



## Aldol condensation of furfural and acetone on zeolites



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### ARTICLE INFO

#### Article history:

Received 26 July 2013

Received in revised form 13 October 2013

Accepted 18 October 2013

Available online 27 November 2013

#### Keywords:

Aldol condensation

Oligomerization

Zeolites

Acidity

Coke formation

Regeneration

### ABSTRACT

Zeolites of different structural types were used as catalysts for aldol condensation of furfural and acetone in batch reaction conditions at  $T=20\text{--}100\text{ }^{\circ}\text{C}$  and time  $0\text{--}24\text{ h}$ . To establish a relation between physico-chemical and catalytic properties of microporous materials, the samples were characterized by SEM,  $\text{N}_2$  adsorption, FTIR and TGA. It was found that the acidic solids possessed appreciable activity in the reaction and resulted in a formation of products of aldehyde–ketone interaction. Nevertheless, furfural conversion decreased rapidly due to coke formation inside zeolite pores. Simultaneously with a general route of the reaction observed for basic catalysts, dimerization of the condensation product on acidic sites occurred. It was supposed that catalytic behavior of zeolites considerably affected by their both structural and textural properties. Experiments with re-used samples showed that zeolites totally restored their activity and selectivity after calcination at  $530\text{ }^{\circ}\text{C}$ .

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### 1. Introduction

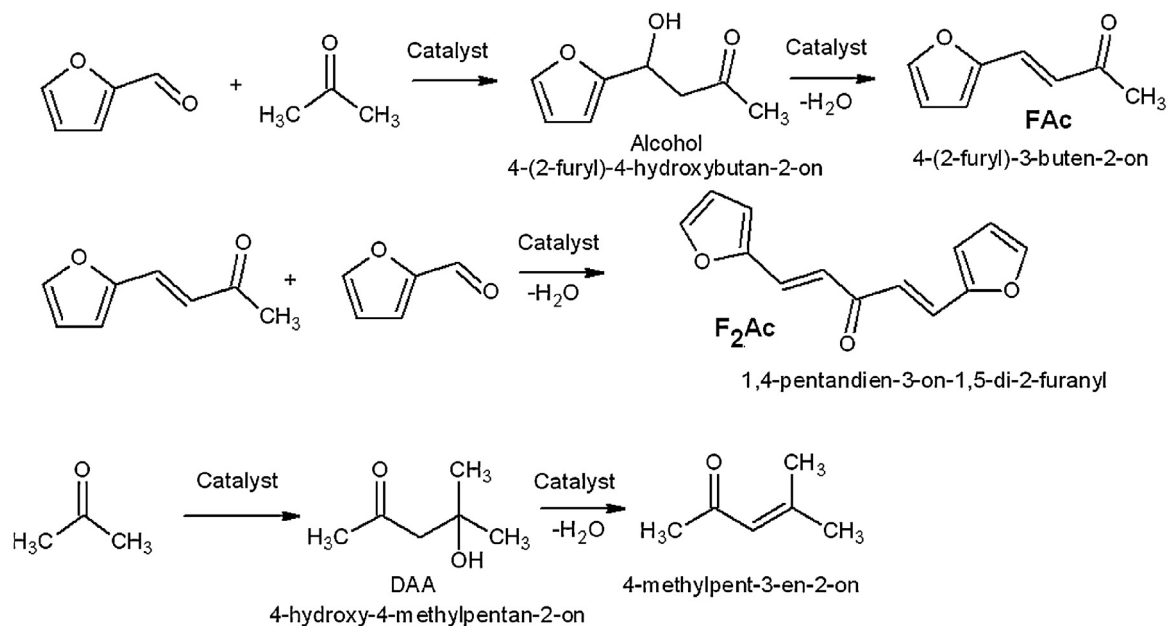
In conditions of unpredictable prices for conventional hydrocarbon sources, it is of a great importance to develop new technologies based on non-traditional, renewable energy supplies. At present, significant research attention is focused on the transformation of waste biomass into fuels and valuable chemicals [1,2]. The primary transformation of biomass can proceed by different routes resulting in a formation of bio-oil (by liquefaction and/or pyrolysis), sugar solutions, etc. [1–6]. Acetone, which is obtained as a product of acetic acid decomposition (ketonization), and furanic compounds that are afforded by sugars hydrolysis are among the final products of the successive transformation steps involved in conversion of the starting complex biomass mixtures. Furanic compounds and acetone, being aldehydes and a ketone by chemical origin, may further react with each other via aldol condensation in the presence of the corresponding catalyst [7–9]. In this respect, aldol condensation seems to be a useful tool to increase a length of carbon chain and to produce heavier reaction products from comparatively light initial reagents. The aldol condensation step is of particular importance in upgrading of bio-oils since these light molecules would be otherwise converted into low-value gaseous products during bio-oil deoxygenation that is necessary to improve its stability and enhance its fuel properties [10].

