

# Supporting Information

## **Insight into the factors affecting the reactivity of sulfonic acid species anchored on hyper-cross-linked polymers in esterification**

Joanna Wolska\* and Lukasz Wolski

*Faculty of Chemistry, Adam Mickiewicz University, Poznań, ul. Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland*

*\* Corresponding author: [j.wolska@amu.edu.pl](mailto:j.wolska@amu.edu.pl) (J. Wolska)*

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## 1. Extended experimental section

### 1.1 Preparation of HCPs

All pristine HCPs polymers were prepared by Friedel-Crafts alkylation [*Macromolecules* 44 (2011) 2410 doi:10.1021/ma200630s.] using triphenylmethane (TPM) and formaldehyde dimethyl acetal (FDA), as a commercially available building block and cross-linker, respectively. In a typical synthesis procedure, TPM (2.44 g, 10 mmol, 1 equiv.) and FeCl<sub>3</sub> (45 mmol, 4.5 equiv.) were dispersed in DCE (60 mL) under an argon atmosphere. Following 15 min of vigorous stirring at room temperature, FDA (3.42 mL, 45 mmol, 4.5 equiv.) was added dropwise to the above suspension resulting in formation of a thick brown gel. The obtained gel was stirred at 40 °C for 5 h, then heated to 80 °C and stirred for another 24 h. During the heating step, the polymer precipitated from the solution as a brown solid. After being cooled to room temperature, the precipitate was separated by Büchner filtration, washed with methanol until a colorless filtrate was obtained, and then with water. The resulting brown product (HCP1) was Soxhlet extracted with methanol for 72 h and then dried under vacuum at 80 °C to constant mass (Yield: 3.0 g, 98%). The HCP2 (Yield: 3.6 g, 96%) and HCP3 (Yield: 4.1 g, 95%) polymers were prepared according to the same experimental procedure, but using a different molar ratio of TPM to FDA (1.0:9.0 and 1.0:13.5 for HCP2 and HCP3, respectively). The % yield of HCPs was calculated using following equation (Eq. S1):

$$\% \text{ yield} = \frac{m_{\text{HCP}}}{m_{\text{TPM}} + m_{\text{methylene linker}}} \quad (\text{Eq. S1})$$

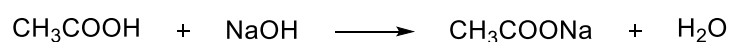
where  $m_{\text{HCP}}$ ,  $m_{\text{TPM}}$  and  $m_{\text{methylene linker}}$  are the mass of the respective HCP (after Soxhlet purification and drying), triphenylmethane used for polymerization and  $-\text{CH}_2-$  moiety (derived from FDA) incorporated into the polymer network, respectively.

## 1.2 Preparation of sulfonated HCPs

Sulfonated HCPs were prepared by a facile post-synthetic sulfonation procedure [ACS Appl. Mater. Interfaces 11 (2019) 22464 doi:10.1021/acsami.9b06295]. For this purpose, the pristine HCP (1.5 g) was stirred into DCE (50 mL) and agitated at room temperature for 1 h to allow the polymer network to swell in the solvent. The resulting suspension was cooled to 0 °C, and then chlorosulfonic acid (10 mL) was added dropwise under vigorous agitation. Following 72 h of intensive stirring at room temperature, the above mixture was poured into 500 mL of deionized water and stirred for 1 h to quench unreacted chlorosulfonic acid. Finally, the sulfonated polymer was separated by Büchner filtration and thoroughly washed with water and methanol until the pH of the filtrate was neutral (no acid residual in the filtrate). The as-prepared dark brown solid was dried under vacuum at 80 °C to a constant mass. The yields were 1.9 g, 1.7 g and 1.6 g for sHCP1, sHCP2 and sHCP3, respectively.

## 1.3 Calculation of acetic acid conversion

The conversion of acetic acid to the corresponding ester (methyl, *n*-butyl, cyclohexyl, or benzyl acetate) as the only product of the esterification was calculated according to Eqs. (S2)-(S3) based on the stoichiometry of the reaction between acetic acid and sodium hydroxide (Scheme S1).



