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Performance of Mesoporous HZSM-5 and Silicalite-1 Coated Mesoporous HZSM-5 Catalysts for Deoxygenation of Straw Fast Pyrolysis Vapors

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Highlights

- Coating of mesoporous ZSM-5 with Silicalite-1 to passivate external acid sites
- Catalyst deactivation was followed during vapor upgrading in tandem micro-pyrolyzer
- Coating of mesoporous HZSM-5 with silicalite-1 reduced the coking propensity

ABSTRACT

Catalytic treating of biomass fast pyrolysis vapors offers a promising route to convert many different types of lignocellulosic biomass into biofuels. Considerable research efforts have focused on using zeolite catalysts, especially the microporous HZSM-5 zeolite. Unfortunately, the zeolite's initial high activity in forming coke and light gases reduces the overall oil yield. In this contribution, we synthesized conventional HZSM-5 zeolite, mesoporous HZSM-5 zeolite, and a core-shell catalyst consisting of mesoporous HZSM-5 zeolite coated with a thin layer (<20 nm) of silicalite-1 zeolite. The catalysts were characterized by inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂ and Ar physisorption, temperature programmed desorption of ammonia (NH₃-TPD), diffuse reflectance infrared fourier transform spectroscopy (DRIFT) spectra, and ²⁷Al nuclear magnetic resonance (NMR). The catalysts were tested in a tandem micro-pyrolyzer system for deoxygenation of wheat straw derived fast pyrolysis vapors in a downstream catalytic fixed bed reactor and the quantitative product analysis was performed with GC-MS/FID/TCD and TGA-MS. The change in yields of different product groups was monitored during catalyst deactivation for an increasing number of pyrolysis vapor pulses and the cumulative carbon recoveries of all product streams (char, vapors, gas, and coke) were compared at different biomass-to-catalyst ratios (~4 and ~1) for catalyst loadings of 2 and 8 mg,

respectively. In addition, the yields were compared for the same number of zeolitic acid sites. Even though the coking propensity was highest for the mesoporous HZSM-5 (5.1% carbon recovery of fed biomass at B:C = 1), it showed improved conversion of oxygenates (wt% O of vapors = 15) and a higher tolerance towards deactivation by coking compared to the conventional HZSM-5 (wt% O of vapors = 20). Coating of mesoporous HZSM-5 with silicalite-1 reduced the number of acid sites per mass of catalyst by ~20%, which is attributed to the addition of the inert silicalite-1 layer and passivation of the external acid sites of the mesoporous HZSM-5. Compared to mesoporous HZSM-5, the added silicalite-1 shell reduced the coke yield by 43% (from 5.1 to 2.9 wt% of fed biomass carbon) for the same catalyst mass and by 8% (4.7 wt% of fed biomass carbon) for the same total number of acid sites. Furthermore, the tolerance towards deactivation observed for the mesoporous HZSM-5 core was largely preserved—especially for conversion of small oxygenates like acids, alcohols and aldehydes, resulting in vapors with 14 wt% O.

ABBREVIATIONS

AC, acids; ALC, alcohols; ALD, aldehydes; ALI, aliphatics; BTX, benzene, toluene and xylenes; CFP, catalytic fast pyrolysis; daf, dry and ash-free; DAR, diaromatics; d.b., dry basis; DTG, derivative thermogravimetry; EST, esters; FID, flame ionization detection; FUR, furans; GC, gas chromatography; KET, ketones; MAR, monoaromatics; MPH, methoxy-phenolics; MS, mass spectrometry; N, nitrogen containing compound; n.d., not determined; PH, phenolics; SUG, sugars; TEM, transmission electron microscopy; TGA, thermogravimetric analysis; TPD, temperature-programmed desorption;

KEYWORDS. Wheat Straw; Biomass; Catalytic Fast Pyrolysis; mesoporous HZSM-5; Passivation; Core-Shell; Silicalite-1;

1 INTRODUCTION

Integration of biomass-derived fast pyrolysis oils in existing oil refineries can decrease our dependence on crude oil and increase the share of renewables in the transport sector [1–4]. Fast pyrolysis processes are generally flexible with respect to biomass feedstocks [5–12]. Short gas residence times (less than 2 s), high heating rates (>500 °C/s), moderate temperatures (400–700 °C), and low pressures (1–5 atm) are required to obtain a high oil yield. The pyrolysis oil contains hundreds of different oxygenated species, which—unfortunately—render the oil acidic and unstable. Catalytic deoxygenation of the biomass pyrolysis vapors prior to condensation reduces the acidity of the oil and improves its chemical stability, heating value, and miscibility with petroleum derived streams [13–17]. However, these improvements come at the expense of carbon loss as light hydrocarbons, CO, CO₂, and coke [18,19]. HZSM-5 zeolite is considered among the most suitable solid acid catalysts for the production of aromatics and gasoline range products from biomass derived pyrolysis vapors since the shape selective micropores (~ 5.5 Å) improve the selectivity to aromatics and limit coke formation [20,21]. Nevertheless, rapid deactivation by coking occurs [15,22].

Previous studies using small scale batch pyrolyzers and a variety of biomass feedstocks generally found that the introduction of mesopores to HZSM-5 zeolite lead to higher yield of monoaromatics while the influence on coke and gas yields was not always investigated or inconsistent results were reported across laboratories [23–26]. Testing mesoporous HZSM-5 zeolite at scales that allowed collection of liquid product indicated that the yield of coke increased for mesoporous HZSM-5 zeolite compared to its microporous version [27–30], but the tolerance towards deactivation by coke improved, leading to extended activity for deoxygenation and aromatization. When monitoring the change in vapor product distribution as function of increasing biomass-to-catalyst

(B:C) ratio using an on-line mass spectrometer, Jia et al. [29] reported higher yields and a broader distribution of mono- and di-aromatics over the mesoporous HZSM-5 zeolite while for the conventional zeolite the yield of olefins and aromatic hydrocarbons decreased faster due to a faster deactivation.