Aldol condensation of aldehydes and ketones is a well-known reaction of organic synthesis and it proceeds in the presence of catalysts with either basic or acidic properties. Most often basic catalysts are used for this reaction because they possess high activity in conversion of reagents and high selectivity toward the desired reaction products (Scheme 1). Sodium hydroxide is a recognized catalyst for aldol condensation, which permits to carry out the reaction even at room temperature [8]. Nevertheless, high corrosivity of this compound and the increasing demands for environmental friendliness of new technologies result in a necessity of using heterogeneous catalytic systems with similar basic properties. Catalysts derived from hydrotalcite-like (HTC) materials as well as other mixed oxide systems were found to be good heterogeneous catalysts with basic properties, which were successively employed as catalysts for aldol condensation [11–14]. It is known that re-hydrated HTC materials allow carrying out aldol condensation between furfural and acetone with high furfural conversion already at  $50\text{--}60\text{ }^{\circ}\text{C}$  [13]. Nevertheless, a number of published works dealing with the properties of HTC materials indicate significant disadvantages of these materials; in particular high sensitivity to the ambient  $\text{CO}_2$  and problems with re-using the HTC-based catalysts in successive catalytic runs [11,15,16].

Solid catalysts with acidic properties are used seldom as catalysts for aldol condensation in comparison with basic heterogeneous catalysts. Zeolites, being materials with pronounced and controllable acidic properties, seem to be suitable materials for this purpose. Indeed, it is known that acidic zeolites

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**Scheme 1.** Aldol condensation between furfural and acetone over acidic or basic catalysts.

of different structural types can catalyze condensation of various aldehydes and ketones [17–19]. However, the examples of using zeolites as catalysts for aldol condensation are still few. Therefore, further investigation to gain deeper understanding of the suitability of these microporous materials as catalysts for reactions of different biomass-derived aldehydes and ketones are required to promote the development of efficient biomass transformation routes into fuel components and valuable chemicals.

The present work aims at understanding of the relationship between the properties of zeolites of different structural type and their catalytic performance in aldol condensation of furfural and acetone. Both activity and selectivity of these materials are correlated with their physico-chemical properties.

## 2. Experimental

### 2.1. Supply and preparation of catalysts

Zeolite samples for the study (NH<sub>4</sub>-ZSM-5(23), NH<sub>4</sub>-ZSM-5(50), NH<sub>4</sub>-BEA(25), NH<sub>4</sub>-BEA(38), NH<sub>4</sub>-MOR(20), HSDUSY(80), HSUSY(5)) were provided by Zeolyst International. The numbers in parentheses designate SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of the samples as given by the manufacturer. The transformation of NH<sub>4</sub>-form of zeolites to the corresponding H-form was carried out by calcination in air at 500 °C for 4–6 h. The effect of chemical composition of the samples on their physico-chemical and catalytic properties was investigated by using materials of the same structural type with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio.

### 2.2. Physico-chemical characterization

The shape and size of the zeolite crystals were determined by scanning electron microscopy (SEM, Jeol, JSM-5500LV). The textural properties of the samples were determined by nitrogen physisorption at 77 K using an ASAP 2020 (Micromeritics) static volumetric apparatus. In order to attain sufficient accuracy in the accumulation of the adsorption data, the ASAP 2020 was equipped with pressure transducers covering the

133 Pa, 1.33 kPa and 133 kPa ranges. The zeolite samples were outgassed under turbomolecular pump vacuum before starting the adsorption experiments. The zeolite samples were outgassed at 110 °C (heating rate 1 °C/min starting from the ambient temperature) until the residual pressure of 0.5 Pa was obtained. After further heating at 110 °C for 1 h the temperature was increased until the temperature 300 °C (heating rate 1 °C/min) was achieved. This temperature was maintained for 6 h.

Acidic properties of zeolites were examined by IR spectroscopy of adsorbed pyridine on Nicolet 6700 spectrometer equipped with MCT detector. Pyridine adsorption proceeded at 150 °C for 20 min at partial pressure 3 Torr, followed by 20 min evacuation at 150 °C. The concentrations of Brønsted and Lewis acid sites were calculated from integral intensities of the individual bands characteristic of pyridine adsorbed on Brønsted acid sites (BAS, at 1545 cm<sup>-1</sup>) and on Lewis acid sites (LAS, at 1455 cm<sup>-1</sup>) and molar absorption coefficients of  $\epsilon(B) = 1.67 \pm 0.1 \text{ cm} \mu\text{mol}^{-1}$  and  $\epsilon(L) = 2.22 \pm 0.1 \text{ cm} \mu\text{mol}^{-1}$ , respectively [20]. The spectra were recorded with a resolution of 4 cm<sup>-1</sup> by collection of 128 scans for a single spectrum. Prior to the adsorption of pyridine, self-supporting wafers of samples were activated in situ by overnight evacuation at temperature 450 °C.

### 2.3. Catalysis

Properties of zeolite samples were investigated in aldol condensation of furfural and acetone. The catalytic experiments were carried out in a 100 ml stirred batch reactor (a glass flask reactor with magnetic stirring for the experiments at 20 and 60 °C, Parr stirred autoclave for the experiments at 100 °C). Before the start of the catalytic runs at 20 and 60 °C, 2 g of catalyst was mixed together with a stirred mixture of 39.5 g acetone and 6.5 g of furfural (acetone/furfural molar ratio 10/1, pre-heated to the desired reaction temperature, 20 or 60 °C) and kept at the reaction temperature for 2–24 h under intensive stirring. For autoclave experiments, 2 g of catalyst was mixed together with the reaction mixture of the above composition and loaded into the autoclave. After initiation of the heating the desired temperature was achieved in

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