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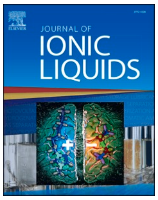

Functionalized ionic liquid coatings in the Pd-catalyzed selective hydrogenation of acetylene in ethylene-rich feeds

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ABSTRACT

This study explores the tuning of a Pd/Al_2O_3 hydrogenation catalyst for the selective removal of trace acetylene from ethylene-rich feeds by coating the catalyst with non-functionalized and functionalized ionic liquids (denoted as SCILL and Advanced SCILL materials, respectively). These materials were tested in an automated continuous hydrogenation rig converting 3300 ppm of acetylene in excess ethylene, a gas mixture mimicking a technical front-end steam cracker feed composition. While the sulfonic-acid-functionalized IL coating resulted in a highly active but very unselective catalyst converting mainly ethylene to ethane, an Advanced SCILL catalyst prepared from a nitrile-functionalized IL reduced the acetylene concentration down to less than 1 ppm, while leaving over 99% of the ethylene untouched. We also examined the potential transformations of the IL layer under reaction conditions by means of ^1H NMR. Except for a ketone-functionalized IL, which was inherently labile, all tested ILs primarily underwent C2-ethylation or remained unaltered. Our findings highlight the great potential of functionalized ILs in modifying heterogeneous hydrogenation catalysts.

Introduction

Although homogeneous catalysts are known for their high selectivities and rational tunability due to their well-defined dissolved metal complex structure, most industrial applications prefer heterogeneous catalysts due to their thermal robustness and the much easier product/catalyst separation (Corma and Garcia, 2008). One attractive way to increase the selectivity of heterogeneous catalysts is the so-called 'solid catalyst with ionic liquid layer‘ (SCILL) concept. Herein, a classical nanoparticle on support catalyst is coated with a thin film of ionic liquid (IL) as shown in Fig. 1 to modify its selectivity and activity (Kernchen et al., 2007). ILs are ideal surface modifiers as they offer a wide variety of coordination and solubility properties combined with their extremely low vapor pressures (Steinrück and Wasserscheid, 2015). Therefore, SCILL systems can be applied in gas-phase processes without loss of the modifying ionic liquid coating over time.

The use of SCILL or SCILL-related catalyst materials has been reported in literature for the selective hydrogenation of cyclooctadiene (Kernchen et al., 2007), citral (Naicker et al., 2022; Arras et al., 2009; Wörz et al., 2011), propylene (Friedrich et al., 2017) and acetylene (Herrmann et al., 2011; Farshidfar et al., 2016; Wang et al., 2021) and often drastic selectivity changes compared to the respective uncoated catalysts have been reported. As reasons for these selectivity effects two aspects are discussed in the literature: a) The IL coating may change the effective concentration of reactant(s), intermediate(s) and product(s) at the active catalytic surface compared to the uncoated solid catalyst. b) The IL may interact with the active catalytic surface and thereby modify its adsorption properties and reactivity (Steinrück and Wasserscheid, 2015). In most cases both aspects are relevant in combination with the relative importance being dependent on applied reactants, active metal and type of ionic liquid.

Selective acetylene removal from excess ethylene is a process of high industrial relevance in the context of purifying the steam cracking product stream for further use. If not removed, acetylene would act as a catalyst poison in the subsequent ethylene polymerization reaction (Rase, 2000). In the production of ethylene via steam cracking, acetylene is formed to an amount of around 3300 ppm. To produce polymerization-grade ethylene, acetylene removal to less than 5 ppm is

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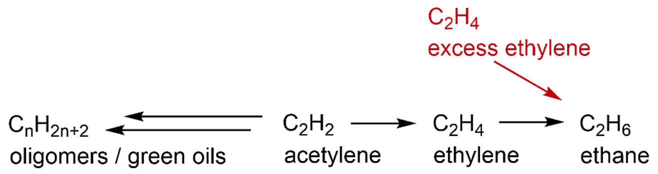
required. The challenge of acetylene removal from excess ethylene is that the undesired hydrogenation of ethylene (present in the feed typically in 30–50%) would not only lead to losses of valuable product but would lead to massive heat formation resulting in even lower selectivity for the desired acetylene hydrogenation. Thus, raising temperatures in the hydrogenation reactor can lead to thermal runaways and the need to shut down the whole steam cracker unit (Jess and Wasserscheid, 2020). Generally, two types of selective acetylene hydrogenation reactors exist, namely the front-end and back-end type. They are named after their position relative to the demethanizing column in the process, where hydrogen and methane are removed from the cracker stream. The back-end process encounters severe problems with the formation of oligomers (so-called green oil) due to the low hydrogen content. To minimize the formation of green oil, which inevitably blocks the catalyst surface, most industrial plants apply the front-end reactor configuration. However, in such a configuration the excess hydrogen together with the high ethylene content favors thermal runaway in the typically adiabatic reactors (Hock et al., 2022). An overview of possible reactions under the discussed conditions is shown in Scheme 1.



Scheme 1. Network of expected reactions in the presented selective acetylene hydrogenation studies (Herrmann et al., 2011).

Previous work in our group in this context demonstrated the effectiveness of PdAg/Al_2O_3-based SCILLs using various non-functionalized ionic liquids. Using the IL [C_2C_1Im][$EtSO_4$], for example, the thermal operation window – defined as the temperature window in which the acetylene concentration is brought down to at most 5 ppm and ethane formation is not higher than acetylene consumption – could be broadened from 15 °C to 50 °C (Williams, 2019).

