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Highly Selective Continuous Gas-Phase Methoxycarbonylation of Ethylene with Supported Ionic Liquid Phase (SILP) Catalysts

Santosh G. Khokarale, Eduardo J. García-Suárez, Rasmus Fehrmann, and Anders Riisager*[a]

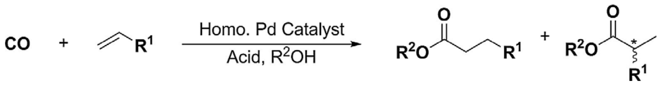
Supported ionic liquid phase (SILP) technology was applied for the first time to the Pd-catalyzed continuous, gas-phase methoxycarbonylation of ethylene to selectively produce methyl propanoate (MP) in high yields. The influence of catalyst and reaction parameters such as, for example, ionic liquid loading, metal concentration, and ligand loadings was studied, and in particular the SILP catalyst activity and stability was found to be strongly dependent on the ligand to metal ratio.

Introduction

After about 15 years of advancement, supported ionic liquid phase (SILP) catalysis is now an established technology, in which a homogeneous catalyst is dissolved in an ionic liquid (IL) film immobilized (non-covalently) on a mesoporous solid carrier material.[1] SILP technology offers an excellent combination of the advantages of homogeneous and heterogeneous catalysts by achieving both high catalyst activity and selectivity—owing to an exceptional large interfacial reaction area created by the thin film approach. In addition, easy product separation and catalyst recovery is also obtained owing to the solid nature of the catalyst at the macroscopic level. Thus, SILP technology allows for efficient catalyst recycling and facilitates homogeneous catalysis to be undertaken with fixed-bed reactor technology, which by far is the preferred process design in the chemical industry.

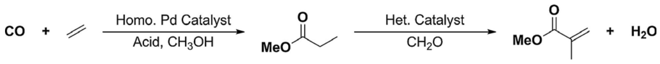
In SILP catalysts the IL film is generally only up to a few nanometers thick. This unique feature minimizes mass transport limitations across the reaction interface, thus allowing an extraordinary high degree of utilization of both the IL and the dissolved catalyst compared with classic IL biphasic systems, in which much larger amounts of ILs are employed as reaction media.[2] Furthermore, the extremely low vapor pressure, characteristic of most ILs, and their suitability to be modified for a specific application make SILP catalytic systems easy tunable for a specific application, in particular, for continuous gas-phase processes.[3]

The applicability of SILP technology for continuous gas-phase processes in fixed-bed reactors has during the last decade successfully been demonstrated for a number of homogeneously catalyzed reactions with industrial importance, such as hydrogenation,[4] hydroformylation,[5–8] carbonylation,[2] water–gas shift (WGS) reaction,[9] and hydroamination,[10,11] etc. However, the SILP technology has—to the best of our knowledge—so far not been applied for alkoxycarbonylation of olefins, which is also a highly relevant industrial reaction. The alkoxycarbonylation of olefins is an atom-efficient reaction for production of commodity alkyl esters and derivatives[12] (Scheme 1).



Scheme 1. General reaction scheme for the alkoxycarbonylation of olefins.

Pd-catalyzed methoxycarbonylation of ethylene (Scheme 1, $R^1 = H$, $R^2 = CH_3$) to produce methyl propionate (MP) is a reaction with special interest owing to the high demand of the product. MP is a key building block for the production of methyl methacrylate (MMA) in the Alpha process conceptually developed in 1990,[13] and explored industrially by Lucite International (now Mitsubishi Rayon Company) (Scheme 2).[14] MMA is a monomer for the preparation of poly-MMA, which is a large-scale transparent thermoplastic used as, for example, a glass alternative and in medical technologies. The first MMA plant based on Alpha technology was commissioned in 2008 in Singapore with an annual production capacity of 120 kt, and a second plant with the largest world production of MMA (250 kt/a) will be operational in Saudi Arabia in 2017.