**Scheme S1.** Acidimetric titration formula for conversion calculation.

$$\text{moles of reacted AcH} = \text{initial moles of AcH} - \text{moles of NaOH used for titration} \quad (\text{S2})$$

$$\text{conversion of AcH} = \text{moles of reacted AcH} / \text{initial moles of AcH} \cdot 100\% \quad (\text{S3})$$

## 1.4 TOF calculation

The turnover frequency (TOF) was calculated using Eq. (S8) as moles of acetic acid converted over one mole of sulfonic groups present on the surface of the catalyst per one hour. The calculations were as follows:

$$n_{\text{AcH}} [\text{mol}] = \text{conversion} [\%] \cdot n_{\text{AcH}_0} [\text{mol}] / 100 [\%] \quad (\text{S4})$$

$$n_{\text{AcH in 1h}} [\text{mol h}^{-1}] = n_{\text{AcH}} [\text{mol}] / t_{\text{reaction}} [\text{h}] \quad (\text{S5})$$

$$-\text{SO}_3\text{H}_{\text{cat}} \text{ content} [\text{g}] = m_{\text{cat}} [\text{g}] \cdot \%S [\%] / 100 [\%] \quad (\text{S6})$$

$$-\text{SO}_3\text{H}_{\text{cat}} \text{ content} [\text{mol}] = -\text{SO}_3\text{H content} [\text{g}] / M_S [\text{g mol}^{-1}] \quad (\text{S7})$$

$$\text{TOF} [\text{h}^{-1}] = n_{\text{AcH in 1h}} [\text{mol h}^{-1}] / -\text{SO}_3\text{H content} [\text{mol}] \quad (\text{S8})$$

where  $n_{\text{AcH}}$ ,  $n_{\text{AcH}_0}$ ,  $n_{\text{AcH in 1h}}$ ,  $t_{\text{reaction}}$ ,  $-\text{SO}_3\text{H}_{\text{cat}} \text{ content}$ ,  $m_{\text{catalyst}}$ ,  $\%S$ ,  $M_S$  stand for moles of converted acetic acid, moles of acetic acid before the reaction, moles of converted acetic acid in 1 h, reaction time in hours, content of the  $-\text{SO}_3\text{H}$  in catalyst (determined by elemental analysis), catalyst mass, the percentage composition of sulfur element in polymer (estimated by elemental analysis, see Table 1) and molecular weight of sulfur element ( $32.06 \text{ g mol}^{-1}$ ), respectively.

## 1.5 Water contact angle measurements

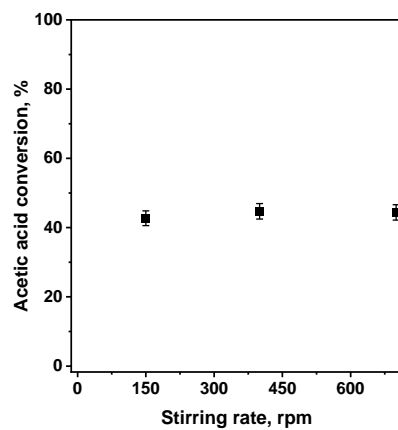
The wettability properties of the catalyst materials were evaluated by measuring the water contact angle (CA) at room temperature and a relative humidity of 12% (DataPhysics Instruments GmbH, OCA 15). It was observed by placing a drop of water on the polymer surface and measuring the angle using the sessile drop type. A camera captured images of the droplets as quickly as possible after their deposition. The droplet after contact with the surface was analyzed to obtain the contact angle values with an accuracy of 0.1 degrees ( $^\circ$ ).

## 1.6 The ion exchange capacity

The sulfonic acid ( $-\text{SO}_3\text{H}$ ) exchange capacity of all HCPs was determined by the acid-base titration method using NaCl aqueous solution as an ion-exchange agent [*Bioresour. Technol.* 270 (2018) 166, doi:10.1016/j.biortech.2018.09.037]. In a typical procedure, 0.100 g of dry polymer (drying conditions: 80 °C for 12 h under vacuum) was immersed in a 2.0 M NaCl aqueous solution (60 mL) and stirred at room temperature for 48 h. The resulting suspension was then filtrated off and the filtrate was titrated with 0.005 M NaOH aqueous solution using phenolphthalein as an indicator. The acid exchange capacity in the polymer was calculated using the following equation (Eq. S9):

$$\text{acid exchange capacity} = C_{\text{NaOH}} \times \Delta V/m \quad (\text{S9})$$

where  $C_{\text{NaOH}}$  represents the concentration of the NaOH solution,  $m$  is an initial mass of polymer and  $\Delta V$  is the volume of the NaOH solution consumed during acid-base titration method.