While the introduction of auxiliary mesoporosity to HZSM-5 zeolite reduces the diffusion restrictions [25,31,32], it also increases the external acidity which lacks space confinements and therefore allows reactive oligomeric species and coke precursors to attach to these sites. The first attempts to limit the external acidity comprised the deposition of a SiO₂ layer by chemical vapor [33,34] or liquid deposition [35–37], which successfully reduced the coke yields and increased the selectivity of p-xylene in the methanol-to-hydrocarbon (MTH) reaction [24] and biomass catalytic fast pyrolysis (CFP) [36]. Unfortunately, a significant reduction in total acidity [36] indicated that some pore entries were blocked by the randomly deposited SiO₂ considering that the number of the external acid sites is much less than that of the internal acid sites [38]. Growing a shell of catalytically inactive aluminium-free silicalite-1 zeolite with the same MFI zeolite framework as HZSM-5 zeolite along the external surface of HZSM-5 core crystal would reduce the external acidity while likely preserving the access and number of internal acid sites [39]. The applications of such core-shell HZSM-5/silicalite-1 materials have been demonstrated for simple reactants [40–44]. With respect to catalytic fast pyrolysis of biomass, Hu et al. [38] recently tested a conventional HZSM-5 coated with silicalite-1 for upgrading of vapors from pine pyrolysis in a fixed bed (550 °C) located ex-situ and reported increased yields of benzene, toluene and xylenes (BTX) and decreased coke yields after silicalite-1 coating. The performance of silicalite-1 coated mesoporous HZSM-5 for the MTH process and in-situ CFP was reported by Li et al. [45]. While an increased lifetime for the MTH reaction was observed, no obvious differences in product yields from CFP were observed apart from an increased p-xylene selectivity.

The work of Li et al. [45] is among the first reports that investigate the performance of silicalite-1 coated mesoporous HZSM-5 for CFP of whole biomass. Unfortunately, catalyst deactivation at increasing B:C ratios was not investigated and the tests were performed with direct contact between the catalyst and biomass (in-situ), which can lead to poisoning of acid sites by the biomass indigenous ash [46]. Transfer of alkali metals to the catalyst can be avoided by placing the catalyst downstream of the pyrolysis section [15,16] (ex-situ), which allows for vapor-phase upgrading of agriculture residues like wheat straw with higher ash content and lower cost compared to woody biomass. To the best of our knowledge, the performance of silicalite-1 coated mesoporous HZSM-5 in ex-situ CFP has not yet been reported. Since in ex-situ CFP the yield of carbonaceous deposits on the catalyst (coke) is determined separately from the char, the coking propensity of catalysts can be compared and correlated with their properties.

In this study, we synthesized conventional HZSM-5 zeolite (Conv-ZSM-5), mesoporous HZSM-5 zeolite (Meso-ZSM-5), and a core-shell catalyst consisting of a core of mesoporous HZSM-5 zeolite coated with a shell of silicalite-1 zeolite (Shell-Meso-ZSM-5). The catalysts were characterized and tested in a tandem micro-pyrolyzer system for upgrading wheat straw derived fast pyrolysis vapors. Product analysis for the catalytic tests was performed with GC-MS/FID/TCD and TGA-MS. We established a correlation between the GC-FID response and the molecular properties of ~50 calibrated vapor compounds. From this correlation, the yield for all vapor compounds could be calculated based on their molecular properties. This approach allowed monitoring the change in the yields of different product groups due to catalyst deactivation for an increasing number of injected biomass samples. The importance of reporting carbon balance was recently stressed [18]. We therefore determined the carbon recoveries of all product streams (char, vapors, gas, and coke) and assessed the performance of the catalysts based on their product yields and tolerance towards deactivation.

2 EXPERIMENTAL SECTION

2.1 Feedstock

The biomass feedstock was obtained by downsizing wheat straw pellets using a hammer mill. Ultimate and proximate characterization for wheat straw particles of the size <1.4 mm was reported earlier [15]. In this study, a sieve fraction of 106–250 μm was used and re-analyzed. The elemental content was determined using an Elementar® elemental analyzer (vario MICRO cube) in CHNS operating mode (ultimate analysis). The temperature of the reduction and combustion tubes was set to 1050 °C and 850 °C, respectively. A thermal conductivity detector (TCD) was used to quantify the amounts of carbon, hydrogen, nitrogen, and an infrared (IR) detector was used to quantify sulfur. Rice flour with known elemental composition was used for calibration, and the reported result represents the average from duplicate analysis. Based on the amount of combustion products and the dry and ash-free (daf) mass of samples loaded, the weight percentages of C, H, N, S, and O (by difference) were calculated to be 48.2%, 5.0%, 1.27%, 0.1%, and 45.4%, respectively.

Proximate analysis was conducted using a Mettler Toledo TG/DSC 1 following the procedure developed by Johnston [47]. About 30 mg of biomass was loaded in alumina crucibles and the temperature was first ramped to 105 °C at 10 °C/min in a nitrogen atmosphere (100 ml/min) and held at that temperature for 40 min in order to determine moisture. For the analysis of volatiles, the temperature was ramped under the same flow conditions in N₂ from 105 to 900 °C at 10 °C/min and the temperature was held at 900 °C for 20 min. For determination of the fixed carbon content, nitrogen was replaced by air and the temperature was held at 900 °C for 30 min. The remaining mass after combustion of fixed carbon was considered ash. The moisture (as received (a.r.)), volatiles (dry basis, (d.b.)), ash (d.b.), and fixed carbon (d.b., by difference) were determined to be 7.1 wt-%, 74.4 wt-%, 9.8 wt-%, and 15.8 wt-%, respectively.

Sulfuric acid hydrolysis was used for the determination of carbohydrates bound in the cellulose and hemicellulose. Klason lignin was determined as the ash free residue after hydrolysis. First, 1.5 ml of 72% H_2SO_4 was added to 0.16 g sample and the sample was pre-hydrolyzed for 60 minutes at 30 °C. Second, after dilution of the hydrolysate with MilliQ water (42 ml), the liquid samples were autoclaved at 120 °C for 60 minutes. Filtered liquids were analyzed on an HPLC column, while the solid residue was heated to 550 °C to determine the lignin ash content. The content of carbohydrates and Klason lignin was determined to be ~68.5 wt-% and 20.2 wt-%, respectively. The contribution of individual carbohydrates is listed in Table S2.

2.2 Catalyst preparation

Used chemicals: Tetrapropylammonium hydroxide (TPAOH, Sigma-Aldrich, 1.0 M in H_2O), tetraethylorthosilicate (TEOS, Sigma-Aldrich, ≥99.0 %), sodium aluminate (NaAlO_2 , Sigma-Aldrich, anhydrous), carbon black particles (BP-2000) with average particle diameter of 12 nm.