Scheme 2. Reaction scheme for the two-step Alpha MMA process.[11]

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[a] Dr. S. G. Khokarale, Dr. E. J. García-Suárez, Prof. Dr. R. Fehrmann, Prof. Dr. A. Riisager
Centre for Catalysis and Sustainable Chemistry
Department of Chemistry
Technical University of Denmark
DK-2800 Kgs. Lyngby (Denmark)
Fax: (+45) 45883136
E-mail: ar@kemi.dtu.dk

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Homogeneous catalyst systems based on Pd–phosphine complexes and strong acid-promoters are most frequently applied in alkoxycarbonylation of olefins to provide high activity under relatively mild conditions. However, the choice of phosphine ligand can strongly influence the reaction selectivity towards esters or polyketones.[13] The catalytic system developed for the Alpha process comprises a strong mineral acid with $pK_a \leq 4$, a Pd^{II} precursor, and the so called "Alpha ligand" 1,2-bis(di-*tert*-butylphosphinomethane)benzene (DTBPMB) developed by Shaw et al.[15] The DTBPMB (P–P) ligand has been shown to be unique for the ethylene methoxycarbonylation reaction, yielding MP with high selectivity (>99.9%) at very high conversion rates, and provides unprecedented stability to the catalytic species involved in the reaction mechanism.[13]

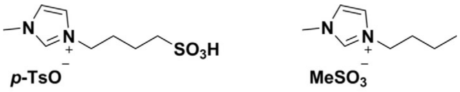
The Alpha process is carried out in homogeneous solution in a continuously stirred tank reactor under moderate reaction conditions. Although the catalyst system is well-established and highly efficient, the product isolation—and mainly the catalyst recovery—still remains challenging as in many other homogeneous catalytic processes. Different approaches (besides SILP technology) have been developed in the past to overcome these inherent drawbacks in homogeneous catalysis including, for example, biphasic systems[16–18] and the use of supercritical CO_2.[19] Indeed, we recently reported an efficient biphasic system for the ethylene methoxycarbonylation by using Brønsted acid ionic liquids (BAILs) as both reaction media and acid promoter, in which excellent recyclability, stability, and recovery of the catalytic system was achieved.[20]

In this work, we report for the first time the application of SILP technology to Pd-catalyzed continuous, gas-phase ethylene methoxycarbonylation. Excellent results in terms of catalytic activity and selectivity towards MP were achieved by using the DTBPMB ligand. Different SILP catalyst formulations with respect to metal loading, ligand loading, IL loading, and nature of the support were investigated to evaluate the catalytic performance and the stability of the SILP system.

Results and Discussion

Preparation and characterization of the SILP catalysts

The SILP catalysts were prepared with the desired amount of BAIL1 and the commercially available IL2 (Figure 1) with support pore filling degrees or IL loading (α) corresponding to 10–30 pore vol% (i.e., $\alpha = 0.1$–0.3). IL2, comprising an analogous alkyl imidazolium cation as BAIL1 except for the sulfonic acid group, was selected for comparative purposes to pinpoint the crucial role of the acid functionalization of BAIL1 in the methoxycarbonylation reaction. The textural properties of the support materials and the prepared SILP catalysts are compiled in Table 1.



[SBMI][*p*-TsO] **[BMIM][$MeSO_3$]**

BAIL1 **IL2**

Figure 1. ILs employed in the SILP preparation.

Table 1. Textural properties of the supports and the prepared SILP catalysts.[a]

Support	Pd [wt%]	IL loading (α)	S_{BET} [$m^2 g^{-1}$]	V_t [$cm^3 g^{-1}$]
SiO_2-100	–	–	347	0.98
	0.08	0.2	204	0.62
	0.16	0.2	187	0.57
	0.23	0.2	210	0.63
	0.31	0.2	196	0.56
	0.38	0.2	198	0.57
	0.26	0.1	242	0.72
	0.34	0.1	252	0.68
	0.22	0.3	165	0.48
SiO_2-500	–	–	360	0.98
	0.23	0.2	208	0.60

[a] SILP formulation: SiO_2-100 or SiO_2-500 support, $Pd(OAc)_2$ precursor, DTBPMB ligand (P–P/Pd = 5:1), IL loading (α) defined as the ratio between the volume of IL and the pore volume of the support.

The BET surface area (S_{BET}) as well as the total mesoporous volume (V_t) decreased regularly by increasing the IL loading although a less significant change was observed with increasing Pd loading, as also expected. TGA of the prepared SILP revealed mass loss in agreement with IL loadings (see the Supporting Information). The pore size distribution of the prepared SILPs (with SiO_2-100 support) revealed a gradually smaller mean average pore diameter with increasing IL, suggesting that the IL homogenously distributed on the support (see the Supporting Information).