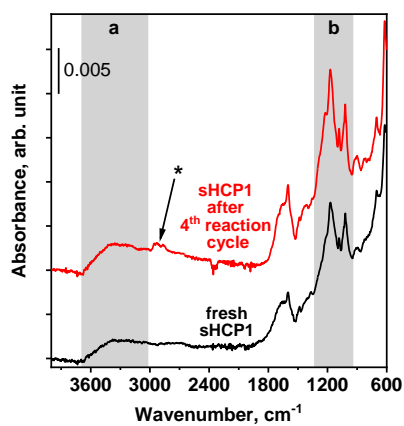


**Fig. S1.** The influence of stirring rate on the conversion of acetic acid in esterification of acetic acid with *n*-butanol in the presence of sHCP3 catalyst. *Reaction conditions:* AcH (3.84 g, 3.66 mL, 1.0 equiv., 64.0 mmol), BuOH (9.49 g, 11.71 mL, 2.0 equiv., 128.0 mmol), 20 mg of sHCP3, 240 min.

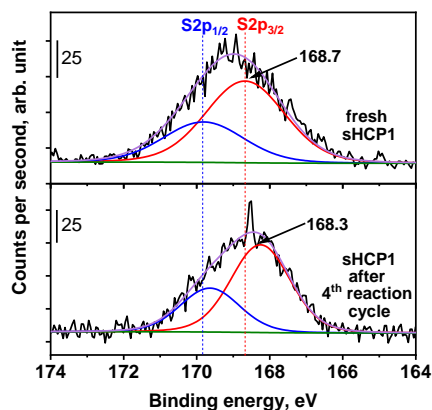
**Table S1:** Comparison of the catalytic activities of various SACs possessing sulfonic acid groups in esterification of acetic acid with *n*-butanol.

Solid acid catalyst	Type of SAC	AcH/ <i>n</i> -BuOH molar ratio	Catalyst loading [wt%]	Temp. [°C]	Time [h]	Conv. [%]	References
<b>sHCP1</b>	Hyper-cross-linked polymer	1.0:2.0	0.22	100	4	75.4	This work
<b>sFAP5</b>	Linear fluoropolymer	1.0:2.0	1.2	80	4	85.3	<i>Mater. Chem. Phys.</i> 273 (2021) 125132, doi: 10.1016/j.matchemphys.2021.125132.
<b>MNPs@CS-SO<sub>3</sub>H</b>	Biopolymer-magnetite nanocomposite	1.0:1.5	1.9	100	3	78.0	<i>Chin. J. Chem. Eng.</i> 39 (2021) 154, doi:10.1016/j.cjche.2021.04.037.
<b>PSSF-mCNTs-GO</b>	Linear polymer grafted carbon nanotube composite with graphene oxide	1.0:4.0	2.0	120	10	70.2	<i>RSC Adv.</i> 5 (2015) 90757, doi: 10.1039/C5RA14813H
<b>S-MIL-101</b>	Metal-organic framework	1.0:1.0	2.2	110	2	99.5	<i>Catal. Sci. Technol.</i> 3 (2013) 2044, doi: 10.1039/c3cy00044c
<b>H-ampsul-SCMNPs</b>	Silica coated magnetite nanoparticles	1.5:1.0	4.5	120	8	71.0	<i>Chem. Asian J.</i> 14 (2019) 1076, doi: 10.1002/asia.201801810
<b>SSA</b>	Silica sulfuric acid	1.0:2.0	5.4	130	2	84.5	<i>Energy Fuels</i> 28 (2014) 4267, doi: 10.1021/ef500129x
<b>MIL-125s</b>	Metal-organic framework	1.0:1.0	6.0	90	7	75.2	<i>Catal. Commun.</i> 100 (2017) 48, doi: 10.1016/j.catcom.2017.06.026





**Fig. S2.** ATR-IR spectra of fresh sHCP1 and material after 4<sup>th</sup> reaction cycle in the range of 4000-600 cm<sup>-1</sup> (region a: stretching vibration of the O-H bonds of the -SO<sub>3</sub>H; region b: asymmetric and symmetric stretching vibrations of S=O bonds in -SO<sub>3</sub>H groups, respectively). Asterisk (\*) corresponds to the band attributed to C(sp<sup>3</sup>)-H stretching vibrations in the alkyl moieties of the adsorbed reactants.



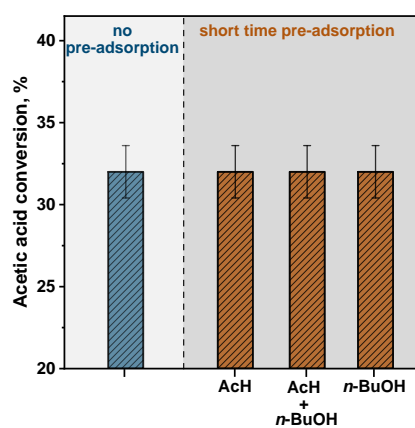
**Fig. S3.** XPS spectra in the S 2p binding energy range for fresh sHCP1 and material after 4<sup>th</sup> reaction cycle.

