Catalysis Today 235 (2014) 176–183

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Prospectives for bio-oil upgrading via esterification over zeolite catalysts

Maria Milina, Sharon Mitchell, Javier Pérez-Ramírez*

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland

ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form 8 February 2014
Accepted 25 February 2014
Available online 27 March 2014

Keywords:
Bio-oil upgrading
Esterification
Zeolite
Hierarchical porosity
Demetallation

ABSTRACT

A promising route to upgrade crude bio-oil prior to hydrotreating is via the catalytic esterification of intrinsic acids and alcohols. This process reduces the acidity and oxygen content of the bio-oil, thereby improving the stability and decreasing the hydrogen consumption in subsequent refining steps. Here, the applicability of microporous zeolite catalysts of different framework type and composition is explored in the liquid-phase esterification between the characteristic bio-oil constituents, acetic acid and *o*-cresol. Ester formation, which is significantly influenced by concurrent coke-forming reactions, is dependent on the reaction temperature and on the size of the zeolite micropores, with maximum yields observed over large-pore beta and faujasite catalysts. The benefits of introducing secondary mesoporosity through demetallation in alkaline media are remarkable for medium-pore ZSM-5 due to the alleviated diffusion constraints, while the enhanced performance of hierarchical faujasite is less pronounced, but still appreciable. Characterization of the spent catalysts by XRD and N_2 sorption evidences the preserved crystallinity and microporosity of the zeolites, while IR spectroscopy of adsorbed pyridine reveals a small reduction in the concentration of Brønsted acid sites. The latter is detrimental for the ester formation upon reuse of ZSM-5 zeolites, while faujasite catalysts preserve their initial activity. These findings highlight both the potential of microporous zeolites and their hierarchical analogs for acid-catalyzed condensation reactions in the field of bio-oil upgrading and some of the possible challenges which could be faced.

1. Introduction

Biomass-derived pyrolysis oils, or bio-oils, are promising candidates to replace petroleum fuels. However, their direct application within existing infrastructure is impeded by their high oxygen content (20–50 wt.%) and acidity (pH = 2.5–3), which impart undesirable properties such as low heating value, immiscibility with hydrocarbon fuels, thermal and chemical instability, high viscosity, and corrosiveness [1,2]. The upgrading of bio-oils to conventional fuels requires the removal of oxygen to within a few wt.%, which can be accomplished by zeolite cracking or hydrotreating [3–5]. While hydrotreating is considered to have the greatest potential to obtain high-grade fuels, its economic viability is limited by the identification of stable catalysts and the hydrogen consumption [6,7]. Currently, a catalytic cascade approach, aimed at exploiting the intrinsic reactivity of the oxygen-containing functional groups (i.e. alcohols, acids, aldehydes, and ketones) prior to hydrotreating (Fig. 1), is seen as a promising solution to facilitate the upgrading process [8]. In this context, the integration of an esterification step would attractively reduce the acid concentration, thereby improving the stability [9]. Additionally, as with other condensation reactions such as ketonization and aldol condensation, this would enable the partial elimination of oxygen in the form of water, benefiting the process economics by reducing the amount of hydrogen required in succeeding steps.

The removal of carboxylic acids from bio-oils via esterification has been commonly approached through the addition of an external alcohol, such as methanol or ethanol [10]. Together with reducing the pH, the alcohol introduced acts as a solvent, immediately decreasing the viscosity and increasing the heating value [11]. Several recent studies have reported enhancements in the bio-oil quality on tandem application of external alcohols with solid acid catalysts, including resins [9,12–14] and zeolites [15]. However, this would bring little benefit upon further hydrotreating of the bio-oil, as the oxygen content is unaltered. Additionally, this route relies on the availability and price of sustainably produced alcohols.

An alternative, but largely neglected, strategy is the direct catalytic esterification of bio-oil constituents. Comprising a major

---

* Corresponding author. Tel.: +41 44 633 7120; fax: +41 44 633 1405.
E-mail address: jpr@chem.ethz.ch (J. Pérez-Ramírez).

http://dx.doi.org/10.1016/j.cattod.2014.02.047

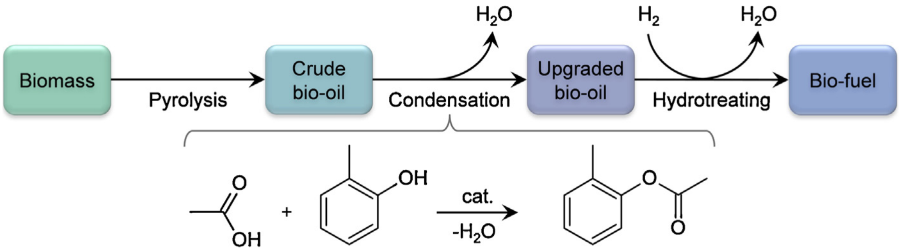

Fig. 1. Cascade approach for the production of fuels from biomass including an intermediate deoxygenation step via condensation reactions. The esterification of *o*-cresol with acetic acid, two characteristic constituents of crude bio-oil, is investigated in this manuscript.

fraction of alcohols in pyrolysis oil (3–22 wt.%) [16], phenolic compounds are considerably less reactive than methanol or ethanol requiring more severe process conditions [17]. In turn, this introduces increased complexity in the design of a suitable esterification catalyst, especially in relation to their stability in aqueous acidic medium. Under these circumstances, acidic zeolites would represent an adequate choice of the catalysts in view of their robustness and synthesis flexibility, resulting in materials with various pore size, Si/Al ratio, acid site distribution, and hydrophobicity [18]. However, due to relatively large size of the phenolic alcohols with respect to the micropore dimensions in zeolites, significant mass transfer limitations can be expected. Consequently, the use of hierarchical zeolites containing an auxiliary network of mesopores could be highly beneficial. Hierarchical analogs of virtually any family of commercial zeolites can now be prepared through the different strategies available [19,20], and have demonstrated superior performance in many traditional and emerging applications, including bioenergy-related processes such as biomass catalytic pyrolysis [21–23] and bio-oil deoxygenation [24,25].