Catalytic performance of SILP catalysts

The prepared SILP catalysts were examined for continuous, gas-phase ethylene methoxycarbonylation at 85 °C and 5 bar pressure by using fixed-bed technology. In a first approach, catalyst parameters such as Pd loading, P–P/Pd ratio, and IL nature and loading were systematically investigated and optimized to achieve the best performance concerning catalytic activity and stability. Notably, with all examined catalyst systems the only detected product was MP, confirming that the reaction selectivity was exceptionally high as also expected for the DTBPMB ligand system (see above).

Composition of the IL

The crucial role of the Brønsted acid functionalization of the IL on catalytic performance was demonstrated by comparing the prepared SILP catalysts with BAIL1 and the non-acidic IL2 under the selected reaction conditions. As shown in Figure 2, the SILP with BAIL1 yielded a high catalytic activity corresponding to a maximum turnover frequency (TOF) of 210 h^{-1} and space time yield (STY) of 0.24 $kg L^{-1} h^{-1}$, but the

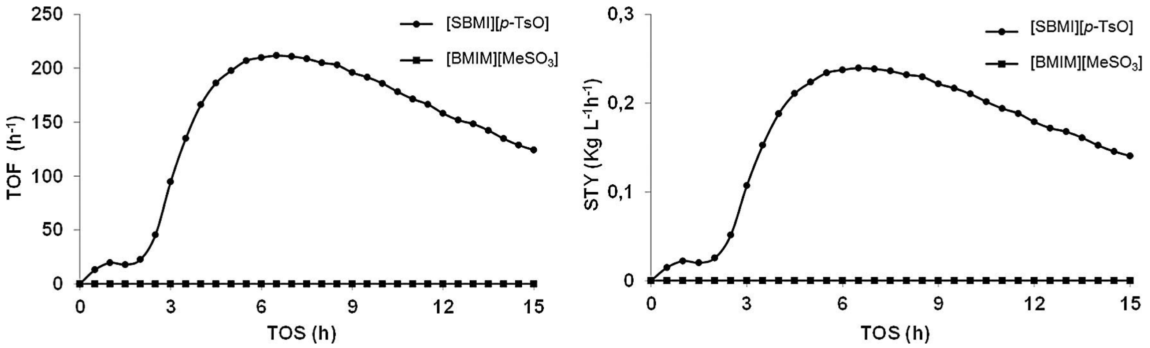


Figure 2. Effect of the IL composition on the TOF (left) and STY (right) in SILP-catalyzed ethylene methoxycarbonylation. SILP catalyst: SiO_2-100, P–P/Pd = 5, Pd = 0.23 wt %, α = 0.2 (BAIL1 or IL2). Reaction conditions: m_{SILP} = 500 mg, P_{total} = 5 bar (C_2H_4/CO/Ar = 2:2:1), T = 85 °C, gas flow rate (STP) = 129 mL min^{-1}, gas hourly space velocity (GHSV) = 9048 h^{-1} (STP), contact time = 0.4 s.

performance gradually decreased with time on stream (TOS). In contrast, the SILP with IL2 (non-acidic) was completely inactive under the applied conditions. These results confirm the essential role of the functionalized IL in the reaction, as also observed in our previous work with the catalyst system in bulk IL phase.[20]

Influence of the SiO_2 support

A commonly used mesoporous SiO_2 (silica gel 100, Merck) was selected as support material for the prepared SILP catalysts. It is well documented that silanol groups present in SiO_2 can affect either negatively[3] or positively[7] hydroformylation SILP catalyst performance and stability depending on catalyst composition. To examine if silanol groups also influenced the performance in the present reaction, thermally treated SiO_2 (500 °C, 12 h; SiO_2-500) was also prepared and used.

The thermal treatment decreased the concentration of silanol groups and hence acidity of the SiO_2-500 (628 μmol g^{-1}) support significantly compared with SiO_2-100 (1297 μmol g^{-1}) as shown by NH_3-TPD analysis (see the Supporting Information). However, the catalytic performances of the corresponding catalysts were quite similar if used in ethylene methoxycarbonylation under the applied conditions, except for an induction period for the catalyst with the SiO_2-100 support (Figure 3), which might be related to an initial wettability difference between the supports. Hence, the more hydrophilic SiO_2-100 support on exposure to dry reactant gas desorbed water during the induction period and became more hydrophobic, achieving a comparable conversion as the pre-calcined catalyst. The SiO_2-100 was chosen for further experiments.

