



Aqueous-phase furfural-acetone aldol condensation over basic mixed oxides

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ABSTRACT

Catalytic aqueous-phase aldol-condensation of acetone and furfural has been studied in this work. Three different mixed-oxides catalysts (Mg–Zr, Mg–Al and Ca–Zr, with different basic sites distribution) were studied, their activity and selectivity being correlated with their physico-chemical properties. Catalysts with the highest concentration of basic sites (especially medium-strength basic sites) are the most active and selective for the C13 fraction, whereas molar ratios of 1:1 yield the highest selectivities for C13 fraction (more than 60% atomic yield for the Mg–Zr mixed oxide). Concerning to reaction mechanism, *cis* isomers are the first ones formed, whereas *trans* isomers are the most abundant at higher reaction times. The main causes of catalysts deactivation are the modification of the physico-chemical properties of catalysts – because of the interaction with water – and in minor extent, the leaching effect; although homogeneous catalytic effects are discarded at studied conditions.

The products formed, and the kinetic dependence on reactant concentration, are consistent with a catalytic mechanism in which the rate-determining step is the formation of the enolate species. The model considers consecutive reversible reactions yielding C8, in the first step, and C13, in the second step; with a first-order dependence on the species with α -hydrogen (acetone and C8), and zero-th order on those species without it (furfural and C13).

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1. Introduction

The depletion of fossil fuel reserves and the increasing concern about global climate change have accelerated the development of fuel production pathways based on renewable resources. Although there is a vast amount of renewable sources for electricity generation (wind, solar, etc.), biomass is the only renewable resource allowing the manufacture of liquid fuels for transportation [1]. On the other hand, the so-called first generation biofuels (biodiesel and bioethanol) are industrially obtained from crops (starch and triglyceride containing seeds, fruits or roots) that compete with food purposes. Therefore, the development of new processes using the whole lignocellulosic biomass is of key interest, because these processes allow using many kinds of wastes (switchgrass, sawdust, low-priced woods, crops wastes, municipal wastes, etc.) as raw materials [2].

Transformation of biomass can proceed by different routes involving biological, thermal, enzymatic or chemical processes [3]. Chemical processes are the most flexible ones, being possible to use the cheapest and most abundant forms of biomass (such as low quality cellulose, and hemicelluloses) as raw material [4]. The first step in these chemical methods is the transformation

of the biomass into sugar solutions useful for enzymatic and biological transformations (such as bioethanol manufacture). However, the presence of bio-incompatible sugar degradation products, such as furfural, as well as the chemical complexity of these solutions, hinders these upgrading procedures [5]. These furanic compounds (furfural or 5-hydroxymethylfurfural), obtained from sugars by catalytic dehydration under mild conditions [6], are valuable chemical platform for manufacturing chemicals and fuels. Direct hydrogenation of these compounds is feasible [7], but it leads to linear C5–C6 hydrocarbons with very poor performance as fuels. However, the aldol condensation of these furanic compounds, or within these compounds and other bioorganic molecules leads to C₁₃–C₁₅ adducts, which can be transformed upon hydrogenation and deep hydrodeoxygenation in high-quality diesel fuels. Therefore, Dumesic and co-workers, proposed a process for obtaining these fuels from furfural and acetone involving the three above-mentioned sequential steps [8,9]. Among these steps, the aldol condensation is the step that determines the overall number of carbon atoms and, hence, the resulting quality of the obtained fuel. This reaction was initially carried out by aqueous NaOH solutions, as homogeneous catalyst [5,10], but present several problems such as the difficult recovery or the corrosion.

Heterogeneously catalyzed aldol condensations have been widely studied in the last decades, but essentially in gas phase. However, aqueous phase environment raises new problems, such as different reaction mechanisms [11], enhanced catalyst leaching

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[12], and solubility problems [9]. Thus, the development of reusable solid catalysts for aqueous reaction having high activity for this reaction, as well as a complete understanding of the reaction mechanism, has generated an increasing interest.

In the present work, the performance of three basic catalysts for the aqueous-phase aldol condensation of acetone and furfural is studied, determining the effect of the reactant concentration and catalyst properties on the condensation efficiency. Reactivity trends were correlated with physico-chemical properties of the materials, proposing a reaction mechanism and a kinetic model for fitting the data. The three selected materials were the Mg–Zr mixed oxide proposed in the works of Dumesic and co-workers [8,9], a mixed oxide obtained from an Al–Mg hydrotalcite, and a Ca–Zr mixed oxide with enhanced basic properties. These materials have been chosen since they have been previously used with promising results in other basic reactions. Mg–Al mixed oxide was used in reactions of aldol condensation of citral and acetone [13], Knoevenagel condensation between glycerinaldehyde acetonide and ethyl acetoacetate [14] or isobutyl alcohol obtained by Guerbet condensation of ethanol [15]. Recent reports approach the use of Mg–Zr mixed oxide in processes as the production of biodiesel by transesterification reaction using microalgae oil as raw material [16], Knoevenagel condensation of benzaldehyde and ethyl acetoacetate [17], as well as this aldol condensation [18].

2. Experimental and materials

2.1. Materials

Mg–Al layered double hydroxide (LDH) with Mg/Al ratio of 3 was synthesized by co-precipitation at low super-saturation conditions – constant pH – [19]. The procedure involves the K_2CO_3 -assisted precipitation of Mg–Al hydroxide from aqueous nitrate solutions in presence of ultrasonication, the drying of the resulting hydroxides, and their subsequent calcination at 723 K. Further experimental details are given in [19].