Conv-ZSM-5. The synthesis of ZSM-5 was based on the work of Thumbayil et al. [48]. NaAlO_2 was dissolved in 7.2 ml TPAOH before 4.4 ml of TEOS was added dropwise (corresponding to nominal Si/Al=40) to the stirring solution. After 1 hour of stirring, the mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 180°C for 24 h. The product was washed with distilled water, calcined for 20 h at 550 °C and ion exchanged to the proton form (see Ion exchange section).

Meso-ZSM-5. Following the procedure reported by Jacobsen et al. [49], carbon black was used to synthesize mesoporous ZSM-5. First, NaAlO_2 was dissolved in 7.2 ml TPAOH and then 2 g of carbon black was impregnated with this solution and dried overnight at room temperature. The dried mixture was impregnated with 4.4 ml of TEOS and dried overnight again at room temperature. Then the beaker was placed in a Teflon-lined stainless steel autoclave with distilled water around the beaker and heated at 180 °C for 72 h. The product was washed with distilled

water and calcined at 550 °C for 20 h. This sample was also ion exchanged to the proton form (*vide infra*).

Shell-Meso-ZSM-5. Following previous work [50], the as-synthesized mesoporous ZSM-5 was impregnated first with TPAOH until incipient wetness in a Teflon beaker and dried overnight at room temperature and then with TEOS until incipient wetness and dried overnight at room temperature. The beaker was placed in a Teflon-lined stainless steel autoclave with distilled water around the beaker and heated at 180 °C for 72 h. The product was washed with distilled water and calcined at 550 °C for 20 h. The final product was ion exchanged (see Ion exchange section).

Ion exchange. 1 g of zeolite was added to 80 ml of 1 M ammonium nitrate aqueous solution and stirring the solution at 80 °C for 1 hour. The process was repeated three times and the last ion exchange was carried out overnight. Finally, the zeolite was collected by centrifugation, washed with distilled water and calcined at 550 °C for 10 h.

2.3 Catalyst characterization

Catalysts were characterized with powder X-ray diffraction in a Huber G670 diffractometer operated in transmission mode with Cu K α irradiation from a focusing quartz monochromator with the scanning rate of 2 °/min.

Scanning electron microscopy (SEM) was carried out on a Quanta 200 ESEM FEG operated at 20 kV and transmission electron microscopy (TEM) was performed on a FEI Tecnai T20 G2 microscope operated at 200 kV to investigate particle sizes and morphology of the catalyst samples.

N₂ physisorption was carried out on a 3FLEX surface area and porosimetry analyzer at liquid nitrogen temperature. Prior to the measurement, samples were outgassed under vacuum at 400 °C overnight. The specific surface area (S_{BET}) was calculated by the BET method in the relative pressure range of 0.05 to 0.3. The total pore volume (V_{total}) was calculated from the amount of adsorbed nitrogen at the relative pressure of $p/p_0 = 0.95$. The BJH pore size distribution was derived

from the adsorption branch of the N₂ physisorption isotherm for calculation of the volume and surface area of mesopores (20–500 Å pore width).

A Quantachrome AsiQ instrument was used for Ar-physisorption measurements. Isotherms from Ar-physisorption were analyzed using the nonlinear density functional theory (NL-DFT) model applied to the adsorption branch of the isotherm.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was done for elemental analysis of the catalysts in an Agilent 720 ICP-OES spectrometer to determine the Si/Al ratios.

Temperature programmed desorption (TPD) of ammonia was performed in a Micromeritics Autochem II 2920. Samples were pre-treated at 550 °C (heating ramp: 20 °C/min) in 20 mL/min He for 1 h to remove moisture. The zeolites were then cooled to 100 °C and NH₃ was adsorbed for 30 min (20 mL/min of 10 vol% NH₃ in He) followed by a flowing He purge for 30 min. The NH₃ desorption while heating the samples to 600 °C using a 10 °C/min ramp in 10 mL/min He was recorded by a thermal conductivity detector (TCD). Curves were normalized using the sample mass. Based on a duplicate analysis, a standard deviation of 0.009 mmol NH₃/g was calculated.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) of pyridine-loaded samples was performed on a Bruker Tensor 27 spectrometer equipped with a Harrick Praying Mantis attachment and a high temperature reaction chamber. The calcined zeolite samples were diluted to 4 wt-% in KBr (stored at 80 °C) and mixed and ground thoroughly with a mortar and pestle to pass a 56 µm sieve. Absorbance from 4000 to 400 cm⁻¹ was collected using 64 scans at a 4 cm⁻¹ resolution. A background spectrum was recorded with pure KBr at 150 °C. Prior to pyridine adsorption, the KBr/zeolite mixture was heated to 450 °C and held at the final temperature for 1 h under 30 ml/min Ar flow to remove moisture. The sample was cooled to 150 °C under continued Ar flow. At 150 °C, a three-way valve was switched to redirect the flow through a bubbler filled with pyridine kept at room temperature and the exiting gas stream was passed through the sample

for 30 min. After pyridine adsorption, the sample was flushed with Ar for 20 min to remove any weakly absorbed species before acquiring the DRIFT spectra. Subsequently, the temperature was increased to 250 °C and held for 30 min, before acquiring the next spectrum. The procedure was repeated for higher temperatures of 350 and 450 °C as long as absorbance bands of pyridine adsorbed on Brønsted (1545 cm^{-1}) and Lewis (1455 cm^{-1}) acid sites were noticeable. The spectra were analyzed with OPUS 7.0 software, compensated for atmospheric CO_2 and H_2O , baseline corrected, and smoothed. The peak height of the Lewis and Brønsted acid peaks at 150 °C was used to determine the ratio of Brønsted to Lewis acid sites (B/L).

