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Nanosized TiO₂—A promising catalyst for the aldol condensation of furfural with acetone in biomass upgrading

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ABSTRACT

Nanosized TiO₂ catalyst was successfully prepared by a simple green procedure and used in liquid phase aldol condensation of furfural with acetone, a key step in bio-fuel processing. In order to determine the effect of calcination temperature on catalytic properties of TiO₂, the as-prepared TiO₂ and calcined TiO₂ (150–900 °C) were studied by XRD, BET, TPD-CO₂/NH₃, TGA/DTG and FTIR evaluation. The catalytic performance of TiO₂ samples in aldol condensation of furfural with acetone was evaluated and compared with that of Mg–Al hydrotalcites and a BEA zeolite. These experiments showed that uncalcined TiO₂ possessed reasonable activity in aldol condensation of furfural to acetone and resulted in commonly produced condensation products. The observed catalytic behavior of TiO₂ could be competitive with that reported for other inorganic solids. The calcination of TiO₂ resulted, however, in a decrease in its catalytic activity due to extensive dehydration and surface dehydroxylation as well as due to changes of textural properties resulting in a decrease in the amount of accessible active sites. Thanks to its advanced properties, nanosized TiO₂ is a promising catalyst for aldol condensation of furfural with acetone and could broaden possibilities for optimizing conditions for bio-fuel production.

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1. Introduction

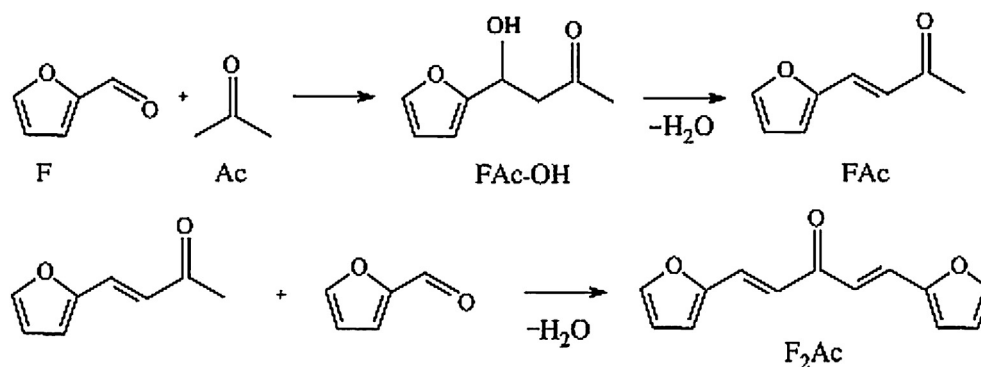
The world's energy system needs to be adapted to a more sustainable one, based on a diverse mix of energy resources, addressing the pressing challenges of energy security supply and climate change [1]. Nowadays, there is a change in the biomass energy uses from traditional and non-commercial ones, such as simple open combustion to produce heat, to modern ones, such as advanced processes to produce electricity and bio-fuels integrated in food and biomaterials industries [2]. The technical and economic potentials of biomass are higher than the current world energy consumption [1,2], thus, the main challenge is in its viable and sustainable use. The most abundant biomass resource is lignocellulosic biomass consisting of cellulose, hemicellulose and lignin [3]. Some other materials such as ash, proteins, pectin, etc. are also found in the lignocellulosic biomass in different proportion depending on the biomass source and origin [4]. In addition to dedicated biomass-for-energy plantations, waste biomass holds enormous potential with a high degree of sustainability. These waste materials can be

categorized based on their source such as industrial waste (sawdust, paper mill discards, food industry residues, etc.), forestry waste (branches, hard and soft wood residues, etc.), agricultural residues (straw, stover, peelings, cobs, stalks, nutshells, non-food seeds, etc.), domestic waste (kitchen wastes, sewage, waste papers, etc.), and municipal solid waste [4,5]. These materials are considered as one of the most promising bio-based feedstocks for the production of fuels and other chemical products as they are not in direct competition with food crops, fodder, and natural habitat [6].

Furanic compounds (e.g. furfural, 5-hydroxymethylfurfural) and acetone are readily available chemicals, which can be produced by the hydrolysis of biomass [7]. Additionally, acetone is available as a by-product in phenol production. Aldehydes and ketones can react by aldol condensation and result in the production of higher added value products from simple and cheap ones. In order to exploit the full potential of furfural as a platform chemical, its transformation by aldol condensation with acetone followed by hydrogenation/deoxygenation has been proposed to afford hydrocarbons, namely C₈ and C₁₃ alkanes [8] (see Scheme 1). Aldol condensation proceeds in the presence of either basic or acidic catalysts [9,10]. The most effective industrially available methods rely on using liquid bases (NaOH or KOH) or mineral acids (e.g. H₂SO₄) as catalysts [9]. However, these catalysts pose a major environmen-