Magnesia–zirconia ($MgO-ZrO_2$) catalyst was synthesized using the sol–gel technique proposed by Aramendía et al. [20]. Magnesium nitrate and zirconyl nitrate aqueous solutions were used as precursors, being the preparation procedure fully described in a previous work [21].

Mesoporous $CaO-ZrO_2$ nano-oxide was prepared by a solid–gel route, according to the method described by Liu et al. [22]. One gram of amphiphilicpoly(alkylene oxide) block copolymers ($PEO_{20}PPO_{70}PEO_{20}$, Pluronic P123) (Aldrich) was dissolved in 40.21 mL of absolute ethanol (Panreac, 99.5%). As the surfactant was completely dissolved, 1.01 g of calcium nitrate (Panreac, 99.0%) was added. To this solution, 4.45 g of zirconium(IV) n-propoxide (Aldrich, 70 wt% solution in 1-propanol) mixed with 0.5 g of acetylacetone (acac) (Panreac, 99%) was added with vigorous stirring. Upon stirring at room temperature for 1 h, 1.8 g of deionized water was added drop wise. The mixture was gelled in a closed vessel at 323 K for 24 h. Then, the products were washed with deionized water and filtered. Finally, the sample was heated in flowing He at a ramping rate of 5 K/min to 973 K.

2.2. Experimental and analysis

2.2.1. Catalysts characterization

The crystallographic structures of the mixed oxides were determined by XRD using a Philips PW 1710 diffractometer, working with the $Cu-K\alpha$ line ($\lambda = 0.154$ nm) in the 2θ range of 5° – 85° at a scanning rate of 2° /min. The textural characteristics of specific surface area and pore volume were estimated by nitrogen physisorption at 77 K in a Micromeritics ASAP 2020 surface area and

porosity analyzer. Physisorption data has been analyzed using BET and BJH approaches for determining surface area and pore volume, respectively.

The strength and distribution of the basic/acid sites were determined by temperature programmed desorption of preadsorbed CO_2 or NH_3 in a Micromeritics TPD/TPR 2900. Samples (10 mg) were treated in He at 723 K for 2.5 h and exposed to a CO_2 or NH_3 (2.5% NH_3 in He) stream at 323 K temperature until saturation coverage was reached. Weakly adsorbed CO_2 or NH_3 was removed by flushing with He at the same temperature for about 1.30 h. The temperature was then increased at a linear rate of 5 K/min from 293 K to 723 K and the rate of CO_2 or NH_3 evolution was monitored by mass spectrometry. The same device has been used for performing TPO analysis of the used catalysts, following CO and CO_2 concentration in the outlet gases.

The nature of basic sites was corroborated by CO_2 chemisorption analyzed by Fourier transform infrared (FTIR) spectroscopy, using a Bruker Vector 22 FTIR spectrophotometer (deuterated triglycine sulfate (DTGS) detector), in the 4000 – 400 cm^{-1} range, with a resolution of 2 cm^{-1} and using 100 scans. The bulk chemical composition of all the samples was determined by ICP-MS, using an octapole HP-7500c. The samples were dissolved in HNO_3 1% (1:250) and Rh was used as internal standard. The surface composition of the mixed oxides was measured by X-ray Photoelectron Spectroscopy (XPS), using a SPECS system equipped with a Hemispherical Phoibos detector operating in a constant pass energy, using Mg– $K\alpha$ radiation ($h\nu = 1253.6$ eV). The samples were fixed to the sample holder using a carbon adhesive tape. The background pressure in the analysis chamber was kept below 4×10^{-9} mbar during data acquisition. Since samples are non-conductors it was needed to use a low energy electron flow gun in order to compensate the charging effects [23]. Correctness of binding energy assignments was checked with the C 1s line.

2.2.2. Reaction studies

Reactions were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE Seal) equipped with a PID temperature controller and a back pressure regulator. The reactor was loaded with 0.25 L of an aqueous solution of furfural (Panreac, 98%) and acetone (Panreac, 99.5%), resulting aqueous solution with 5 wt.% of organic compounds for the 1:1 ratio. 500 mg of the catalyst was added (with an average particle diameter of 50–80 μm) and air is purged out by adding nitrogen up to 55 bar for three times before starting the condensation reaction. The reactor was pressurized to 10 bar with N_2 , heated to reaction temperature, and stirred at 1000 rpm for 24 h [23].

Samples were withdrawn from the sampling port during the condensation reaction, filtered, extracted in ethyl acetate (using a volume relation of 1:1) and analyzed by capillary GC in a Shimadzu GC-2010 equipped with a FID detector, using a 15 m long CP-Sil 5 CB capillary column as stationary phase and quantitative responses were determined using standard calibration mixtures. The calibration samples were prepared with known concentrations of each compound in aqueous phase and carrying out the extraction with the same ratio ethyl acetate/water that was going to be used in the sample analysis. Peak assignment was performed by GC–MS in a HP 6890/5973 instrument, using a 15 m long CP-Sil 5 CB capillary column as stationary phase. The C8 compound was identified checking the mass fractionation in the NIST database and C13 compound was identified comparing the retention time and the mass fractionation of the peaks in the mixture sample and the peaks obtained with commercial standard.

Deactivation studies were carried out by collecting the solution obtained after the first reaction with the catalyst in suspension and subjected it to filtration with a 2 μm mesh. The catalyst thus obtained was used in a new reaction with fresh reagents, keeping

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