The ^{27}Al NMR spectra were acquired with 8k scans (8·1024). The AVII-600 NMR spectrometer features a wide bore 14.1 tesla superconducting magnet and an Avance II spectrometer console from Bruker Corporation (Billerica, MA and Karlsruhe, Germany). The proton frequency for this field is 600.13 MHz and the ^{27}Al frequency is 156.38 MHz. All datasets were acquired with a rotor-synchronized Hahn echo pulse sequence (90-tau-180-tau-acquire) at 6 kHz magic-angle spinning speed and a two rotor period tau delay (330 μs). The 90° pulse was 2.5 μs and the spectra were acquired under 62.5 kHz proton decoupling. The free induction decay contained 1024 points with an acquisition time of 5.5 ms and a recycle delay of 1.5 s. Resultant data were processed in TopSpin software (Bruker) using a Gaussian window function.

2.4 Micro-pyrolyzer

The experiments were carried out using a single-shot tandem micro-pyrolysis system (Rx-3050tr, Frontier Labs, Japan) and analyzed by GC-MS/FID/TCD (see Fig. S1) using He as carrier gas at a flow rate of 60 mL/min and a split ratio of 1:56. A detailed description of the experimental set-up can be found in the work of Nolte et al. [51]. The top pyrolysis reactor and the bottom catalytic reactor were maintained at 530 °C and 500 °C, respectively. 0.59 ± 0.1 mg of wheat straw was loaded into calcined and reduced (550 °C) stainless steel sample cups and the cups were

introduced into the pyrolysis zone via an autosampler. The catalytic reactor, located ex-situ of the pyrolysis reactor, contained a quartz tube loaded with a mixture of 60 mg quartz beads (150–215 μm , acid washed and calcined at 550 $^{\circ}\text{C}$) and the catalyst (2–11.5 mg, 36–125 μm). The dilution of the catalyst with quartz beads prevented channeling or bypass flow and maintained similar bed lengths across different catalyst loadings. The catalyst bed was secured between two quartz wool plugs in order to be placed within the temperature-controlled isothermal zone of the tandem-reactor.

2.5 Product analysis

The GC (Agilent 7890B) separation was completed using an initial oven temperature of 35 $^{\circ}\text{C}$ for 7.5 min followed by ramping at 10 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$. Condensable species were separated using a medium polarity 1701 column (Agilent VF-1701 ms) and identified by MS (Agilent 5977A) and quantified using FID. The chromatograms were processed using MassHunter Workstation Software (Agilent) and the identification of mass spectra peaks was achieved by using the NIST library (Version 2.0 f). Calibration of the FID detector was performed for 54 model compounds of various functionalities (aromatics, acids, ketones, aldehydes, phenols, methoxyphenols, furans etc.) as listed in Table S1. The FID response factor of compounds not available for calibration was estimated based on the positive correlation (Fig. S2) between the FID response determined for the calibrated compounds and the molecular response factor (MRF) of each compound that was calculated based on its combustion enthalpy and molecular structure [52].

While each FID chromatogram comprised peaks of >100 compounds, the compounds were grouped into aliphatics (ALI), monoaromatics (MAR), di-aromatics (DAR), phenols (PH), aldehydes (ALD), acids (AC), ketones (KET), methoxy-phenols (MPH), furans (FUR), alcohols (ALC), and nitrogen containing compounds (N). Table S4 to S16 provide an overview of the compounds contained in each product group along with their respective MRF.

The light gases and hydrocarbons were separated using a GasPro column (Agilent GS-GasPro) and quantified using TCD. Analysis of light gas species was conducted by calibrating the TCD detector of the GC. Calibration was performed by injection of increasing volumes of a gas mixture containing CO, CO₂, C₁₋₅ alkanes and C₂₋₅ alkenes with a gas-tight 1 mL syringe and correlating the resulting TCD peak areas with the moles injected.

To test the repeatability of the product analysis, three biomass injections were performed replacing the catalyst with 2 mg of SiC as highly inert material. Table S3 lists the individual product standard deviations based on these three repeated injections.

The char yields were determined gravimetrically by weighing the sample cups and biomass before and after fast pyrolysis in the micro pyrolyzer.

Coke yields were determined by combustion of the coke in a TGA (Netzsch STA449 F1) coupled with an MS (QMS 403 D Aëolos[®]). The content of the quartz tubes (catalyst plus glass beads) was emptied in alumina crucibles. Using 40 ml/min total flowrate, the samples were first heated in Argon to 350 °C (10 °C/min, held at 350 °C for 5 min) in order to remove moisture. The gas was adjusted to 20 vol-% oxygen (balance Ar) and the temperature was held for an additional 5 min at 350 °C before ramping to 600 °C at 10 °C/min and holding the final temperature for 10 min. Besides the weight loss monitored during the coke combustion, the mass of carbon and hydrogen in the coke was obtained by recording the evolving CO, CO₂ and H₂O during combustion with the MS. The response of the MS detector for CO, CO₂ and H₂O was calibrated by decomposition of a known amount of calcium oxalate (Sigma-Aldrich, 99.999 % trace metal basis) when ramping the temperature at 20 °C/min to 900 °C in 40 ml/min Ar. The relative deviation between the mass loss determined by TGA and the sum of the mass of H and C contained in the combustion gas species was less than 10%, indicating that the carbon content of coke was ~90%.

3 RESULTS

3.1 Catalyst properties

Powder X-ray diffraction results confirm the crystallinity of zeolite samples synthesized in this work. All zeolite samples show characteristic diffraction peaks of MFI structure at 7.9° , 8.8° , 23° , 23.9° and 24.4° (see Fig. S3), confirming the high crystallinity of the synthesized catalysts [53]. Since silicalite-1 and HZSM-5 have the same MFI topology structure, no additional XRD peaks were observed after coating with a shell of silicalite-1 zeolite.

Table 1 provides an overview of the physicochemical properties of the three catalysts tested in this study. Applying the NL-DFT model to the adsorption branch of the isotherm from high-resolution low temperature Argon pore characterization (Fig. S5) shows that Meso-ZSM-5 contained smaller mesopores in the range of 30-100 Å but also a large amount of mesopores >100 Å. After silicalite-1 coating the amount of larger mesopores >100 Å decreased, while a shift towards smaller mesopores was observed. A likely explanation for this observation could be that the silicalite-1 coating (partly) filled mesopores. Thus, it can be expected that acid sites that were located in the mesopores were successfully covered.