Besides varying the cation-anion combination, it is also possible to add additional functional groups to the cation of the IL to tailor its properties for specific applications. The concept of functional group carrying ionic liquids has been introduced by Davis et al. and the term 'task-specific ionic liquids' (TSIL) has been introduced for such functionalized ILs (Visser et al., 2001; Davis, 2004). Literature primarily focuses on the use of TSILs in separation technologies, e.g. heavy metal extraction (Visser et al., 2002), metal oxide solubilization (Nockemann et al., 2006), or CO_2 absorption (Bates et al., 2002). Only very few reports are known on the use of TSILs in SCILL or SCILL-related catalysis leading to so-called 'Advanced SCILL' systems. One example is the use of functionalized ILs as catalyst modifiers for the selective hydrogenation of citral demonstrated by the group of Claus (Claus et al., 2009). Comparing nitrile-, ester-, and alcohol-functionalized ILs, these authors demonstrated that the nitrile group leads to the highest selectivities of the supported Pd catalyst towards the desired product citronellal. Another example deals with the coating of strongly Lewis-acidic ILs on Pt-catalysts in alkane isomerization (Meyer et al., 2012) and arene hydrogenation reactions, leading to an increased activity (Lijewski et al., 2017). Other groups have reported the successful use of functionalized ionic liquids as catalyst modifiers, but have not explicitly compared different functionalities under otherwise identical reaction conditions (Konnerth and Prechtl, 2016; Hu et al., 2009; Prechtl et al., 2009). Spectroscopic and mechanistic studies have been published for the example of an ester-functionalized imidazolium IL binding to various cobalt oxide surfaces. Whereas the carboxylate-anchored IL film did readily form on CoO(100), the reaction was not observed on Co_3O_4(111) as a result of the different arrangement of Co^{2+} ions on the two surfaces. The highly structure-sensitive binding of functionalized ILs onto reactive surfaces thus opens a large potential for the targeted modification of catalytic surfaces using functionalized ILs (Xu et al., 2017; Xu et al., 2017).

On the basis of the promising results for selective acetylene hydrogenation using non-functionalized SCILLs and the large potential of functionalized ILs in catalysis in general, we investigate in this study the performance of a variety of functionalized and non-functionalized ILs (shown in Fig. 2) in the selective acetylene hydrogenation. To elucidate the effect of the functionality, we not only vary the functionality of the ILs under investigation (keeping the cation backbone as well as the anion constant), but also investigate possible in-situ transformation or decomposition reactions of the coating ILs under different reaction conditions.

Experimental

General remarks

All chemicals were purchased from VWR, Merck, abcr, Alfa Aesar, Sigma-Aldrich, Roth and BLDpharm and used without further purification. All pure or pre-mixed gases were purchased from Linde Gas or Air

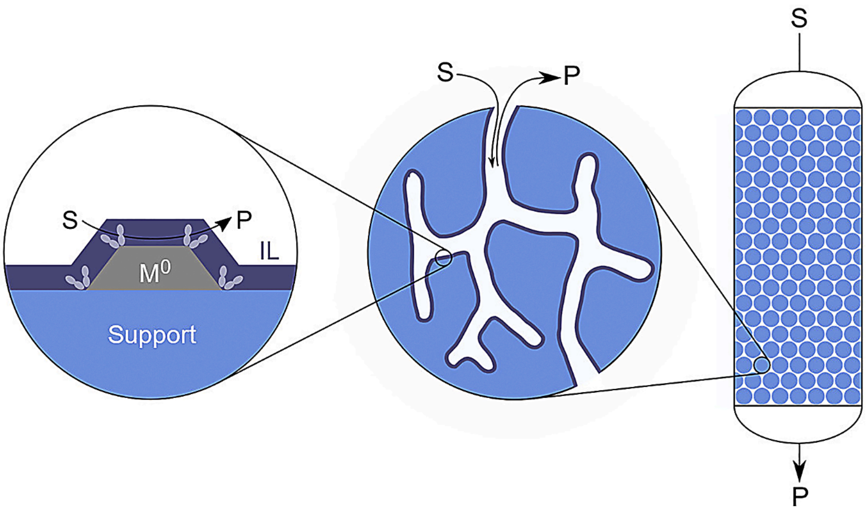


Fig. 1. Schematic representation of a SCILL consisting of a supported metal catalyst coated with a thin film of IL. The so prepared material can be macroscopically treated as classical heterogeneous catalyst and used in many continuous processes, while the IL microscopically interacts with the catalyst sites (here the edges) fine tuning its selectivity in the reaction from substrate to product.

