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Heterogeneous basic catalysis for upgrading of biofuels

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ABSTRACT

The liquid product (biofuel) obtained from biomass pyrolysis has a very complex composition that consists of a mixture of different organic compounds. This mixture presents a high content of oxygenated groups (aldehydes, acids, esters, etc.) that reduce the quality of the biofuel. The deoxygenation of these biofuels improves their quality, reducing the viscosity, increasing the calorific value and improving their thermal stability. In this sense, the deoxygenation of methyl octanoate was carried out over different catalysts with basic properties such as FAU zeolites, SBA-15 ordered mesoporous silicate and clays like sepiolite and hydrolacite. Enhancement of its basic properties was carried out by ion-exchange and/or by impregnation with CsOH. Among these catalysts only over X zeolite was obtained good activity and selectivities to the desired products (C_6, C_7 and C_8 hydrocarbons), especially over the ones with low silicon/aluminum molar ratio. The decrease of the electronegativity of the exchangeable cation in the X zeolite (KNaX1 and CsNaX1) allowed to improve the selectivity to C_6 and C_7 hydrocarbons (60%). Furthermore, the presence of cesium hydroxide (10 wt%) on the zeolite (CsI-NaX1) produced significant conversion of methyl octanoate (70%) with high selectivity to alkenes (53%) reaching a desired/undesired product ratio of 7.3.

1. Introduction

The interest in renewable fuels as replacements for fossil fuels has rapidly increased over the past few years [1–3]. These biofuels have been compared to fossil fuels and the results show partial agreement with fossil fuel specifications.

Biomass is an abundant and carbon-neutral renewable energy resource for the production of biofuels, moving the market dependence away from fossil-based energy sources. There are four primary ways to make biofuels: direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification [4]. Production of biofuel by fast pyrolysis of biomass has received renewed attention in recent years [5–8]. This kind of biofuel typically contains a complex mixture of acids, alcohols, aldehydes, esters, ketones, phenols, alkenes, aromatics, and heavier oxygenates compounds [9]. The presence of aldehydes, acids, esters, etc. is undesirable because they reduce the quality of the biofuel, so that the removal of oxygen atoms or deoxygenation is necessary to use it as fuel. Deoxygenation upgrades the biofuel since the heating value, the chemical and thermal stability are increased and the viscosity and corrosiveness are reduced. In addition, the deoxygenation would allow obtaining an economic biofuel which could be used in transport reducing the toxic carbonyl emissions into the atmosphere from engines running [10].

Deoxygenation of biofuels has been attempted via metal-catalyzed hydrotreating, conducted at high pressure with large consumption of hydrogen [11]. Several attempts have been made to reduce hydrogen consumption and reaction severity [12,13]. For example, acidic catalysts, such as silica–alumina or acid zeolites, have been found to promote deoxygenation of biofuels at lower pressures. However, in all these studies, coke and tar were observed as undesirable by-products. On the other hand, deoxygenation can also be carried out by decarboxylation or decarbonylation using heterogeneous basic catalysis with relatively low hydrogen consumption, as compared to metal catalysts. It is known that, in addition to the need for strong basicity, an active catalyst requires the co-existence of acid and basic sites. In this sense, basic zeolites (low silicon/aluminum ratio) can be used in these reactions since they conjugate acid–base pairs. The exchangeable alkali cation can act as Lewis acid site and the oxygen in the framework near the exchangeable cation has basicity [14].

The purpose of this work is to investigate the deoxygenation reactions over different catalysts with basic properties such as FAU zeolites with low silicon/aluminum molar ratio, using methyl octanoate as a model feed. The effect of the silicon/aluminum ratio, the influence of the cation in the framework and the comparison between basic zeolites and others materials (sepiolite, hydrotalcite and SBA-15) was studied.

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2. Materials and methods

2.1. Materials

Sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) were obtained from Aldrich and sodium aluminate ($NaAlO_2$) from Carlo Erba. Water was purified in a Milli-Q plus 185 instruments. Sodium and cesium chlorides (CsCl, 99%) and cesium hydroxide ($CsOH{\cdot}H_2O$, 99.9%) from Aldrich were employed in the ionic exchange and impregnation, respectively. Chemicals used in the catalytic reactions were methyl octanoate ($CH_3(CH_2)_6COOCH_3$) from Aldrich and methanol (CH_3OH) from Carlo Erba.

2.2. Catalyst preparation

X zeolite syntheses with different silicon/aluminum molar ratio were carried out via the hydrothermal method according to previous studies [15]. In this method, sodium aluminate was dissolved in water and then a mixture of sodium hydroxide and potassium hydroxide was added. Finally, sodium silicate was slowly added to the sodium aluminate–alkaline metal hydroxide solution. The solids were washed with 0.01 M sodium hydroxide or potassium hydroxide solution to avoid protonation and dried at 373 K overnight. Aging and crystallization was carried out at 343 K for 14 h to obtain low silica X zeolite with ratios in the mixture gel of: $SiO_2/Al_2O_3 = 2.2$, $(Na_2O + K_2O)/SiO_2 = 3.25$, $H_2O/(Na_2O + K_2O) = 17$ and $Na_2O/(Na_2O + K_2O) = 0.77$. This zeolite was named KNaX1. The gel mixture was aged at 343 K for 3 h and the crystallization was carried out at 373 K to obtain a zeolite with silicon/aluminum molar ratio of 1.4. In this case, molar ratios in the mixture gel were $SiO_2/Al_2O_3 = 3.44$, $(Na_2O + K_2O)/SiO_2 = 1.32$, $H_2O/(Na_2O + K_2O) = 39.8$ and $Na_2O/(Na_2O + K_2O) = 1.0$. This zeolite was named NaX1.4.