Influence of Pd loading

To examine the effect of metal loading, SILP catalysts with Pd loadings up to 0.38 wt % were prepared and tested in the ethylene methoxycarbonylation. The MP yield and catalyst TOFs increased with the amount of Pd content to well above 330 h^{-1}, though not linearly as could be expected (Figure 4). The reason for this unusual behavior is at present not clear. Moreover, an increased amount of Pd (and ligand) seemed to shorten the induction period, although less significantly than in the case of the different supports as shown above. Possibly this change may also be a result of a surface wettability effect, here induced by the ligand, that is, a higher ligand concentration results in a more hydrophobic system. A reference SILP catalyst without Pd was not catalytically active in the reaction, clearly demonstrating that the metal is the catalytically active inventory. The SILP catalyst with 0.23 wt % Pd was selected for

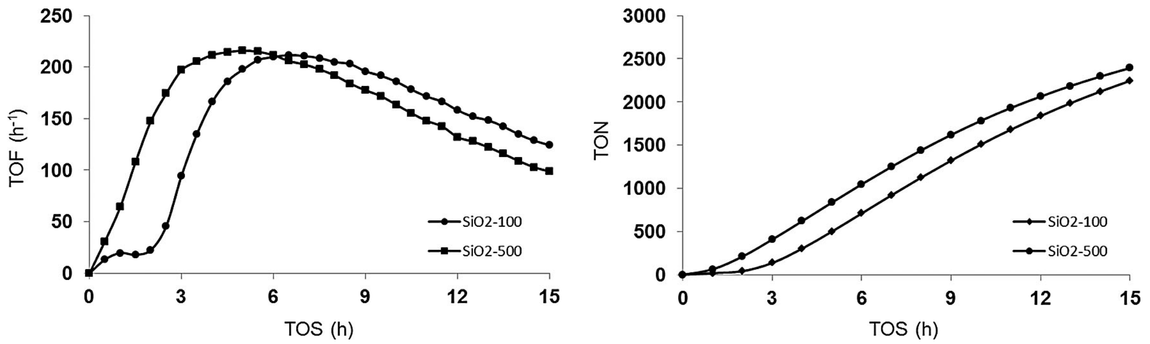


Figure 3. Effect of the SiO_2 support on the TOF (left) and TON (right) in SILP-catalyzed ethylene methoxycarbonylation. SILP catalyst: SiO_2-100 or SiO_2-500, P–P/Pd = 5, Pd = 0.23 wt %, α = 0.2 (BAIL1). Reaction conditions: m_{SILP} = 500 mg, P_{total} = 5 bar (C_2H_4/CO/Ar = 2:2:1), T = 85 °C, gas flow rate (STP) = 129 mL min^{-1}, GHSV = 9048 h^{-1} (STP), contact time = 0.4 s.