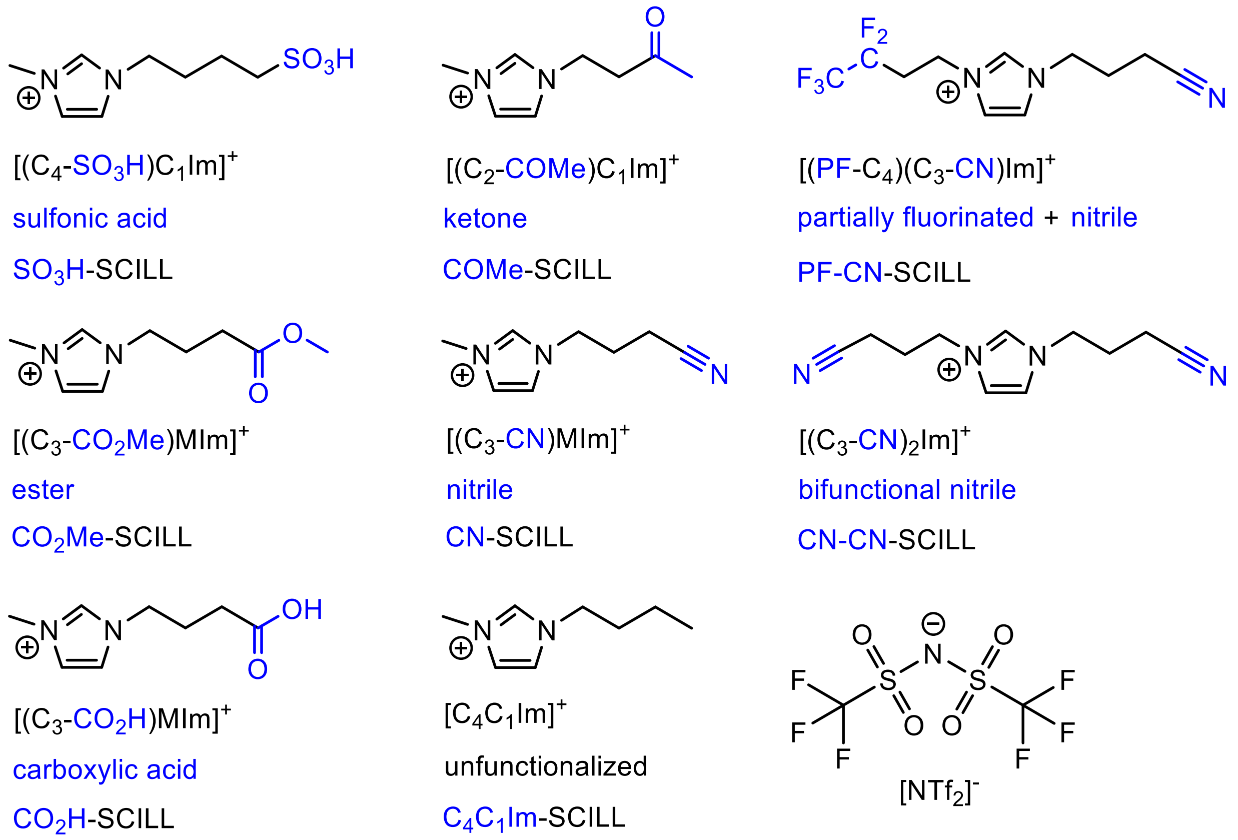


Fig. 2. Functionalized ionic liquids used in this work. Functional groups, their names, and abbreviations as used throughout this paper are highlighted in blue. All cations were combined with the [NTf_2] anion that is also shown.

Liquide. Additional information on the used methods can be found in the electronic supporting information.

IL synthesis

[C_4C_1Im][NTf_2] (99% purity) was purchased from Iolitec and used without further purification. All other ionic liquids (for molecular structures see Fig. 2, full IUPAC names are provided in the electronic supporting information) were synthesized in our laboratory using highest purity standards. We ensured, for example, the use of entirely grease-free equipment in order to prevent any contamination with surface-active substances.

SCILL catalyst preparation

For this work, a commercial catalyst from Heraeus was used, which consisted of 2–4 mm alumina (Al_2O_3) spheres with 5 $m^2 g^{-1}$ BET surface area impregnated with 0.25 wt.-% palladium in an eggshell mode. This material is herein referred to as 'blank catalyst'.

All SCILL materials tested throughout the work were based on ILs with the anion bis(trifluoromethylsulfonyl)imide ([NTf_2]$^-$), which is an easy to metathesize and thermally stable anion (Ngo et al., 2000). SCILL preparation was performed using the wet impregnation technique. Acetone was used for the impregnation of the catalyst, as it proved to dissolve all tested ILs sufficiently. It furthermore was found to lead to a good penetration depth of the IL into the catalyst pellet in the previous work of Williams (Williams, 2019) enabling full coverage of at least the Pd containing shell of the used egg-shell catalyst. The typical loading of ionic liquid was set to 10 wt.-% for stability tests under hydrogen or nitrogen atmosphere and to only 3 wt.-% for the selective hydrogenation experiments in order to reduce the risk of pore blocking.

In a typical SCILL synthesis, the respective weight of IL was dissolved in 0.8 ml of acetone for each gram of fresh SCILL to be synthesized. The resulting solution was subsequently added onto the blank catalyst and the solvent was removed using a rotary evaporator, followed by thoroughly drying the SCILL under vacuum for three days. The so-obtained catalyst is herein referred to as 'fresh SCILL'.

Continuous gas-phase reactions

Both stability tests as well as selective hydrogenation experiments were carried out in a continuous gas-phase tubular reactor equipped with a PFA polymer lining to inhibit blind activity of the stainless steel. Pressure was controlled via a manual backpressure regulator, temperature by measuring the catalyst bed temperature and via a heating mantle and a Eurotherm control unit. Gas dosing was realized using Bronkhorst MFCs for each gas, i.e. nitrogen (Air Liquide, 99.999% purity), hydrogen (Air Liquide, 99.999% purity), ethylene (Air Liquide, 99.95% purity), acetylene gas-mix (Linde, composition: acetylene (1.01%), methane (0.983%; used as internal GC standard) in nitrogen (rest)), and carbon monoxide gas-mix (Air Liquide, composition: carbon monoxide (909 ppm, 99.997%) in nitrogen (rest, 99.9999%)). Both gas dosing and temperature were controlled with the software Flexlab. A flowsheet of the complete setup can be found in the electronic supporting information, Figure S1-S2.

In a typical experiment, 0.8080 g of blank catalyst or fresh SCILL was loaded into the reactor tube, which was equipped with an inert PFA inlay to reduce blind activity, and held in place by a Teflon frit, additionally fixed with the help of glass wool from the top. The tube was then mounted using ½" VCR fittings with silver-coated metal gaskets. After purging the reactor and supply lines with nitrogen thrice, automated gas dosing and temperature control was started (details see Table S1), as well as product monitoring via gas chromatography. In general, a total volume flow of 69 ml_n/min was set, corresponding to a gas hourly space velocity (GHSV) of 3250 h^{-1}. For selective hydrogenation experiments at ambient pressure, the gases were mixed to obtain the following composition: 0.33 mol-% acetylene, 24.5 mol-% ethylene, 202 mol-ppm carbon monoxide, 20.0 mol-% hydrogen, 0.33 mol-% methane, and 54.8 mol-% nitrogen. For stability tests, either pure hydrogen or pure nitrogen was used with the same flow of 69 ml_n/min, but at a constant temperature of 80 °C and 10 bar pressure for 16 h.

The product stream was analyzed with a Shimadzu GC2030 online gas chromatograph equipped with a Shimadzu SH/AluminaBond Na_2SO_4 column (50 m length, 0.53 mm ID, 10 µm film thickness). 1 mL gaseous sample was injected (split ratio 1:10) with nitrogen (column flow rate 5.79 ml_n min^{-1}) as carrier gas. The temperature ramp (100 °C, 1.0 min; ramp 15 °C min^{-1} to 180 °C, 1.0 min hold time) allowed good separation of ethylene, ethane and acetylene and detection of all volatile hydrocarbons being emitted as side products.

After the experiments, the catalyst (referred to as 'H_2 treated SCILL' after stability tests under hydrogen, as 'therm. treated SCILL' after stability tests under nitrogen, or as 'used SCILL' after selective hydrogenation experiments, respectively) was removed from the reactor and weighed. For analyzing the IL film, the SCILL materials were leached by sonicating 300 mg of the catalyst with 1 ml of acetone-d_6 for 15 min followed by filtering the extract through a syringe filter and measuring ^1H NMR spectra of the resulting solution. As a reference, the corresponding fresh SCILL was leached in the same manner.