Nitrogen physisorption (Fig. S4-A) shows that there is a steep nitrogen uptake at partial pressures up to $p/p_0 = 0.01$, which is an evidence for presence of micropores in all three samples with MFI structures. Conv-ZSM-5 zeolite has the characteristic type I isotherm (according to IUPAC classification) characteristic for microporous materials [54,55]. Meso-ZSM-5 zeolite showed a type IV isotherm with a hysteresis loop at approximately $p/p_0 = 0.85$. This observed hysteresis loop with upward curvature is known to be caused due to the presence of mesopores [56,57]. The core-shell zeolite similarly shows a type IV isotherm but a different hysteresis loop, of type H2. This hysteresis loop has a sharp closure at relative pressure of 0.45 that indicates the presence of inkbottle pores [58]. The inkbottle phenomenon indicates encapsulated mesopores inside the microporous shell. The sharp peak at ~ 40 Å pore width observed for Shell-Meso-ZSM-5 when

deriving the BJH pore distribution from the desorption branch (see Fig. S4-B+C) is considered an artifact based on the tensile strength effect [59]. For Meso-ZSM-5, the BJH analysis (Fig. S4-B) reveals that the width of mesopores is between 100–500 Å.

While the microporous volume was in the range of 0.18–0.19 cc/g for the three catalysts, clear differences in mesoporous volume (V_{meso}) were observed. Ar-physisorption indicated that Meso-ZSM-5 zeolite had 0.28 cc/g compared to only 0.06 cc/g for the Conv-ZSM-5 zeolite. After silicalite-1 coating, V_{meso} decreased to 0.11 cc/g, which indicates that the addition of silicalite-1 filled some of the mesopores. Similar conclusions are derived from nitrogen physisorption data, for which V_{meso} was determined to 0.08 cc/g for Conv-ZSM-5 and V_{meso} decreased from 0.24 cc/g for Meso-ZSM-5 to 0.12 cc/g for Shell- Meso-ZSM-5, along with a decrease in total pore volume from 0.34 to 0.27 cc/g at $p/p_0 = 0.95$ (before the onset of interparticle nitrogen condensation).

SEM images show uniform particle size distribution for Conv-ZSM-5, which is less than 300 nm, while the particle size of Meso-ZSM-5 is around 2000 nm (Fig. S6-A+B). From different TEM images (Fig. S8-C+D and Fig. S10) the thickness of the silicalite-1 layer is estimated to be less than 20 nm. Based on the SEM images the addition of the thin shell did not have an observable effect on the particle size (Fig. S6-C).

Ammonia-TPD results (Fig. S11) show that Conv-ZSM-5 has less acid sites in comparison with the mesoporous ZSM-5 zeolite although these zeolites have similar Si/Al ratios based on ICP-OES results. The reason is speculated to be the limitations in the synthesis approach of conventional zeolite for low Si/Al ratios that result in forming more extra-framework Al. As expected, by addition of the non-acidic silicalite-1 layer the overall concentration of acid sites in the material decreased for the core-shell ZSM-5 compared to the parent mesoporous ZSM-5. The effect of adding a silicalite-1 layer to the Meso-ZSM-5 is also observed in ICP-OES results as the Si/Al ratio increases from 53 in the Meso-ZSM-5 zeolite to 74 for the Shell-Meso-ZSM-5 zeolite.

The Brønsted/Lewis (B/L) acid site ratio obtained from the pyridine DRIFT spectra was very similar amongst the catalysts: For conventional HZSM-5 and mesoporous HZSM-5 zeolites, the ratio was 6.4, while the core-shell HZSM-5 had B/L = 6.2. When increasing the temperature, the adsorption band related to Lewis acid sites disappeared at temperatures above 250 °C (see Fig. S12). Brønsted acidity on the other hand extended to higher acid strength. Especially the Meso-ZSM-5 and Shell-Meso-ZSM-5 maintained a peak at $\sim 1530\text{ cm}^{-1}$ attributed to pyridine adsorbed on Brønsted acid sites for temperatures up to 450 °C. For Conv-ZSM-5 zeolite, the strength of Brønsted acid sites appeared weaker as its peak had decreased appreciable at 350 °C.

A comparison of the ^{27}Al solid-state NMR spectra—scaled to the same peak areas—is shown in Fig. S13. The peak at $\sim 54\text{ ppm}$ corresponds to framework Al in tetrahedral AlO_4 and is an indirect measure for Brønsted acid sites. Peaks at 20-30 ppm and -5-10 ppm are both extra-framework aluminate (EFAL) domains corresponding to AlO_5 and AlO_6 , respectively. Furthermore, the line shape give indications on the degree of local order/disorder around the Al nucleus, with highly ordered environments resulting in sharp peaks. Thus, the Conv-ZSM-5 zeolite showed both a higher fraction of EFAL (15.1%) compared to Meso-ZSM-5 (7.8%)/Shell-Meso-ZSM-5 (2.3%) and a higher degree of disorder around the framework Al nucleus (see Fig. S13).

Table 1 Physicochemical characterization of the conventional HZSM-5, mesoporous HZSM-5, and silicalite-1 coated mesoporous HZSM-5 (core-shell). V_{micro} and S_{micro} were determined by high-resolution low temperature Argon physisorption (87 K), while all other textural parameters were derived from nitrogen adsorption data. Total acidity was determined by NH_3 -TPD.

	Conv-ZSM-5	Meso-ZSM-5	Shell-Meso-ZSM-5
V_{micro}^a [cc/g] from Ar	0.173	0.186	0.179
S_{micro}^a [m ² /g] from Ar	1310	1420	1360
V_{meso}^b [cc/g] from N ₂	0.077	0.242	0.123
S_{meso}^b [m ² /g] from N ₂	71	81	80
V_{total} at $p/p_0=0.95$ from N ₂	0.20	0.34	0.27
BET area (N ₂) [m ² /g]	375	426	419

Total Acidity [mmol NH ₃ /g]	0.171	0.247	0.199
B/L ratio ^c	6.4	6.4	6.2
Si/Al ^d	51	53	74

^aobtained from NL-DFT of adsorption branch; ^bobtained from BJH analysis of adsorption branch; ^cdetermined from pyridine FT-IR; ^dcalculated from ICP-OES results;

3.2 Product distribution

Non-catalytic reference. Table S17 shows the structure of the 34 most prevalent compounds identified in the vapors from fast pyrolysis of wheat straw at 530 °C without catalytic upgrading. Note that all compounds contain at least one oxygen functionality. Aldehydes (ALD), ketones (KET), and furans (FUR) had the highest number of group members with 5+ members per group. Esters (EST) and methoxy-phenols (MPH) contained four members, respectively, while alcohols (ALC), sugars (SUG), acids (AC) and phenols (PH) contained 1–2 group members. PH and MPH are attributed to the decomposition of the lignin component of wheat straw, while anhydrosugars and smaller oxygenates result from the pyrolysis of hemicellulose and cellulose [60–62].