Synthesis of SBA-15 was carried out according to the method of Zhao [16] using tri-block copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) $EO_{20}PO_{70}EO_{20}$ as templating agent and tetraethoxysilane as silicon source in acidic medium. Mass ratio in the synthesis medium were $EO_{20}PO_{70}EO_{20}$: 2 M HCl: TEOS: $H_2O = 2$: 60:4.25:15. The mixture was stirred at 313 K, and then heated at 373 K overnight. The solid product was filtered off and calcined at 773 K for 5 h.

Sepiolite (SP) was supplied by TOLSA, S.A and previously was treated according to Ref. [17]. Hydrotalcite (HTC) was synthesized according to Ref. [18].

NaX1 and CsNaX1 zeolites were prepared by conventional ion-exchange [19] from the KNaX1 zeolite. In this method, one ion-exchange was performed for 24 h at 293 K using 0.05 M NaCl or CsCl solution with a solid–liquid ratio of 50 ml g^{-1}. After ion-exchange, the samples were filtered and washed until absence of chloride with 0.01 N NaOH or CsOH solutions to avoid the protonation and dried at 323 K overnight.

Impregnation of NaX1, SBA-15, sepiolite and hydrotalcite was carried out with cesium hydroxide solution by the incipient wetness method. By this method, only that volume of water which will fill the pores of the material is used, leaving the external areas of the material dry. The amount of CsOH dissolved corresponded to that desired in the final catalysts (zeolite, SBA-15, sepiolite or hydrotalcite). The cesium hydroxide solution was added dropwise to the material with continuous stirring to obtain a good dispersion of the hydroxide in the bulk. Finally, the catalysts were dried at 353 K overnight [19]. All catalysts were impregnated by 10% of Cesium. Hereafter, the catalysts loaded with cesium hydroxide were labeled as CsI-NaX1, CsI-SBA-15, CsI-SP and CsI-HTC.

2.3. Characterization

N_2 adsorption–desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020. X-ray diffraction (XRD) patterns were recorded on a PHILIPS diffractometer (X'PERT MPD) with CuKα radiation and Ni filter. The scanning range of 2θ was set between 5° and 50° with a step size of 0.1. Chemical composition was determined by X-ray fluorescence (XRF) using a PHILIPS PW-1480 instrument.

2.4. Deoxygenation of methyl octanoate

Deoxygenation of methyl octanoate was employed as catalytic test to examine the properties of the different materials in the upgrading of biofuels. The reaction was carried out at atmospheric pressure, in a fixed bed flow reactor made with 1/2″ stainless steel tube under a nitrogen atmosphere. Previously, the catalysts were calcined at 450 °C in nitrogen stream for 1 h, and cooled to the reaction temperature 425 °C. The reactant feed of 10 wt% methyl octanoate in methanol solvent was introduced into the reactor using a syringe pump ($W/F = 200$ g h/mol). Samples from the reaction were analyzed using a GC-FID equipped with a capillary HP-5 column, following a temperature program to optimize product separation.

The methyl octanoate conversion and the selectivity to products were defined as follows: methyl octanoate conversion (%) = moles of consumed methyl octanoate/moles of fed methyl octanoate × 100, selectivity to product (%) = moles of product/moles of consumed methyl octanoate × 100.

3. Results and discussion

3.1. Catalysts characterization

XRD patterns of the zeolites (not shown) displayed the FAU framework with the characteristic peaks of this structure and the normal reduction in the intensity of the signal corresponding to the presence of potassium and cesium (impregnated or ion-exchanged) in the zeolite. The behavior was similar in the others catalysts. This reduction was not linked to the collapse of the structure [19,20]. The characteristics of all catalysts are presented in Tables 1 and 2. In the impregnated catalysts the effect of the cesium hydroxide on the structure was observed in the BET surface area (Tables 1 and 2). BET surface area decreased as the cesium hydroxide was loaded.

3.2. Catalytic activity

The deoxygenation of methyl octanoate over basic catalysts yields several products such as hydrocarbons (C_6, C_7 and C_8, alkanes and alkenes), oxygenated (octanal, octanol, octanoic acid, etc.),

Table 1
Physical properties of the zeolitic catalysts.

	NaX1.4	NaX1	KNaX1	CsNaX1	CsI-NaX1
Si/Al[a] (mol)	1.41	1.04	1.08	1.04	1.02
%Na[a] mol	12.7	22.2	17.4	16.3	17.9
%K[a] mol	0	0	7.4	0	0
%Cs[a] mol	0	0	0	7.1	5.5
S_{BET}[b] (m^2/g)	702	675	452	511	482

[a] Composition determined from XRF data.
[b] Specific surface calculated from N_2 adsorption data applying BET method.

Table 2
Physical properties of non-zeolitic catalysts.

	HTC	CsI-HTC	SP	CsI-SP	SBA15	CsI-SBA15
%Cs[a] mol	0	5.1	0	5.4	0	4.9
S_{BET}[b] (m^2/g)	169	151	158	101	631	359

[a] Composition determined from XRF data.
[b] Specific surface calculated from N_2 adsorption data applying BET method.