Reproducibility test experiments were exemplarily performed using a selection of SCILL materials, i.e. the CN-, CO_2Me-, CO_2H-, and SO_3H-functionalized materials. The results are shown in Figure S11 of the ESI.

Evaluation of catalytic performance

Catalyst performance is evaluated in terms of activity and selectivity. The definition of these parameters is based on the reaction network presented in Scheme 1, assuming, that green oil forms from acetylene oligomerization, only (Margitfalvi et al., 1981; Leviness et al., 1984; Zhang et al., 2016).

Hydrogen conversion X_{H_2} was calculated from the formed ethane and the consumed acetylene with $c_{Ethane,0}$ and $c_{Ac,0}$ being the corresponding concentrations of ethane and acetylene in blind activity experiments:

$$X_{H_2} = \frac{c_{Ethane} - c_{Ethane,0} + c_{Ac,0} - c_{Ac}}{c_{H2,0}} * 100\% \tag{1}$$

For the determination of the ethylene selectivity it is first necessary to define the oligomer selectivity S_{Ol} and the ethane selectivity S'_{Ethane}:

$$S_{Ol} = \frac{c_{Ol}}{c_{Ac,0} - c_{Ac}} * 100\% \tag{2}$$

$$S'_{Ethane} = \frac{c_{Ethane} - c_{Ethane,0}}{c_{Ac,0} - c_{Ac}} * 100\% \tag{3}$$

The ethane selectivity S'_{Ethane} can get larger than 100% in case more ethylene is converted to ethane than acetylene was consumed, implying that parts of the ethylene present in excess in the feed is also over-hydrogenated.

Finally, the ethylene selectivity S'_{Et} can be calculated:

$$S'_{Et} = \left(1 - S'_{Ethane} - S_{Ol}\right) * 100\% \tag{4}$$

If all acetylene is hydrogenated without any formation of ethane or oligomers, S'_{Et} is 100%, while it is 0% if the total amount of ethane and oligomers formed matches the amount of acetylene consumed. Note that this definition allows for negative S'_{Et} values if the amount of ethane and oligomers formed exceeds the amount of acetylene consumed.

Results and discussion

IL stability investigations

Imidazolium based ionic liquids are known for their tendency to undergo several decomposition reactions at elevated temperatures, especially when in contact with certain metals (Chen and Huang, 2023) and gases (Maton et al., 2013). Prior to their use in the selective hydrogenation of acetylene, the SCILL materials were therefore tested for their thermal and chemical stability under exposure to different gases and at elevated temperatures. So-treated SCILL materials were leached and the obtained IL solution was studied by ^1H NMR spectroscopy. This study was carried out for coating ILs with functionalities, that were expected to be most susceptible towards transformations under typical hydrogenation conditions, i.e. nitrile-, ester-, carboxylic-acid-, and ketone-functionalized ILs. SCILL materials prepared with these ILs were exposed to an atmosphere of pure nitrogen, to pure hydrogen, and to the gas mixture used in our catalytic studies. As a reference, a freshly prepared SCILL was also leached. Fig. 3 compares the stability of $[(C_3\text{-CN})C_1Im][NTf_2]$ leached from the respective SCILL in the fresh state, after thermal treatment, after hydrogen treatment and after selective hydrogenation in the presence of acetylene, ethylene, and ethane (for the extended spectrum see Figure S3; for the NMR spectra of the leachates of the other tested SCILLs see Figures S4-S10).

Thermal stability of the coating ILs

Compared to the fresh CN-SCILL (black spectrum in Fig. 3), the thermally treated SCILL (red spectrum) does not show any new peaks in the ^1H NMR spectrum. The same can be stated for the other tested ILs except for $[(C_2\text{-COMe})C_1Im][NTf_2]$, which showed signs of retro-Michael decomposition (shown in Scheme 2) forming 1-methylimidazole (see Figure S4). Note that the observed reaction is the inverse reaction to the Michael-type addition that was used to prepare this specific IL in the first place (Bösmann et al., 2007). The coupling product 3-butene-2-one could not be detected, most likely due to its high volatility. Interestingly, the decomposition reaction of $[(C_2\text{-COMe})C_1Im][NTf_2]$ already happens under extremely mild conditions (ambient pressure, room temperature) when impregnated onto the Pd catalyst. This was concluded from the fact that the fresh SCILL with $[(C_2\text{-COMe})C_1Im][NTf_2]$ contained 1-methylimidazole in the IL film, that was not present in the neat IL (purple spectrum in Figure S4). Obviously, the interaction with the Pd surface lowers the thermal stability of $[(C_2\text{-COMe})C_1Im][NTf_2]$ quite significantly.

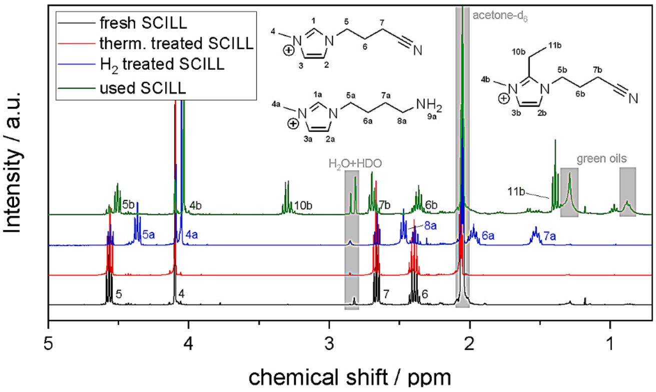
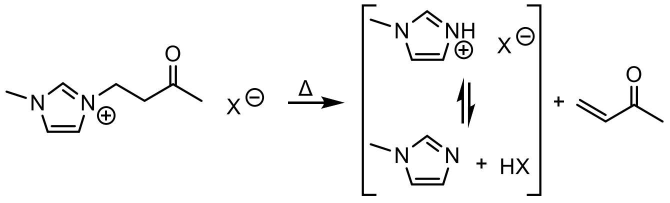


Fig. 3. NMR spectra of IL films leached from CN-SCILL catalysts after thermal treatment (red), exposure to hydrogen (blue), and after 44 h under reaction conditions using feed gas (green) in comparison with the leachate extracted from the freshly prepared catalyst (black).



Scheme 2. Retro-Michael decomposition of [(C_2-COMe)C_1Im][NTf_2].

