Deoxygenation of bio-oil over solid base catalysts: From model to realistic feeds

Begoña Puértolas [1], Tobias C. Keller [1], 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

ABSTRACT

This study investigates the design of mild base catalysts for the deoxygenation of bio-oil *via* aldol condensation paths. The first part rationalizes the active, selective, and stable performance of supported MgO catalysts in the vapor phase condensation of propanal, which is maximized upon the mechanochemical activation of a siliceous USY zeolite (Si/Al = 405) with 1 wt.% $Mg(OH)_2$. Infrared spectroscopic studies of the interaction with CO and CO_2, reveal that the presence of 4-coordinate Mg likely localized in framework defects on the zeolite surface, and the avoidance of MgO formation are key to moderating the basicity with respect to the bulk oxide. The second part compares the best-performing MgO/USY catalyst with the most promising previously reported catalysts: K-grafted USY and Ca-hydroxyapatite. A detailed kinetic analysis of the conversion of individual bio-oil constituents (propanal or acetic acid) and binary mixtures thereof (propanal with acetic acid, methanol, or water) provides insights into the reaction network, rate-limiting steps, and relative surface coverage of reactants and products over each catalyst. This enables the anticipation of the aldol-condensation performance in simulated and real bio–oil mixtures. A significant inhibitory effect is observed in the presence of acetic acid, but the K-grafted USY zeolite is found to preserve its stability and retain the highest activity due to the weaker adsorption of acidic compounds. The presence of water has no pronounced effect on the observed reaction rates, while methanol is found to selectively poison Ca-hydroxyapatite due to the competitive adsorption on the active sites. The attained results under real bio-oil conditions demonstrate the effectiveness of this simplified approach to bridge the complexity gap between the study of model compounds and real bio-oil.

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1. Introduction

One of the primary challenges in the sustainable production of second-generation biofuels is the development of more efficient routes for the deoxygenation of crude pyrolysis oils (30–50 wt.% oxygen) than the direct hydrodeoxgenation (HDO) or cracking. A promising upgrading strategy comprises a cascade deoxygenation process, wherein the pyrolysis vapors are subjected to catalytic deoxygenation prior to HDO, thereby reducing the H_2 usage by *ca.* 50% [1]. The intermediate step(s) exploit the intrinsic reactivity of the bio-oil constituents to eliminate oxygen as water or carbon oxides *via* condensation reactions as esterification, aldol condensation, and ketonization [2–5]. Aldol condensations are particularly attractive [6], as the low-boiling aldehydes and ketones,

which account for up to 25 wt.% of the crude bio-oil [7], can be converted into gasoline- and diesel- range compounds, increasing the yield of liquid fuels and thus, the carbon efficiency. In contrast to traditional strong solid bases such as alkaline earth metal oxides and activated hydrotalcites which prompt rapid deactivation due to the formation of coke [8,9], a number of mild base catalysts have been identified to yield stable performance in aldol condensation such as supported alkali [10,11] or alkaline earth metals [9,12–16], other supported metal oxides [17], and calcium hydroxyapatites [18]. In the case of alkaline earth metal oxides, it is known that the basic strength can be moderated by supporting it on an appropriate material such as SiO_2 [9,12,13], zeolites [14,15] or carbons [16], leading to the weaker bonding of the adsorbed species, and thus facilitating the desorption of the products from the catalyst surface. However, whereas previous studies reported the origin of the moderating effect for supported alkali and calcium hydroxyapatites [11,18], in the case of supported alkaline earth metal catalysts, different synthesis methods, MgO loadings, and types of support have

been used in each case, leaving the optimal preparation conditions and catalyst composition unclear.

Pyrolysis oils comprise complex mixtures of over 400 different components, 15–35 wt.% water and 0.01–3 wt.% solid particles, which presents significant challenges for the development of catalytic routes for their deoxygenation [19]. Owing to the difficulty in rationalizing the compositional changes based on the individual reaction pathways, and especially the interactions of the different functional groups on the catalyst surface, this is typically approached through the study of model compounds instead of real pyrolysis oils [20]. In particular, for the vapor phase aldol condensation, several studies have been devoted to the investigation of the reaction network for individual aldehydes such as acetaldehyde or butanal over acidic, basic, or bifunctional catalysts either through the *in situ* spectroscopic evaluation [9] or by a full *ex situ* product analysis [4]. Whereas monofunctional (basic) catalysts usually attain a rather simple product distribution [21], for multifunctional materials various side reactions including hydrolysis, cracking, oligomerization, and aromatization [22] are known to compete with aldol condensations, resulting in complex product mixtures consisting of aromatics, linear hydrocarbons, and phenolic compounds among others [23]. However, the mechanistic understanding of the transformation of pure aldehydes in vapor phase is limited [24], and the influence of major bio-oil constituents on the reaction rates remains unaddressed. Accordingly, insights into the interactions of promising catalysts with single bio-oil constituents *versus* complex mixtures can assist in bridging the complexity gap between model components and crude bio-oil.

Herein, we investigate the design of mild base catalysts for bio-oil deoxygenation *via* aldol condensation. To gain insight into the moderate basic strength and performance of supported alkaline earth metal oxides, the first part of the manuscript tackles the preparation of supported MgO catalysts, which is approached by the mechanochemical activation of a high-silica USY zeolite with Mg(OH)$_2$. In-depth characterization provides unprecedented understanding of the nature of the active sites in the resulting MgO/USY catalysts, while their active, selective, and stable performance is confirmed in the self-condensation of propanal. The second part of the manuscript compares the deoxygenation activity of the best-performing MgO/USY with that of previously reported Ca-hydroxyapatite [18], and K-grafted USY catalysts [11]. A comprehensive kinetic analysis of the effect of the addition of representative bio-oil constituents such as acetic acid, methanol, and water on the rate of propanal conversion enables the identification of the mechanistic paths governing the performance of each system in simulated feed mixtures, which is further corroborated under real bio-oil conditions.