Catalyst vapor upgrading: The repeated injection of biomass cups allowed monitoring the change in product distribution for each injection and calculating integral yields at a certain cumulative weight ratio of injected biomass (daf) to loaded catalyst. Initially, the performance of the three catalysts was compared for catalyst loadings of 2 mg and 8 mg, respectively. For a series of 16 biomass injections of ~0.5 mg daf wheat straw per injection, a cumulative B:C ratio of ~4 was reached when loading 2 mg of catalyst, while B:C ~1 was reached when 8 mg catalyst was loaded. Fig. S14 shows how the product yields of the different product groups developed with increasing amounts of biomass injected. With 2 mg catalyst loading, Conv-ZSM-5 zeolite showed some initial activity by decreasing yields of oxygenates and increased MAR and DAR yields; however, its activity had decreased to a negligible level at B:C ~1 which can be attributed to catalyst deactivation by coking. Meso-ZSM-5 on the other hand showed significantly higher initial acidity and appeared more tolerant towards deactivation since the yield of MAR decreased less steeply and oxygenates continued to increase up to B:C ~2.5. After adding the silicalite-1 shell,

the yield of MAR decreased slightly steeper compared to Meso-ZSM-5 and the yield of oxygenates continued to increase until B:C $\sim$ 2. Table S18 compares the cumulative yields at B:C $\sim$ 4 when using 2 mg catalyst. Meso-ZSM-5 was most active as it achieved the highest yield of MAR (0.72 wt-%) and C₂₋₃ olefins, concomitantly with achieving the lowest yield of acids (1.44 wt-%) and methoxy-phenols (0.54 wt-%) amongst the three catalysts. The higher activity of Meso-ZSM-5 agrees with its higher acidity and better accessibility of the active sites (**Table 1**).

Increasing the catalyst loading to 8 mg increased the conversion and therefore allowed for monitoring the differences in deactivation behavior up to B:C $\sim$ 1 at a higher resolution. For Conv-ZSM-5 zeolite (Fig. S14b), the yield of MAR decreased in an exponential decay function, while the yield of oxygenates started to increase after the first injection. For Meso-ZSM-5 zeolite on the other hand, the MAR yields were almost stable for the first three injections after which the MAR yields decreased linearly indicating a high tolerance toward deactivation (see Fig. S14d). Likewise, the yield of oxygenates increased moderately and AC and MPH were completely converted up to B:C $\sim$ 0.5. For the Shell-Meso-ZSM-5 material (Fig. S14f), the yield of MAR decreased slightly steeper. While MPH started to slowly break through above B:C $\sim$ 0.3, acids were similarly effectively converted compared to Meso-ZSM-5. **Table 2** provides an overview of the product yields obtained with 8 mg of catalyst loading. Compared to a loading of 2 mg catalyst (Table S18), the four times higher catalyst loading led to higher conversions as seen by the increased MAR yields and reduced yields of oxygenates like acids and methoxy-phenols when comparing the product yields at B:C $\sim$ 1. Higher catalyst loading also increased gas formation, especially CO and ethylene/propylene. Note that while Shell-Meso-ZSM-5 showed similar performance as the meso-HZMS-5 in converting smaller oxygenates like ALD, AC, and ALC, it was least effective in converting MPH. This agrees with the fact that MPH are bulky compounds that cannot enter the

micropore structure of HSZM-5 and therefore have to be converted at external acid sites, which were blocked by the inert silicalite-1 layer.

To obtain a comparison of the catalytic performance for the same number of acid sites, the reactor loading was adjusted to 11.54 mg and 9.95 mg for the Conv-ZSM-5 and the core-shell catalyst, respectively. Since the amount of biomass per injection was kept constant, the number of injections was increased from 16 to 20 and 23 for the core-shell and conventional HZSM-5, respectively. Fig. S15–S17 show a comparison of the FID chromatograms for the first and last injection of wheat straw over the three different catalysts, respectively. For all three catalysts, the main product species observed at the first injection ($B:C = 0-0.05$) were simple mono- and di-aromatics like substituted benzenes, naphthenes, and naphthalenes, as well as small oxygenates like acetaldehyde, furan, and acetone. For the last injection close to $B:C \sim 1$, the peak height of MAR and DAR decreased and additional oxygenates were observed. However, clear differences in the extent of catalyst deactivation was observed when comparing the chromatograms at $B:C \sim 1$ amongst the different catalysts. This is in accordance with **Fig. 1** monitoring the change in product yields with increasing biomass injections for the same number of acid sites. For all three catalysts, similar MAR yields of ~ 8 wt-% were obtained for the first injection. The conventional HZSM-5 was the least efficient catalyst as seen by the rapid decline in aromatization activity and rapid breakthrough of oxygenates, whereas the oxygenates increased at a lower rate for Meso-ZSM-5 (**Fig. 1b**) and Shell-Meso-ZSM-5 (**Fig. 1c**). For Conv-ZSM-5 the AC and MPH started to break through at $B:C \sim 0.3$. For Meso-ZSM-5, on the other hand, the AC and MPH were completely converted until $B:C \sim 0.6$, and for the core-shell catalyst the breakthrough of MPH occurred earlier (0.5) while acids were effectively converted up to $B:C \sim 0.7$. Comparing the cumulative yields at $B:C \sim 1$ for the same number of acid sites (**Table 2b**) indicates that the Shell-Meso-ZSM-5 obtained the highest cumulative yield of MAR/DAR and the lowest yields of AC.

A comparison of the monoaromatic selectivities for the different catalyst types is shown in Fig. S18. With increased catalyst loading to 8 mg, higher BTX selectivities were obtained compared to a loading of 2 mg catalyst. No clear differences in the selectivities to different monoaromatic species could be discerned amongst the three catalysts, indicating similar shape selectivity of the bulk microporous volume.