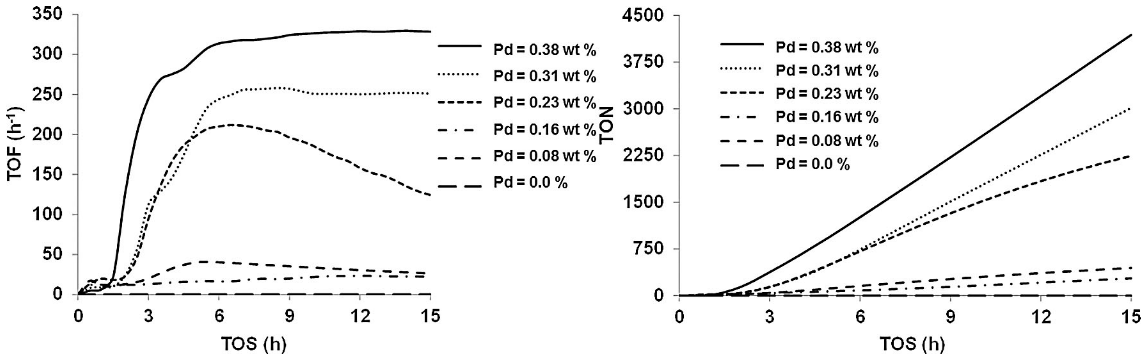


Figure 4. Effect of the Pd loading on the TOF (left) and TON (right) in SILP-catalyzed ethylene methoxycarbonylation versus time on stream (TOS). SILP catalyst: SiO_2-100, P–P/Pd = 5, Pd = 0–0.38 wt %, $\alpha = 0.2$ (BAIL1). Reaction conditions: $m_{SILP} = 500$ mg, $P_{total} = 5$ bar (C_2H_4/CO/Ar = 2:2:1), $T = 85\,^{\circ}C$, gas flow rate (STP) = 129 mL min^{-1}, GHSV = 9048 h^{-1} (STP), contact time = 0.4 s.

further studies, as this metal content allowed the ligand and the corresponding complexes to be solubilized in the IL phase, whereas solubility limitations, in some cases, were observed if using larger Pd amounts.

Influence of variations in IL loading (α)

IL loading (α) in SILP catalysts describes the IL pore filling degree of the employed support. The α value allows estimation of the IL film thickness on the support by calculation if an even surface distribution of the IL is assumed. The IL film thickness is of great importance for the catalyst activity, as mass transfer limitations—usually associated with the use of bulk amounts of ILs—can be avoided or enhanced depending on the IL loading. Hence, relatively low α values are expected to eliminate mass transfer limitations and facilitate higher catalytic activity. In contrast, absence of IL (i.e., $\alpha = 0$) is expected to result in a catalytically inactive system, as the acid functionalization contained in the IL is essential for the methoxycarbonylation reaction. For the examined SILP catalysts (Figure 5), the expected trends were observed, and the highest TOF around 400 h^{-1} was found for the catalyst with the lowest IL loading ($\alpha = 0.1$). Notably, this catalyst was apparently also the most stable of the examined catalysts, reaching a turnover number (TON) around 4500.

Effect of ligand amount

In homogeneous catalysis, it is well-known that an insufficient amount of ligand leads to incomplete formation of the catalytic active species, whereas an excessive amount of ligand can result in the formation of highly stable species with relatively low catalytic activity. Therefore, the ligand content is an important parameter to examine in SILP catalysis with dissolved homogeneous complex catalysts.

The SILP catalyst activity and stability was enhanced in the ethylene methoxycarbonylation if the P–P/Pd ratio was increased, reaching a TOF > 650 h^{-1} and TON > 9000 if using a P–P/Pd ratio of 10 (Figure 6). Possibly the high ligand content may act as a ligand reservoir and help stabilize the catalytically active species by rapidly replacing ligands dissociated from the metal center by side reactions that can occur during the catalytic cycle, for example, protonation or oxidation.

Encouraged by these results, catalysts with P–P/Pd ratios of 20 and 30 were also prepared. Notably, for these catalysts the Pd loading had to be reduced to 0.08 wt % to keep the required relatively large amounts of ligand dissolved in the IL layer. The results obtained with these catalysts clearly confirmed that an increasing ligand amount significantly improved both catalyst activity and stability, and very high TOFs of up to approximately 900 and 1500 h^{-1} was reached with the

