

Preparation of solid acid catalysts and their application in Friedel-Crafts type acylation reactions

PhD thesis

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Introduction

Nowadays in the applied technologies the environment friendly processes are preferred. These technologies involve the reduction or elimination of the by-product formation, the transformation or and neutralization of the formed secondary products.

Moreover, energy saving and proper efficiency are needed in the processes.

None of the conventional Friedel-Crafts catalysts (halogenides of transition metals and of earth metals) can be regenerated after their use. Conventional Friedel-Crafts acylation thus produces high amount of non-regenerable, useless chemicals. Consequently, researches to find fully regenerable and efficient catalysts have a great importance.

Due to the high specific surface area and to the special chemical environment inside the solid acid catalysts, they have strong catalytic activity. They have been playing thus important roles in several chemical technologies. Because their acidity arises from the inner acidic functional groups, solid acids can be treated easily and are very efficient catalysts.

After catalyzing the reaction, the solid acids can be removed from the reaction mixture by a simple way, with a mechanic filtration for example.

Recently, in the industrial technologies, application of solid acid catalysts has been spread for special syntheses. Several chemical reactions have been conducted with high conversion, and great selectivity has also been achieved. Production of dangerous polluting by-products has been minimized.

The aim of my research work was to find a new, heterogeneous catalytic way for the Friedel-Crafts acetylation of the benzo-15-crown-5 crown ether. On the basis of literature data, two types of acylating catalysts have been selected: (a) montmorillonite-based catalysts whose structure had already been characterized and (b) sulfated zirconias prepared by myself. In the latter case (b) the way of the preparation of the catalysts as well as their physical and chemical characterization were targeted. The relation between the catalytic activity and the structural features of the catalysts has also been studied.

Methods

The physical and chemical properties of the catalysts have been studied with the following methods: chemical analysis, thermal analysis (TG, DTA, DTG), measuring the specific surface area, temperature programmed ammonia desorption (TPD-NH₃) and reflexion FT-IR spectroscopy. The chemical reactions were followed with HPLC chromatography.

New scientific results

1. On the basis of my investigations it can be stated that there are significant differences between structure and properties of sulfated zirconia catalysts prepared by one-step and of those prepared by two-step methods.

Catalysts prepared by the two-step method:

- contain only one sulfate species (corresponding to the DTG curves) which decomposes in a higher range of temperature;
- they have greater sulfur content, but during the calcination process they lose a greater part (87%) of it;
- after calcination they don't contain strongly acidic hydroxyl groups which can be linked with sulfate groups;
- evaluating the IR spectra recorded after adsorption of benzene, one can realize that these types of catalysts contain less amount of strongly acidic disulfate groups than weakly acidic monosulfate groups.

Catalysts prepared by the one-step methods:

- contain two sulfate species even before calcination;
- after calcination they contain in higher proportion the strongly acidic disulphate species;
- the acidity of their OH groups linked to Zr-atoms corresponds to that of the HX-zeolite.

2. Sulfated zirconia catalysts prepared by the two-step method show relatively lower activity either in the acylation of anisole by acetic anhydride or in that of benzo-crown-ether than the catalysts prepared by sol-gel methods. This experience corresponds well to the measured lower acidity of the former type catalysts than that of the latter one.
3. It has been shown that there are significant differences between the two subtypes of catalysts prepared by the one-step methods:
 - If the sulfuric acid is mixed first with water and then added to zirconium propoxide, the hydrolysis is not completed, there is always some residual organic material in the gel (independently of the type of solvent). The strongest acid (characterized by the total number of acidic sites measured by TPD-NH₃) is the catalyst prepared in n-propanol and then calcined. This acidity corresponds to medium acidic sites.

- If the sulfuric acid is dissolved in zirconium propoxide and after that water is added to the mixture, the resulted product has definitely greater specific surface area than the previous one, has a heterogeneous pore distribution and contains the highest number of acidic sites.

One can therefore conclude that H_2SO_4 is not only a source of sulfur but it plays an important role in the mechanism of the hydrolysis.

4. A novel method has been elaborated to the heterogeneous catalytic acylation of benzo-15-crown-5 with acetyl chloride. Although according to calculations diffusion control is out of question, no relations were found between acidity and activity of the catalysts (namely K10 and its ion-exchanged derivatives). The best results could be achieved by Sn^{2+} -K10 and Fe^{3+} -K10 (the latter gave 55% preparative yield). One can notice that these catalysts contain variable valency metals. The fact that catalysts ion-exchanged by variable valency metals showed outstanding activity, led us to propose – following literature analogies – a redox mechanism initiated by a radical attack.
5. It has been found that in the case of acylation of benzo-15-crown-5 by acetyl chloride the quantity of by-products grows continuously during the reaction. The existence of consecutive reactions has been experimentally verified. The structure of a major by-product was determined by LC-MS: this triacetyl compound presumably formed by ring-cutting followed by successive acetylation.
6. For the acetylation of benzo-15-crown-5 a method with acetic anhydride has also been elaborated. This reaction gave optimal result without solvent, at the boiling point of the acylating agent itself. Best result could be achieved with Sn^{2+} -K10 catalyst (57% preparative yield). Only few by-products and no triacetyl derivative were found in the final mixture. By studying the effect of the heat treatment of the ion-exchanged K10 catalysts one could conclude that the activity of such catalysts are determined by their Brønsted acidity.
7. In these two types of acetylation of crown ethers sulfated zirconia catalysts gave different results, however the best yields could be obtained with catalysts prepared by sol-gel method (water added to the mixture of zirconium propoxide + H_2SO_4), independently of the used solvent. These catalysts applied in acetic anhydride gave almost the same performance as Sn^{2+} -K10 (in accordance with the Brønsted-acidity); on the other hand they gave poor

results with acetyl chloride. This fact can be an indirect approval of the proposed redox mechanism initiated with a radical attack.

Publications

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