Fig. 1 Carbon yields of the different product groups for the same number of acid sites per reactor loading. The catalyst loading of conventional HZSM-5 (a) and silicalite-1 coated mesoporous HZSM-5 (c) was increased to 11.5 mg and 10 mg in order to match the number of acid sites of 8 mg mesoporous HZSM-5 (b). Shown are the momentary carbon yields for each biomass injection. The abbreviations in the legend refer to aliphatics (ALI), monoaromatics (MAR), di-aromatics (DAR), phenols (PH), aldehydes (ALD), acids (AC), ketones (KET), methoxy-phenols (MPH), furans (FUR), alcohols (ALC), and nitrogen containing compounds (N). The yield of ALC and N was multiplied by 10 for better visibility.

Table 2 Yields of species at a cumulative fed dry and ash-free biomass to catalyst ratio of B:C ~1. **Table 2a** shows the yields obtained with 8 mg of catalyst while **Table 2b** shows the yield obtained for the same number of acids sites, for which the loading of conventional and core-shell catalysts was increased to 11.5 and 10 mg, respectively. Results obtained with SiC as a highly inert solid shown for reference. Vapors and gas were analyzed by GC-FID and GC-TCD, respectively.

		Vapors										Gas					
		ALI	MAR	DAR	PH	ALD	AC	KET	MPH	FUR	ALC	N	CO	CO ₂	C ₁₋₃	C ₂₋₃ olefins	C ₄₊
(a)	SiC	0.06	0.04	0.00	0.13	1.76	2.44	3.91	0.88	1.05	0.75	0.00	7.1	17.1	0.1	0.3	0.3
	Conv-ZSM-5	0.88	1.22	0.08	0.38	1.66	0.90	2.49	0.11	1.37	0.33	0.33	8.4	17.2	0.1	0.6	0.6
	Meso-ZSM-5	0.78	2.87	0.41	0.51	1.11	0.26	1.52	0.09	0.90	0.15	0.21	10.3	18.0	0.0	1.3	1.0
	Shell-Meso-ZSM-5	0.71	2.49	0.40	0.37	1.18	0.20	1.95	0.19	1.22	0.16	0.24	9.5	18.0	0.1	1.1	0.9
(b)	Conv-ZSM-5	0.68	1.95	0.26	0.53	1.68	0.51	2.34	0.33	1.41	0.29	0.28	12.6	20.0	0.1	2.6	1.3
	Meso-ZSM-5	0.78	2.87	0.41	0.51	1.11	0.26	1.52	0.09	0.90	0.15	0.21	10.3	18.0	0.0	1.3	1.0
	Shell-Meso-ZSM-5	0.50	3.11	0.50	0.42	1.11	0.14	1.73	0.11	0.59	0.14	0.18	12.2	16.5	0.0	3.0	0.9

Table S19 and **Table 3a** show a comparison of the carbon recoveries of vapors, gas, and coke when using 2 and 8 mg of catalyst, respectively, while **Table 3b** provides a comparison based on the same number of acid sites. Char yields of 18.3 wt-% (± 0.08) of fed wheat straw (daf) were determined, which is in agreement with char yields of 18-21 wt-% (daf) observed for the same feedstock and pyrolysis temperature at a fast pyrolysis bench scale unit [1,2]. The amount of recovered char using the micro-pyrolyzer was insufficient to conduct proximate and elemental analysis. In view of the similar char yields observed at micro- and bench-scale, the elemental composition of the char from the micro-pyrolysis was assumed to be the same as determined in bench scale, namely 80 wt-% C, 4 wt-% H, 2 wt-% N, and 14 wt-% O (by difference) on a daf basis. Based on the estimated carbon content of char, the carbon recovery of char was ~31 wt-%

for all tests. As such, the carbon closure was in the range of 61 wt-% for the non-catalytic case, while it was improved to ~81% when using a catalyst due to increased carbon recoveries of gas, vapors and coke. These observations agree with earlier work [6] which reported ~90% carbon closure for pyrolysis of cellulose, lignin, and corn stover using the micro-pyrolyzer, while passing the vapors over an active catalyst increased the carbon closure to ~100%. We note that multiple peaks in the FID chromatogram with low intensity could not be identified and quantified properly and that the sum of these non-identified compounds may constitute an important fraction of the missing carbon. Moreover, the missing carbon is attributed to deposits of oligomeric species with highly reactive functionalities that may polymerize and deposit at the interface between the reactors (300 °C), the GC-inlet (270 °C), and the guard column inlet (see Fig. S19). A comparison of Table S19 and **Table 3** shows that an increase in catalyst loading increased the carbon recovery of gas and coke. The highest carbon losses to coke resulted for Meso-ZSM-5 (5.1 C wt-% at B:C ~1), while the Conv-ZSM-5 showed the lowest coking propensity (**Table 3**).

The quality of the never-condensed vapors is expected to correlate to some extent with the quality of condensed bio-oils. Parameters regarded essential for the assessment of bio-oil quality are the oil's acidity, oxygen content, and effective hydrogen index (EHI). Those parameters were introduced for assessment of the quality of the never condensed vapors. The acidity of the vapors was defined as (mass of acids in vapors)/(mass of vapors) and is expected to correlate with the total acid number of the condensed vapors [16,17]. The oxygen content of the vapors—defined as (mass of oxygen in vapors)/(mass of vapors) —gives an indication on the effectiveness of deoxygenation and serves as an indicator for the chemical stability of bio-oils. When oxygen is released as water during the cracking of oxygenates in bio-oils over acidic catalysts, hydrogen is depleted which leads to enriched aromatics content in the products but also rapid coke formation. The effective hydrogen to carbon ratio (EHI) as defined by Chen et al. [63] can be used to assess

the coking propensity of the product mixture. EHI is defined as $(H - 2O - 3N - 2S)/C$, where H, C, O, N, and S are atoms per unit weight of sample of hydrogen, carbon, oxygen, nitrogen and sulfur, respectively.

Both Meso-ZSM-5 and Shell-Meso-ZSM-5 zeolite were significantly more effective in reducing the acidity as compared to the conventional HZSM-5 zeolite (see **Table 3**). The core-shell catalyst was most effective in reducing the acidity. Similar conclusions can be drawn for the overall oxygen content of the vapors as the core-shell catalyst reduced the oxygen content the most (from 37.1 wt-% to 14 wt-% O) when comparing the catalysts at the same number of acid sites. The EHI index was lowest for Conv-ZSM-5 (~1) and highest for Meso-ZSM-5 (~1.1,) while it was 1.05–1.07 for the core shell catalyst.