Stability of the coating ILs under hydrogen atmosphere

Exposure of the SCILL materials to hydrogen at 80 °C for 16 h showed more drastic changes for two of the ILs under investigation. [(C_3-CN) C_1Im][NTf_2] (blue spectrum in Fig. 3) was hydrogenated to its amine-derivative to a large extent, while the IL backbone appeared to stay intact, as no other species were found. Similarly, the newly formed amine functionality appeared to be stable under the conditions discussed and for the short time window observed, although rearrangement reactions induced by the nucleophilic amine functionality might play a role at elevated temperatures or prolonged reaction times. Like [(C_3-CN) C_1Im][NTf_2], [(C_2-COMe)C_1Im][NTf_2] (Figure S4) showed considerable conversion to yield a secondary alcohol, next to its decomposition to 1-methylimidazole as already described above. [(C_3-CO_2Me)C_1Im][NTf_2] (Figure S5) did not seem to be affected to the same extent showing only traces of new species, too little to be conclusively analyzed by means of ^{1}H NMR spectroscopy. Like its structural relative, also [(C_3-CO_2H)C_1Im] [NTf_2] (Figure S7) remained stable with only minor amounts of new species detected.

Stability of the coating ILs under selective acetylene hydrogenation conditions

Especially interesting is the behavior of the coating ILs under reaction conditions, i.e. when exposed to the gas mixture containing acetylene, ethylene, and hydrogen, here exemplarily shown for [(C_3-CN) C_1Im][NTf_2] (green spectrum in Fig. 3). A very prominent difference compared to the fresh SCILL is the presence of broader signals around 1.29 and 0.88 ppm in the ^{1}H NMR spectrum (marked with gray boxes in Fig. 3). Both the chemical shift (Li et al., 2015) and the integral ratio of these two signals match the typical signature of linear alkanes. Such linear alkanes are formed in significant amounts as part of the green oil resulting from an oligomerization reaction of acetylene at the precious metal catalysts (Zhang et al., 2016). [(C_3-CN)C_1Im][NTf_2] itself was converted to a large extent to a new IL with an ethyl moiety in C2-position. This reaction was already investigated in previous work by Bauer, who used a similar gas mixture and the unfunctionalized IL [C_2C_1Im][$EtSO_4$] impregnated onto Pd/Al_2O_3 as catalyst (Bauer et al., 2017). It was proposed in this earlier work that the tendency of C2-acidic imidazolium-ILs to form surface carbenes with Pd can lead to the formation of C2-ethylated species via insertion of ethylene into the carbene C-Pd bond and subsequent reductive elimination. It is interesting that the same reaction occurs at the functionalized IL investigated in our studies. It is also remarkable that the nitrile functionality remains intact in presence of the C2 reactants while hydrogen alone was showing the reduction of the nitrile group to the amine (comparison of the blue and the green spectra in Fig. 3). To exclude that the different reaction conditions of the stability tests and the selective hydrogenation experiments (a detailed side by side comparison of the reaction conditions can be found in Table S2) are responsible for the described results, we performed an additional stability experiment (entry 'low p H_2 treatment' in Table S2) applying the temperature program of the selective hydrogenation experiments but replacing all hydrocarbons and carbon monoxide with nitrogen (see blue spectrum in Figure S6). Similar to the standard stability test under hydrogen (red spectrum in Figure S6), the nitrile group was transformed to the amine to a large extent. Therefore, it can be concluded that the protection of the functionality in selective hydrogenation tests can be traced back to the added gases and therefore to a modification of the active sites by either the adsorbed hydrocarbons or CO. To see how much the co-fed CO in the selective hydrogenation experiment contributes to the protection of the IL against nitrile hydrogenation, another stability experiment (entry 'low p H_2 + CO treatment' in Table S2) was performed with added CO, but without the presence of the C2 hydrocarbons. The corresponding leachate (green spectrum in Figure S6) showed no obvious nitrile conversion to the amine, indicating that the presence of CO in the feed protects the nitrile from hydrogenation.

Very similar to the CN-SCILL, the leachate of used CO_2Me-SCILL (Figure S5) showed the formation of the C2-ethylated species together with some green oil formation. Green oil formation could also be detected for the used CO_2H- (Figure S7) and COMe-SCILL (Figure S4), however, the formation of the C2-ethylated IL was here only found for the COMe-SCILL in traces, albeit a definite assignment could not be made. While decomposition to 1-methylimidazole was the dominant reaction with [(C_2-COMe)C_1Im][NTf_2] (as discussed earlier), [(C_3-CO_2H)C_1Im][NTf_2] appeared to be unchanged after exposure to the hydrocarbon-containing gas mixture and no C2-ethylation was detectable in this case. A possible explanation for this behavior is the acidic nature of the IL, which can counteract the deprotonation of the C2-position of the imidazolium and thereby possibly hindering the carbene formation and subsequent ethylation. The same explanation is valid for the SO_3H-SCILL (see Figure S8) where only green oil formation and no C2-ethylation was found, as expected from such a Brønsted-acidic IL that prevents carbene formation.

Along the lines of this rational, we found C2-ethylation for the non-acidic SCILL systems with [(C_3-CN)$_2$Im][NTf_2] (Figure S9) and [(PF-C_4) (C_3-CN)Im][NTf_2] coatings (Figure S10). However, while for [(C_3-CN)$_2$Im][NTf_2] green oil formation was in the same range as for most of the other ILs, [(PF-C_4)(C_3-CN)Im][NTf_2] showed very little green oil in the utilized SCILL (red spectrum in Fig. 4). This difference could also be pinpointed by comparing the weight gains of the different utilized SCILL systems. While most SCILLs except for the highly active SO_3H-SCILL gained 0.6 to 1.4% in weight (see Table 1), the SCILL prepared from [(PF-C_4)(C_3-CN)Im][NTf_2] remained almost weight stable (weight gain $< 0.1\%$). To conclude our stability tests, a [C_4C_1Im][NTf_2]-coated SCILL material was also studied after contact with the reaction mixture and, as expected, C2-ethylation of the coating IL was observed (Figure S10).