2. Experimental

2.1. Catalysts

The parent high-silica USY zeolite (P-USY) was obtained in protonic form from Tosoh Corporation (HSZ-390HUA, Si/Al = 405). MgO/USY zeolites were prepared by dry and wet impregnation, spray deposition, and mechanochemical activation. For the dry impregnation, an aqueous solution (0.25 M, 4 cm^3) of Mg(NO$_3$)$_2$·6H$_2$O (99%, Fluka) was added dropwise to the USY zeolite (4 g) at 298 K, which was subsequently dried at 338 K overnight, resulting in sample 1MgO/USY-DI. In the case of wet impregnation, the USY zeolite (4 g) was added to a vigorously stirred aqueous solution of Mg(NO$_3$)$_2$·6H$_2$O (0.05 M, 20 cm^3) at 298 K. The resulting mixture was slowly dried in a rotary evaporator (Büchi RE-111) yielding sample 1MgO/USY-WI. The spray deposition method [25] was performed with a Büchi Mini Spray Dryer B-290 equipped

with a two-fluid nozzle of 1.4 mm in diameter. The USY zeolite (8 g) was added to a stirred aqueous solution of Mg(NO$_3$)$_2$·6H$_2$O (0.025 M, 80 cm^3) at 298 K. The resulting suspension was pumped (3 cm^3 min^{-1}) into the nozzle (T_{inlet} = 493 K, T_{outlet} = 363 K, aspiration rate = 35 m^3 h^{-1}) together with a spray air flow (0.5 m^3 h^{-1}) and the dried powder (1MgO/USY-SD) was separated by a cyclone. For the mechanochemical activation, the zeolite (4 g), the desired amount of Mg(OH)$_2$ (99.9%, Fisher Chemicals), and deionized water (2 cm^3) were milled in a NanBei QM-1SP4 planetary ball mill (500 rpm, 30 min) to reach nominal MgO contents of between 0 and 20 wt.%. The resulting powders (coded xMgO/USY, where x refers to the nominal MgO content in wt.%), were dried at 338 K. A reference sample subjected to ball milling in the absence of Mg(OH)$_2$ was denoted BM-USY. For comparative purposes, SiO$_2$ (99.5 wt.%, Sigma–Aldrich) was also used as support (1MgO/SiO$_2$). All the catalysts were subsequently calcined for 2 h in flowing air at a temperature (T_c) of 873 K unless otherwise specified (heating rate 5 K min^{-1}).

The preparation of the benchmark catalysts, K-grafted USY and Ca-hydroxyapatite, is reported in detail elsewhere [11,18]. Briefly, for the K-USY, the zeolite (2 g) was introduced into a KOH solution (0.1 M, 60 cm^3, 85%, Fisher Chemicals) in methanol (99.8%, Sigma–Aldrich) at room temperature, stirred at 500 rpm for 10 min, filtered, washed thoroughly with the same solvent, dried at 338 K, and subsequently calcined in static air (823 K, 5 h, heating rate 5 K min^{-1}). The calcium hydroxyapatite (coded Ca-HA) was precipitated by the dropwise addition of aqueous (NH$_4$)$_2$HPO$_4$ (0.4 M, 98%, Sigma–Aldrich) into a stirred aqueous solution of Ca(NO$_3$)$_2$·4H$_2$O (0.6 M, 99%, Sigma–Aldrich) at room temperature and constant pH (9.5), which was adjusted by the addition of ammonia solution (25% in H$_2$O, Sigma–Aldrich). The precipitate was stirred at the same temperature for 24 h, before it was isolated by filtration, thoroughly washed with deionized water, dried at 383 K for 12 h, and calcined in static air (873 K, 2 h, heating rate 5 K min^{-1}).

2.2. Methods

X-ray diffraction (XRD) patterns were measured on a PANalytical X'Pert PRO-MPD diffractometer using Ni-filtered Cu Kα radiation (λ = 0.1541 nm). Data were recorded in the 2θ range of 5–70° with an angular step size of 0.05° and a counting time of 8 s per step. N$_2$ and Ar sorption at 77 K were undertaken in Micromeritics TriStar II and Micromeritics 3Flex instruments, respectively. Prior to the measurement, the samples were evacuated at 573 K for 3 h. Fourier transform infrared spectroscopy (FTIR) of adsorbed CO (99.998%, Messer) and CO$_2$ (99.998%, Messer) were measured in a Bruker IFS 66 spectrometer (650–4000 cm^{-1}, 2 cm^{-1} optical resolution, co-addition of 32 scans). Self-supporting wafers of the sample (5 ton m^{-2}, 50 mg, 1 cm^2) were evacuated to 10^{-3} mbar for 4 h at 693 K, saturated with CO$_2$ at room temperature, and subsequently evacuated at different temperatures (298–423 K) for 10 min, before the individual spectra were recorded. CO (ca. 2 mbar) was adsorbed on the samples at 77 K, followed by evacuation to different pressures, equilibration, and acquisition of the individual spectra. High-angle annular dark field scanning transmission electron (HAADF-STEM) micrographs as well as energy dispersive X-ray spectroscopy (EDS) element maps were acquired on a FEI Talos instrument operated at 200 kV. The samples were dispersed as dry powders onto lacey carbon coated copper grids. As zeolites are known to gradually amorphize upon prolonged exposure to electron radiation, the mapping experiments were typically performed with beam currents of around 70 pA and with a dwell time of 10 ms to further protect the specimen. The magnesium content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Horiba Ultima 2 instrument equipped