No significant changes in electronic properties of sulfonic acid species were found after 4<sup>th</sup> reaction cycle. Slight shift of the S 2p peaks toward lower binding energy values observed for the reused catalyst results most probably from the presence of interaction between the  $-\text{SO}_3\text{H}$  groups and adsorbed reactants. The presence of the adsorbed reactants on the surface of sHCP1 polymer was revealed by FTIR analysis (see Fig. S2).

**Table S2:** Sulfur content in fresh sHCP1 and material after 4<sup>th</sup> reaction cycle.

Catalyst	Sulfur content [mmol/g] <sup>a</sup>
fresh sHCP1	2.22
sHCP1 after 4 <sup>th</sup> reaction cycle	1.76

<sup>a</sup> Average values derived from three measurements determined based on EA



**Fig. S4.** The effect of reactant short pre-adsorption (5 min) on acetic acid conversion in the esterification of acetic acid with *n*-butanol in the presence of sHCP1 catalyst. *Reaction conditions:* AcH (3.84 g, 3.66 mL, 1.0 equiv., 64.0 mmol) or/and *n*-BuOH (9.49 g, 11.71 mL, 2.0 equiv., 128.0 mmol), 20 mg of the sHCP1, 400 rpm, 100 °C, 60 min.

**Table S3:** Relative polarity of alcohols used in the esterification reaction with acetic acid.

Alcohol	Relative polarity <sup>a</sup>
MeOH	0.762
BnOH	0.608
<i>n</i> -BuOH	0.586
CyOH	0.509

<sup>a</sup>The values for relative polarity are normalized from measurements of solvent shifts of absorption spectra [*Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Publishers, 3rd ed. (2003) doi: 10.1002/9783527632220].

**Table S4:** Comparison of TOF with relative TOF values for esterification of acetic acid with different alcohols over series of sHCPs (sHCP1-sHCP3).

Catalyst	MeOH <sup>a</sup>		BnOH <sup>b</sup>		<i>n</i> -BuOH <sup>c</sup>		CyOH <sup>d</sup>	
	TOF <sup>e</sup> [h <sup>-1</sup> ]	relative TOF <sup>f</sup> [%]	TOF <sup>e</sup> [h <sup>-1</sup> ]	relative TOF <sup>f</sup> [%]	TOF <sup>e</sup> [h <sup>-1</sup> ]	relative TOF <sup>f</sup> [%]	TOF <sup>e</sup> [h <sup>-1</sup> ]	relative TOF <sup>f</sup> [%]
sHCP1	2.49	76.15	3.46	55.99	7.79	68.57	1.45	58.00
sHCP2	2.93	89.60	4.87	78.80	8.78	77.29	1.99	79.60
sHCP3	3.27	100.00	6.18	100.00	11.36	100.00	2.50	100.00

<sup>a</sup> Reaction conditions: AcH (3.84 g, 3.66 mL, 1.0 equiv., 64.0 mmol), MeOH (4.10 g, 5.18 mL, 2.0 equiv., 128.0 mmol), 20 mg of catalyst, 400 rpm, 50 °C, 240 min;

<sup>b</sup> Reaction conditions: AcH (3.84 g, 3.66 mL, 1.0 equiv., 64.0 mmol), BnOH (13.84 g, 13.25 mL, 2.0 equiv., 128.0 mmol), 20 mg of catalyst, 400 rpm, 100 °C, 240 min;

<sup>c</sup> Reaction conditions: AcH (3.84 g, 3.66 mL, 1.0 equiv., 64.0 mmol), *n*-BuOH (9.49 g, 11.71 mL, 2.0 equiv., 128.0 mmol), 20 mg of catalyst, 400 rpm, 100°C, 60 min;

<sup>d</sup> Reaction conditions: AcH (3.84 g, 3.66 mL, 1.0 equiv., 64.0 mmol), CyOH (12.82 g, 13.52 mL, 2.0 equiv., 128.0 mmol), 20 mg of catalyst, 400 rpm, 100°C, 240 min;

<sup>e</sup> TOF was calculated as mole of AcH converted over 1 mol of sulfonic acid sites (determined by acid-base titration method) per 1 h (see Supplementary Data, Eqs. (S4)-(S8));

<sup>f</sup> Calculated assuming that the highest TOF value observed for sHCP3 catalyst is equal to 100%.