Overall, all functionalities tested in this work – with the exception of the thermally labile ketone functionality – appeared to be decently stable under the reaction conditions present in the selective hydrogenation of acetylene. Hydrogenation of the imidazolium-based functionalized ILs has not been an issue. Instead, C2-ethylation was found to be a major transformation path for all ILs (60 to 86 % yields) except for

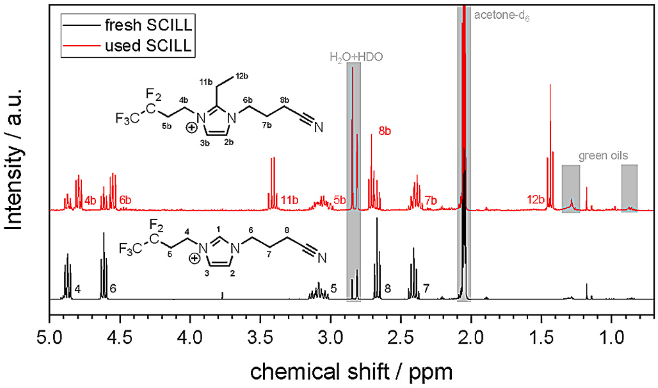


Fig. 4. NMR spectra of IL films leached from PF-CN-SCILL catalysts after 44 h under reaction conditions using feed gas (red) in comparison with the leachate extracted from the freshly prepared catalyst.

Table 1
Comparison of the extent of C2-ethylation (as measured by NMR integral ratios) as well as the weight gain found in the used SCILLs.

SCILL	C_4C_1Im	CN	SO_3H	CO_2H	CO_2Me	CN—CN	PF-CN
IL ethylation	62%	86%	0%	0%	61%	60%	69%
SCILL weight gain	1.4%	0.9%	0.1%	0.6%	0.9%	1.0%	< 0.1%

the Brønsted-acidic ILs, as summarized in Table 1.

Catalytic studies

With this knowledge of the stability and possible structural changes under reaction conditions, the performance of the respective Advanced SCILL systems in the selective acetylene removal from an ethylene-rich feed has been studied. Fig. 5 shows the concentrations of the various gas components as measured by online-GC during the course of a typical hydrogenation experiment, here exemplified for the unfunctionalized C_4C_1Im- and the functionalized CN-SCILL. Generally, with increasing temperature over time on stream (TOS), acetylene and oligomer concentrations drop and ethane formation increases. Comparing the SCILLs using unfunctionalized $[C_4C_1Im][NTf_2]$ vs. functionalized $[(C_3\text{-CN})C_1Im][NTf_2]$, it can be seen, that oligomer concentrations drop to the same extent as a function of temperature regardless of the coating IL. Using $[(C_3\text{-CN})C_1Im][NTf_2]$, however, the acetylene removal is more effective and ethane formation at comparable temperature is lower. Thus, the coating with the functionalized IL leads to a more selective catalyst. Note, that steady-state conditions were sometimes not reached after the 10 h holding time at 40 °C. It is interesting that for each temperature step, the catalyst performance appears to improve over time with decreasing ethane formation being observed until steady-state is reached. One possible explanation for this behavior might be the ongoing C2-ethylation of the IL, which was discussed before.

To enable a more convenient comparison of the catalytic performance of the different SCILLs, ethylene and oligomer selectivities (S'_{Et} and S_{Ol}) as well as the total hydrogen conversion X_{H_2} were calculated for

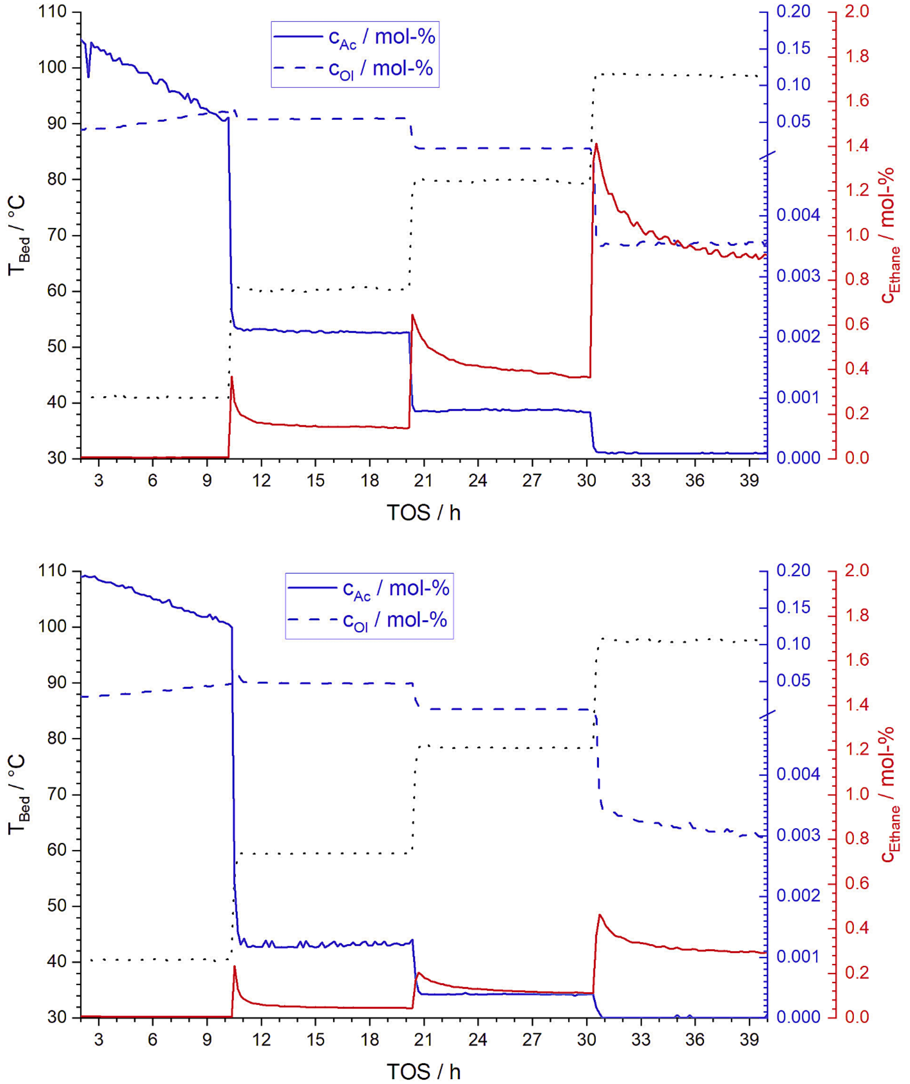


Fig. 5. Acetylene (solid blue line), oligomer (dashed blue line), ethane concentration (red line) and catalyst bed temperature (dotted black line) as a function of time-on-stream (TOS) for the SCILLs based on the unfunctionalized $[C_4C_1Im][NTf_2]$ (top) and functionalized $[(C_3\text{-CN})C_1Im][NTf_2]$ (bottom). Conditions: GHSV 3250 h^{-1}, 1 bar, 0.8 g of catalyst (3 wt% IL on Pd/Al_2O_3). Feed composition: 24.5% ethylene, 20% hydrogen, 0.33% acetylene, 0.33% methane, 0.02% CO and balance nitrogen.