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Scheme 1. Reaction scheme of aldol condensation of furfural with acetone.

tal threat due to waste water production and equipment corrosion. In addition, solid catalysts with acid-base character are recognized as a promising alternative to homogeneous catalysts for aldol condensation of furfural with acetone. Among solid catalysts, double layered hydroxides (hydroxalclites) with basic character are considered as the most promising catalysts for this reaction [8,11–15]. The essential disadvantages of such basic catalysts are their high sensitivity to ambient CO₂, which transforms them into catalytically inactive carbonates, and the lack of reliable methods for recovering their catalytic properties after regeneration [16–18]. Recently, zeolites have been reported as catalysts for aldol condensation of furfural with acetone [19]. It was shown that by using zeolites the disadvantages of basic catalysts i.e. susceptibility to CO₂ and poor regenerability could be avoided. On the other hand, their activity in aldol condensation of furfural with acetone is lower than that of hydroxalclites. Moreover, they are rapidly deactivated due to coke formation during the reaction [19]. Therefore, along with the optimization of the properties of the solid basic catalysts, attention is currently being focused on alternative solid catalysts for aldol condensation of furfural with acetone.

Titanium dioxide (TiO₂) is one of the most common materials in our daily life; in addition to its application in water and air purification and in pigments, it has emerged as an excellent photocatalyst for environmental purification applications [20]. TiO₂ exists mainly in three different crystalline phases: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic), out of which rutile is the most thermodynamically stable phase [21]. The main advantages of TiO₂ are its high chemical stability when exposed to acidic and basic compounds, nontoxicity, relatively low cost and high oxidizing power, which make it a competitive candidate for many photocatalytic applications [22].

To the best of our knowledge, no research study has examined the reaction of aldol condensation of furfural with acetone over nanosized titanium oxides up to date. The aim of this work is to investigate a reusable solid TiO₂ catalyst suitable for aqueous phase environment having high activity in aldol condensation. The research is focused on the following key objectives: (1) preparation of TiO₂ catalysts by co-precipitation from environmentally friendly and low-cost raw materials; (2) in-depth characterization of the prepared materials; and finally (3) a description of the effect of pretreatment temperature of the TiO₂ catalysts on their activity and selectivity in aldol condensation of furfural with acetone.

2. Experimental and materials

2.1. Materials

All chemicals were reagent grade and used as received. Titanium (IV) oxysulfate TiOSO₄ (Precheza a.s.) and urea CH₄N₂O (Lach: Ner,

p.a.) were used for synthesis of TiO₂. Mg–Al hydroxalclites (HTC) with Mg to Al molar ratio of 3 was prepared according to [23]. BEA zeolite (Si/Al = 12.5) was received from Zeolyst Int. (CP 814-E). Commercial sample TiO₂ P25 (Aeroxide® P25, Titanium (IV) oxide nanopowder) was obtained from Sigma–Aldrich. Acetone (Lach: Ner, p.a.) and furfural (Acros Organics, 99%) used for the catalytic experiments were dried using a CaA molecular sieve prior to the experiments.

2.2. TiO₂ synthesis

The nanosized TiO₂ was prepared by hydrolysis of TiOSO₄ in aqueous solutions using urea as the precipitation agent. In a typical process, TiOSO₄ was dissolved in distilled water. The pellucid solution was heated to 95 °C for 1 h, then mixed with urea and continuously heated at 100 °C for 5 h under stirring until pH reached 7.02. The formed precipitate was decanted, filtered and dried at 100 °C and the obtained white powder was denoted as “as-prepared TiO₂” sample. In order to study the effect of calcination temperature on the catalytic performance, the as-prepared TiO₂ sample was calcined in air at different temperatures in the range 150–900 °C for 2 h. All the samples were denoted as “TiO₂–T”, where T represents the calcination temperature.

2.3. Physico-chemical characterization

The catalysts were characterized by several techniques to assess their structure, composition, surface area and pore volume. The crystallographic structures of TiO₂ catalysts were determined by X-ray powder diffraction using a Philips MPD 1880, working with the Cu–Kα line (λ = 0.154 nm) in the 2θ range of 5–70° at a scanning rate of 2θ of 2.4 °/min. The XRD crystal size was calculated by using Scherrer equation as follows [24]:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where *k* is a constant equal to 0.89; λ is the X-ray wavelength, β is the full width at half maximum intensity (FWHM) and θ is the half diffraction angle. The phase composition of the samples was calculated by using the following equation:

$$\text{Rutile phase (\%)} = \frac{100}{[1+0.8 (IA/IR)]}$$

where IA and IR are integrated intensities of the anatase (1 0 1) and rutile (1 1 0) diffraction peaks, respectively.

Chemical analysis of as-prepared TiO₂ sample was performed with WDXRF spectrometer Philips PW 1404 with rhodium tube. The measurement was aimed to control the content of residual sulfate groups on TiO₂ surface after hydrolysis and washing stages.

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