Table 3. Comparison of carbon recoveries of vapors, gas, and coke for (a) the same catalyst mass and (b) the same number of acid sites at B:C ~1. Carbon recovery of char was ~31 wt-%. The table further compares the acidity, EHI, and oxygen content of the vapors and shows the molar CO/CO₂ ratio of the gas.

		C-% vapors	C-% gas	C-% coke	Acidity vapors (wt-%)	EHI vapors	wt-% O vapors	CO/CO ₂
(a)	SiC	12.6	17.3	~0	22.1	0.67	37.1	0.66
	Conv-ZSM-5	13.6	26.4	1.9	9.2	1.00	23.4	0.94
	Meso-ZSM-5	13.9	30.5	5.1	2.9	1.09	14.7	1.09
	Shell-Meso-ZSM-5	14.0	29.3	2.9	2.2	1.05	16.6	1.07
(b)	Conv-ZSM-5	15.0	29.5	3.4	4.9	0.98	20.4	0.99
	Meso-ZSM-5	13.9	30.5	5.1	2.9	1.09	14.7	1.09
	Shell-Meso-ZSM-5	13.6	27.1	4.7	1.6	1.07	14.0	1.16

4 Discussion

For the same mass of catalyst (8 mg), more than twice as much carbon deposited on Meso-ZSM-5 zeolite compared to Conv-ZSM-5 zeolite, whereas only ~30% more carbon had deposited on the core-shell catalyst compared to Conv-ZSM-5 catalyst. From the derivative curves of the weight loss during coke combustion (Fig. S20), two peaks could be discerned. The low temperature peak below ~475 °C is sometimes referred to as ‘soft’ or ‘thermal’ coke. This peak is considered to

contain higher H/C ratios and more oxygenated compounds, mostly derived from lignin derivatives because of their greater ability to re-polymerize [64,65]. This soft coke is deposited on the meso- and macroporous structure of the catalyst and combusts more readily. The coke combusting at higher temperatures ($>500\text{ }^{\circ}\text{C}$) is considered ‘hard’ or ‘catalytic’ coke which is mainly deposited inside the micropores. It is formed by cyclization, aromatization and condensation reactions of reactants and products [66,67] and thus consists of less hydrogenated polyaromatic structures. Interestingly, coke deposited on the Conv-ZSM-5 and core-shell Meso-ZSM-5 catalysts showed similar contributions of low and high temperature coke. For Meso-ZSM-5, the contribution of catalytic coke was more pronounced, which could indicate that the micropores were filled with coke to a greater extent due to their better accessibility through the auxiliary mesopore network.

Li et al. [45] reported higher aromatic carbon yields close to 14% compared to maximum aromatic yields of $\sim 8\text{ C-}\%$ observed in this study. The differences can likely be attributed to the different operating modes (in-situ vs. ex-situ), a higher catalyst temperature of $550\text{ }^{\circ}\text{C}$ used by Li et al. [45], and the larger amounts of catalyst used to achieve full deoxygenation. The pronounced increase in para selectivity amongst xylenes observed by Li et al. [44] (from 28 to 84%) could not be confirmed in this study when using a silicalite-1 coated Meso-ZSM-5 for ex-situ CFP.

Hu et al. [38] tested a core-shell catalyst of silicalite-1 coated conventional HZSM-5 and investigated the change in carbon yield of BTX and olefins with increasing amount of biomass fed. In agreement with our results, there were no obvious changes in the carbon yields of gas after catalyst modification. A slight decrease in BTX yields was reported after silicalite-1 coating. While these authors did not report the acidity of the catalysts, the tests were performed for a constant catalyst mass and thus it is very likely that the addition of the inert silicalite-1 layer had decreased the number of acid sites per reactor loading. For the core-shell catalyst used by Hu et al. [38], the carbon recovery of coke decreased by 22.1% (from 15.2% to 11.9%) compared to the same mass

of conventional HZSM-5. In our study, the addition of the silicalite-1 layer reduced the carbon losses to coke by 43% compared to the same mass (8 mg) of Meso-ZSM-5. The even more pronounced effect may be attributed to the higher coking propensity of mesoporous HZSM-5 compared to conventional HZSM-5 [30]. Comparing the coking propensity for the same total number of acid sites shows that the carbon recovery of coke decreased by ~8% after silicalite-1 addition.

5 Conclusion

Conventional ZSM-5 zeolite, mesoporous ZSM-5 zeolite and mesoporous ZSM-5 zeolite covered with a non-acidic silicalite-1 layer were synthesized. For the first time we tested mesoporous HZSM-5 coated with silicalite-1 for the deoxygenation of biomass fast pyrolysis vapors in ex-situ configuration and provide detailed product yields obtained using a micro-pyrolyzer. Moreover, the deactivation behavior of the core-shell catalyst was compared to a mesoporous and conventional HZSM-5 catalyst. Even though the coking propensity was highest for the mesoporous HZSM-5, it showed improved conversion of oxygenates and a higher tolerance towards deactivation by coke. Coating of mesoporous HZSM-5 zeolite with silicalite-1 reduced the number of acid sites per mass of catalyst by ~20%, which is attributed to the addition of the inert silicalite-1 layer and passivation of the external acid sites of the mesoporous HZSM-5. Compared to mesoporous HZSM-5, the added silicalite-1 shell reduced the coke yield by 43% for the same catalyst mass and by 8% for the same total number of acid sites, while the tolerance towards deactivation observed for the mesoporous HZSM-5 core was largely preserved—especially for conversion of small oxygenates like acids, alcohols and aldehydes.

ASSOCIATED CONTENT

Supporting Information

Reactor scheme, List of calibrated compounds and molecular response factors, XRD patterns, sorption isotherms, TEM image of catalysts, NH₃-TPD profiles, wheat straw analysis by sulfuric acid hydrolysis, experimental uncertainty for repeated injections, list of vapor compounds according to product group, instant and cumulative carbon yields of each vapor group, exemplar FID chromatograms, documentation of carbonaceous deposits observed at equipment, Selectivities of monoaromatics, Derivate curves of weight loss during combustion

AUTHOR INFORMATION

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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