each SCILL at 40 °C, 60 °C, 80 °C and 100 °C. This was carried out using the gas concentrations under steady-state, i.e., in the last hour of each temperature step as shown in the concentration plot in Fig. 5, and with the help of formulas (1), (2), and (4) for X_{H_2}, S_{Ol}, and S'_{Et}. The results are plotted in Fig. 6. In all cases, ethylene selectivity decreases with temperature due to the increasing over-hydrogenation towards ethane. It is also immediately visible that the different IL coatings tested in this work lead to drastically different performances. While the blank catalyst almost consumes all hydrogen leading to extreme ethylene over-hydrogenation even at the lowest temperatures investigated, the reference catalyst coated with the unfunctionalized $[C_4C_1Im][NTf_2]$ (green curve) results in ethylene selectivities of 43% at 60 °C and of −172% at 100 °C. It should be emphasized here that S'_{Et} includes the potential hydrogenation of excess ethylene in the feed. A selectivity of −172% implies that 2.7x as much ethylene is hydrogenated to ethane as acetylene is consumed. Considering that ethylene was present in a 74x excess to the feed compared to acetylene, also the SCILL coated with the unfunctionalized $[C_4C_1Im][NTf_2]$ IL performs quite selectively.

Remarkably, $[(C_3\text{-}CN)C_1Im][NTf_2]$ (red curve) leads to a strongly improved ethylene selectivity of 74% at 60 °C and 12% at 100 °C. To investigate, if a higher nitrile concentration leads to an even better performance, the bifunctional $[(C_3\text{-}CN)_2Im][NTf_2]$ was synthesized, bearing an additional cyanopropyl side chain instead of the usual methyl group. Its performance could not outperform the monofunctionalized $[(C_3\text{-}CN)C_1Im][NTf_2]$, however. $[(PF\text{-}C_4)(C_3\text{-}CN)Im][NTf_2]$ bearing a partially fluorinated butyl-chain as well as a nitrile-functionalized side-chain, in contrast, performed even better than $[(C_3\text{-}CN)C_1Im][NTf_2]$. This IL coated on the Pd on alumina catalyst showed an impressive ethylene selectivity of 88% at 60 °C and still 54% at 100 °C, where the acetylene concentration was reduced down to below 1 ppm (see Figure S12 for the concentration plot) forming only 0.15 mol-% of ethane despite the large excess of ethylene in the reactor. This corresponds to over 99% of the ethylene not being over-hydrogenated. Whether this increase in selectivity can be traced back to solubility differences of one or several gases in the ionic liquid, thereby altering their concentrations at the active sites, or to selective adsorption effects at the catalyst active sites is still subject of further research in our laboratory. Besides an increased ethylene selectivity, $[(PF\text{-}C_4)(C_3\text{-}CN)Im][NTf_2]$ stands out regarding its low oligomer selectivity in comparison to almost all of the other ILs, which all perform very similar (see Fig. 6, center). The reduced tendency of green oil formation was already observed by means of ^1H NMR in the leachate of the used SCILL, see above. The increased ethylene selectivity and dramatically reduced oligomer selectivity of $[(PF\text{-}C_4)(C_3\text{-}CN)Im][NTf_2]$ demonstrate the almost infinite combinatorial possibilities when using tailor-made, functionalized ILs in SCILL applications.

Interestingly, some functional IL coatings showed decreased ethylene selectivities compared to the non-functionalized $[C_4C_1Im][NTf_2]$ coating, such as the CO_2Me-, COMe-, CO_2H-, and SO_3H-SCILL systems. The COMe- and the CO_2H-coatings performed similar in terms of ethylene selectivity and hydrogen conversion compared to the non-functionalized coating. For $[(C_2\text{-}COMe)C_1Im][NTf_2]$, a rapid drop in selectivity and increase of hydrogen conversion with temperature was observed and can be explained by the previously described thermal instability of this IL. Obviously with IL decomposition and evaporation of the volatile decomposition products the selectivity-enhancing effect of the IL coating fades away.

An extreme and very different behavior was observed for the SCILL system with the SO_3H-functionalized IL coating. This system performed almost identically to the blank catalyst without IL in terms of ethylene selectivity and hydrogen conversion, but also regarding to oligomer selectivity. A possible reason for the low oligomer formation observed is that the very high hydrogenation activity leaves no acetylene behind that could undergo oligomerization. The overall very similar performance of the two catalysts was at first a very surprising result for us, as we expected at least a slightly deactivated catalyst after IL coating due to the additional diffusion barrier created by the IL coating.

A detailed analysis of the leachate obtained after reaction gave us a valuable hint to understand the mode of action of this particular SO_3H-functionalized IL coating: While the IL extracted from the used SCILL material was found not to be altered in its chemical structure, the leachate was isolated as an extremely dark, but clear liquid, see Fig. 7, left.

The Pd content of the leachate was therefore determined using ICP-AES, showing that around 18% of the initial Pd loading of the catalyst was dissolved into solution next to small amounts of Al from the support. This and the very dark, but clear appearance of the leachate indicated that IL stabilized Pd nanoparticles were extracted from the catalyst. DLS measurements confirmed these findings by showing nanoparticles with a size of 15 nm in the freshly sonicated leachate after the use of the SCILL in the reaction, as can be seen in the black spectrum in Fig. 7, right.