Here, we assess the potential of zeolite catalysts for bio-oil upgrading via esterification in the liquid-phase reaction between acetic acid and *o*-cresol, two characteristic bio-oil components (Fig. 1). Firstly, the esterification performance of various microporous zeolites of distinct framework-type (FER, MFI, MOR, BEA, FAU) and composition (Si/Al = 3–1000) is studied at different temperatures. Secondly, the influence of introducing intracrystalline mesopores is evaluated. For this purpose, hierarchical faujasite and ZSM-5 zeolites were prepared by means of alkaline treatment followed by an optional sequential acid wash. The relative impact of the mesopore surface area is assessed in relation to the extent of diffusion constraints. Additionally, we address the important aspect of catalyst reusability and stability in the acidic reaction medium.

2. Experimental

2.1. Catalyst preparation

An overview of the various commercial ferrierite (FER), ZSM-5 (MFI), mordenite (MOR), beta (BEA), and faujasite (FAU) zeolites applied in this work, including the sample codes, manufacturers, chemical composition, and textural properties, is provided in Table 1. An amorphous silica-alumina (ASA) was also evaluated as a non-zeolitic reference. The zeolites in NH_4-form were calcined at 823 K for 5 h with a heating ramp of 5 K min^{-1} in static air to attain the H-form. The FAU15 and MFI40 zeolites were alkaline treated in stirred aqueous NaOH solutions (0.1–0.3 M, 338 K, 30 min, 30 cm^3 per gram of zeolite) in the absence (MFI40) or presence (FAU15) of tetrapropylammonium bromide (TPABr, 0.2 M) using an Easymax^{TM} 102 (Mettler Toledo). The suspensions were then quenched in ice-water and filtered, and the isolated solids were washed extensively with distilled water and dried at 338 K. This yielded the alkaline-treated samples denoted AT*x*, where *x* relates to the NaOH concentration applied (i.e. 1 = 0.1 M). MFI40-AT*x* samples were subjected to acid washing in aqueous HCl solution (0.1 M, 338 K, 6 h, 100 cm^3 per gram of zeolite) resulting in MFI40-AT*x*-AW catalysts. Acid washing of FAU15-AT*x* samples was undertaken by treatment in aqueous ethylenediaminetetraacetic acid disodium salt (Na_2H_2–EDTA, 0.03 M, 373 K, 6 h, 15 cm^3 per gram of zeolite). The alkaline and acid-treated zeolites were converted into the protonic form by three consecutive ion exchange treatments in aqueous NH_4NO_3 (0.1 M, 298 K, 12 h, 100 cm^3 per gram of zeolite), followed by calcination as described above.

2.2. Catalyst characterization

The concentrations of silicon and aluminum in the solids were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Horiba Ultima 2 instrument. Powder X-ray diffraction (XRD) was conducted in a PANalytical X'Pert-Pro diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å). Data were recorded in the 3–60° 2θ range with an angular step size of 0.05° and a counting time of 8 s per step. The lattice parameter (a_0) of desilicated faujasite zeolites was determined according to the ASTM D3942-03 protocol based on the (4 4 4), (5 3 3), (6 4 2), and (5 5 5) reflections. N_2 isotherms at 77 K were measured in a Quantachrome Quadrasorb-SI analyzer following evacuation of the samples at 573 K for 10 h. Fourier transform infrared spectroscopy (FTIR) of adsorbed pyridine was conducted in a Bruker IFS 66 spectrometer (650–4000 cm^{-1}, 2 cm^{-1} optical resolution, co-addition of 32 scans). Self-supporting wafers of zeolite (5 ton cm^{-2}, 20 mg, 1 cm^{-2}) were degassed under vacuum (10^{-3} mbar) for 4 h at 693 K, prior to adsorbing pyridine at room temperature. Gaseous and weakly adsorbed molecules were subsequently removed by evacuation at 473 K for 30 min. For selected samples, the evacuation temperature was raised to 693 K in order to assess the relative strength of the Brønsted acid sites. The total concentrations of Brønsted (c_B) and Lewis (c_L) acid sites were calculated from the band areas of adsorbed pyridine at 1545 cm^{-1} and 1454 cm^{-1}, using the extinction coefficients, $\varepsilon(B) = 1.67\ cm^{-1}\ mol^{-1}$ and $\varepsilon(L) = 2.22\ cm^{-1}\ mol^{-1}$, determined previously [26].

2.3. Catalytic tests

The esterification of *o*-cresol with acetic acid was undertaken in glass-pressure tubes (10 cm^3 working volume) between 433 and 493 K under autogenous pressure. In a typical experiment, the powdered catalyst (50 mg) was added to a mixture comprising *o*-cresol (4 mmol, Acros Organics, 99%), acetic acid (2 mmol, Acros Organics, ≥99.7%), an internal standard (*n*-octane, 1 mmol, Sigma–Aldrich, ≥99%), and a solvent (*p*-xylene, 41 mmol, Sigma–Aldrich, ≥99%). Following the desired reaction time, the reactors were cooled, and liquid samples were collected and analyzed using a gas chromatograph (HP 6890, Hewlett Packard) equipped with a HP-5 capillary column and FID. Reactants and products were calibrated using pure standards. The assignments were confirmed by GC–MS (HP 5973,