a gradual loss of sulfate groups and the formation of ε-iron oxide nanoparticles at 900 °C. We can propose that complex iron(III) compounds containing hydroxide and sulfate anions exhibit high catalytic activities toward benzene benzylation, while ε-Fe_2O_3 particles are not active despite their nanosized character.

Figure 1 shows the conversion of benzyl chloride as a function of reaction time in the presence of the 4FS400 catalyst at

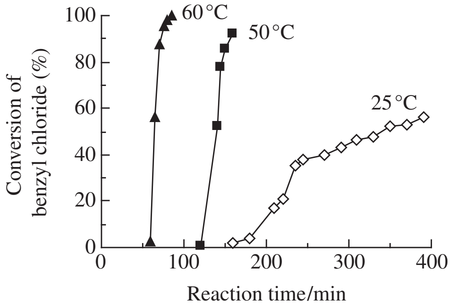

Figure 1 Effect of reaction temperature on the conversion of benzyl chloride in the benzylation of benzene over the 4FS400 catalyst.

[†] The catalysts were prepared using KSKG silica (KhromAnalit; specific surface area, 287 $m^2\ g^{-1}$; average pore diameter, 141 Å; pore volume, 0.81 $cm^3\ g^{-1}$). Silica powder with a grain size of 0.25–0.50 mm was impregnated with an aqueous solution of iron(II) sulfate heptahydrate (Acros Organic) and dried at room temperature for 24 h and then at 110 °C for 4 h. Portions of the dried samples were calcined at 300, 400, 500, 600, 700 and 900 °C for 4 h. The chemical composition of the catalysts was determined by inductively coupled plasma atomic emission spectrometry using an OPTIMA 4300DV spectrometer from Perkin Elmer.

The liquid-phase benzylation of benzene with benzyl chloride was carried out at 25–60 °C in a magnetically stirred round-bottomed flask fitted with a reflux condenser and heated in a precisely controlled water bath. In a typical run, 5 ml of benzene and 0.45 ml of benzyl chloride were added to the catalyst (0.05 g, activated at 110 °C for 30 min). To follow the reaction, the liquid was sampled at regular intervals and analysed by gas-liquid chromatography (Agilent 6890N instrument equipped with a 19091S-916 HP-1MS capillary column, 60.0 m × 320 μm × 0.24 μm, and a JAS atomic emission detector). The reaction products were identified by GC-MS. The primary reaction product is diphenylmethane, and the by-products are *o*-, *p*- and *m*-dibenzylbenzenes. Because benzene was in an excess, the catalytic activity of the iron-containing samples was characterised by the conversion of benzyl chloride. The selectivity was expressed as the ratio of the moles of diphenylmethane formed to the moles of benzyl chloride consumed in the reaction. The heterogeneity of the catalytic action was confirmed by the observations that the filtrate obtained after the catalytic reaction was inactive, and it did not contain paramagnetic species (detected by ESR). Moreover, the elemental analysis data for the catalysts indicated that the Si/Fe ratio is identical for a sample before and after reaction.

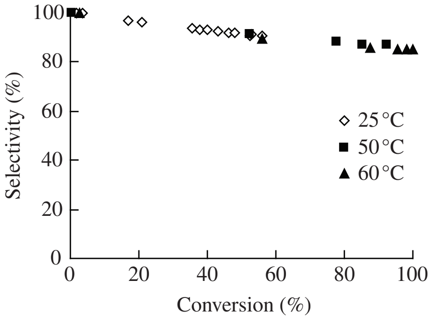

Figure 2 Selectivity for diphenylmethane formation as a function of benzyl chloride conversion over the 4FS400 catalyst.

different reaction temperatures. The reaction usually started after an induction period and then proceeded rapidly, especially at temperature of 60 °C. The 4FS400 sample ensured 100% conversion of benzyl chloride in 60 min at 60 °C; decreasing the reaction temperature beyond this point reduces the catalytic activity. For example, at 50 °C, the reaction was completed after 180 min; the induction period increased by a factor of 2, but approximately the same time was needed for the conversion of benzyl chloride. The sample storage and pretreatment conditions and the water content of the reagent (benzene) also influenced the induction period. A thorough drying of the catalytic sample and benzene shortened the induction period, and the reaction did not proceed at all if the water content of benzene exceeded 100 ppmw. The dependence of the induction period duration on catalyst humidity and reaction temperature was observed earlier.[2,6,9] The selectivity of diphenylmethane formation decreased with the conversion of benzyl chloride. At 100% conversion, the selectivity was approximately 86%. The difference in the reaction temperature and the catalyst pretreatment conditions did not have a significant effect on the selectivity for a fixed molar ratio of reagents (Figure 2).

The influence of iron content on the catalytic activity of the iron-containing silica-supported samples in the benzene benzylation reaction was assessed using catalysts containing 2.1, 4.4 and 6.0 wt% Fe. The growth of the iron content from 2.1 to 4.4 wt% increased the catalytic activity, but a further increase in iron loading up to 6 wt% did not improve the catalytic properties (Figure 3). The selectivity of diphenylmethane formation was not affected by the iron content of the catalysts.

The iron-containing catalysts lost their activity after the first run, and they should be regenerated by burning out the carbon-containing organic deposition formed on the surface.[8,12] The regeneration of the 4FS400 catalyst by calcination at 400 °C for 4 h in an air flow preserved the selectivity for diphenylmethane formation (86%) but the activity of the regenerated catalyst decreased. After the first regeneration, the complete conversion of benzyl chloride at 60 °C was achieved in 180 min instead of 60 min for the as-synthesized 4FS400 catalyst. After the second regeneration, the complete conversion of benzyl chloride required 300 min. Despite the decreased activity in the second experiment relatively to the first one, the proposed catalytic system can be practically applicable due to its simple, reproducible and green preparation, which is performed without organic solvent and with cheap and readily available materials. It is well known that, in the production of fine and specialty chemicals, where the high added-value of the final compounds may account for the use of valuable and costly reactants, the solid catalyst is often considered as a consumable reagent.[18]

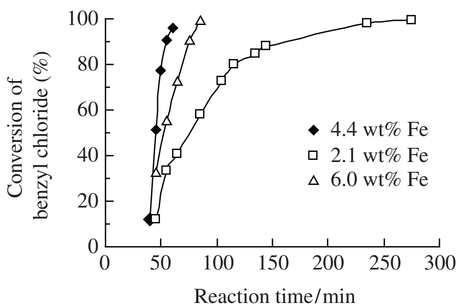

Figure 3 Conversion of benzyl chloride in the benzylation of benzene at 60 °C over the FS400 catalysts with different iron contents.

In summary, the benzylation of benzene with benzyl chloride was investigated in a temperature range of 25–60 °C over silica-supported Fe-containing catalysts prepared by the impregnation of silica with aqueous $FeSO_4$ and the subsequent drying and calcination. The calcination temperature is the primary factor determining the catalytic activity: the catalysts show high activity toward the reaction of benzene with benzyl chloride after calcinations at 400 °C, whereas the catalysts calcined at other temperatures did not exhibit any activity. The selectivity of diphenylmethane formation reaches 86% at a 100% conversion of benzyl chloride and does not depend on the reaction temperature and iron content. The proposed catalytic system seems promising for practical use due to its facile and environmentally safe preparation with the use of cheap and readily available materials.

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