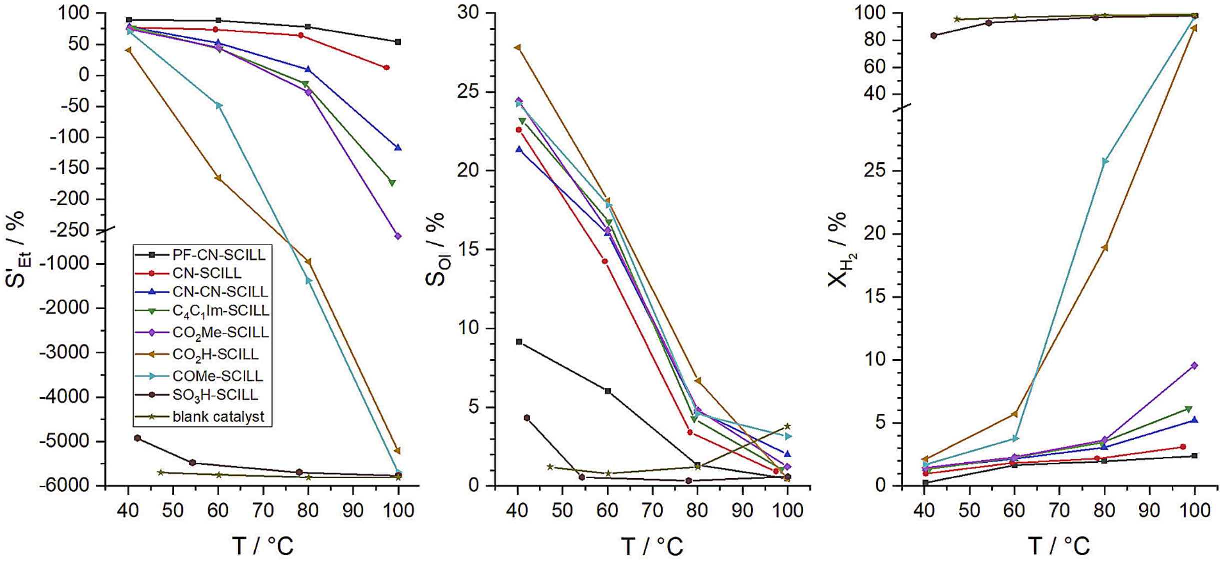


Fig. 6. Ethylene (left) and oligomer selectivity (center) as well as hydrogen conversion (right) for different SCILL systems and the blank catalyst. All selectivity data are plotted over the catalyst bed temperature. Conditions: GHSV 3250 h^{-1}, 1 bar, 0.8 g of catalyst (3 wt% IL on Pd/Al_2O_3). Feed composition: 24.5% ethylene, 20% hydrogen, 0.33% acetylene, 0.33% methane, 0.02% CO and balance nitrogen.

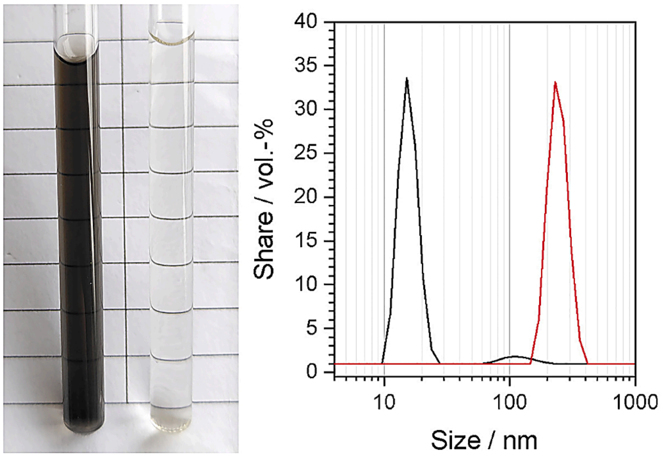


Fig. 7. Left: Comparison of the leachate of the used SO_3H- and CN-SCILLs: while most leachates were isolated in form of clear and colorless liquids, as here seen for the CN-SCILL case (right tube), the one prepared from the SO_3H-SCILL showed a strong brownish-blackish color (left tube); right: DLS measurements of the freshly sonicated (black; 15 nm particles) and the aged leachate (red; 230 nm particles) extracted from the used SO_3H-SCILL.

Leaving the leachate untouched for 5 days (aged leachate) lead to clustering of the nanoparticles (which was reversible via sonication) to form larger particles of around 230 nm. These could be removed via filtration using a 0.2 μm syringe filter, leaving behind an almost colorless solution. ICP of the filtered solution showed a significant decrease of the Pd:Al ratio from 1.9:1 to 0.03:1. These observations confirm colloidal Pd nanoparticles as the origin of the dark discoloration, while the Al seems to be homogeneously dissolved into solution. Overall, it appears that $[(C_4\text{-}SO_3H)C_1Im][NTf_2]$ corrodes the Al_2O_3 support and creates IL stabilized Pd nanoparticles in the supported IL film that are highly active hydrogenation catalysts but pretty unselective in the here-investigated acetylene hydrogenation in excess ethylene.

Conclusion

In this work, we have investigated the coating of functionalized ILs onto a commercial Pd/Al_2O_3 hydrogenation catalyst to modify activity and selectivity in the selective hydrogenation of acetylene from ethylene-rich feeds. The performance of the resulting Advanced SCILL systems ranged from unselective total hydrogenation of acetylene and ethylene in case of a sulfonic-acid-functionalized IL to an impressively high ethylene selectivity for a partially fluorinated and nitrile-functionalized IL. In the latter case, the Advanced SCILL system was able to reduce the acetylene concentration from 3300 ppm to below 1 ppm while leaving over 99% of the ethylene untouched.

We also investigated and explained potential transformations of the IL layer under reaction conditions. Except for the ketone-functionalized IL, which was inherently labile even under inert gas, all tested ILs primarily underwent C2-ethylation, which did not seem to impair catalyst performance, or even stayed unaltered. Hydrogenation of the functionalities, which was observed for several ILs under pure hydrogen atmosphere, was efficiently hindered when catalytic sites were occupied by the reactive adsorbates during reaction.

Our results show the great potential of Advanced SCILL systems. We anticipate other application areas for this technically highly attractive catalyst modification concept beyond the use of precious metal catalysis and also for other types of reactions.

CRediT authorship contribution statement

Daniel Kremitzl: Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. **Karoline Röhrs:** Methodology, Investigation. **Marc B. Williams:** Methodology, Investigation. **Peter S. Schulz:** Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Peter Wasserscheid:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

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.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jil.2024.100092.

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