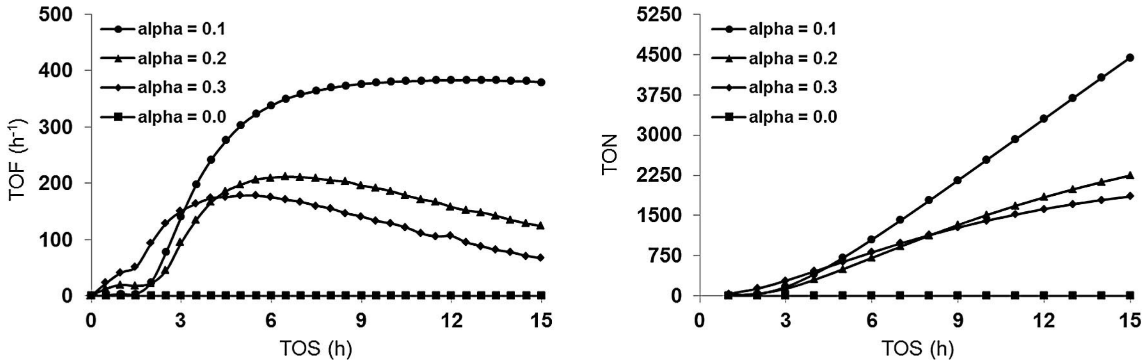


Figure 5. Effect of IL loading on the TOF (left) and TON (right) in SILP-catalyzed ethylene methoxycarbonylation. SILP catalyst: SiO_2-100, P–P/Pd = 5, Pd = 0.23 wt %, $\alpha = 0$–0.3 (BAIL1). Reaction conditions: $m_{SILP} = 500$ mg, $P_{total} = 5$ bar (C_2H_4/CO/Ar = 2:2:1), $T = 85\,^{\circ}C$, gas flow rate (STP) = 129 mL min^{-1}, GHSV = 9048 h^{-1} (STP), contact time = 0.4 s.

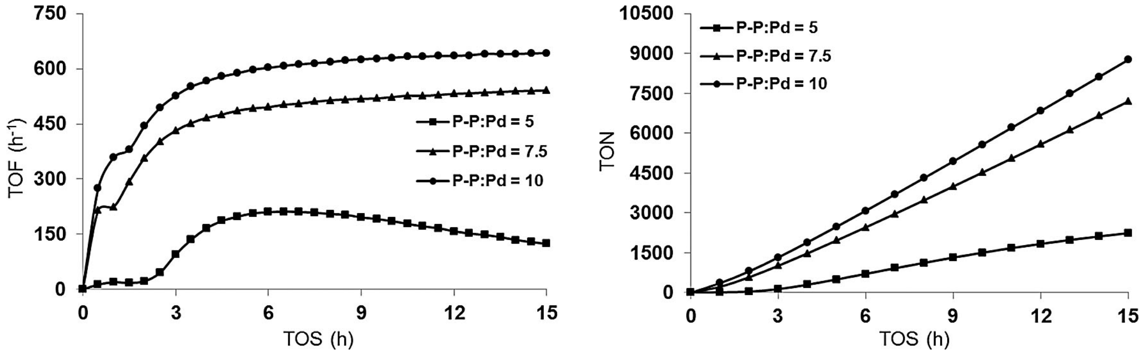


Figure 6. Effect of P–P/Pd ratio on the TOF (left) and TON (right) in SILP-catalyzed ethylene methoxycarbonylation. SILP catalyst: SiO_2-100, P–P/Pd = 5–10, Pd = 0.23 wt %, $\alpha = 0.2$ (BAIL1). Reaction conditions: $m_{SILP} = 500$ mg, $P_{total} = 5$ bar ($C_2H_4/CO/Ar = 2:2:1$), $T = 85\,^{\circ}C$, gas flow rate (STP) = 129 mL min^{-1}, GHSV = 9048 h^{-1} (STP), contact time = 0.4 s.

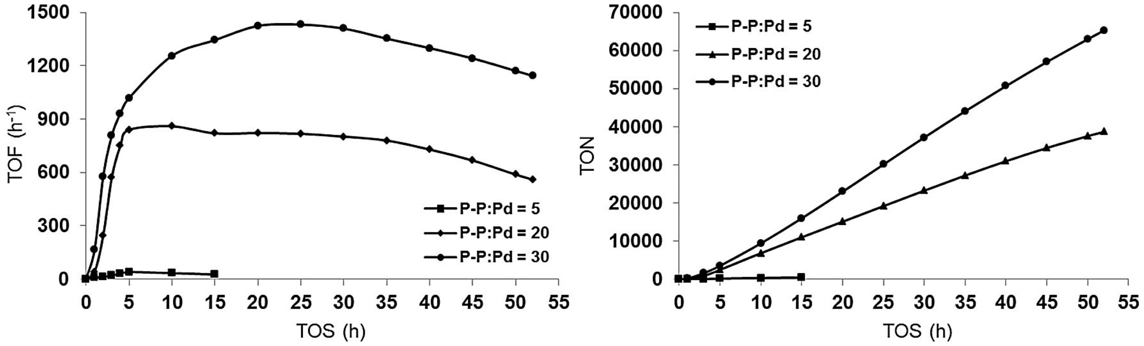


Figure 7. Effect of P–P/Pd ratio on the TOF (left) and TON (right) in SILP-catalyzed ethylene methoxycarbonylation. SILP catalyst: SiO_2-100, P–P/Pd = 5, 20, or 30, Pd = 0.08 wt %, $\alpha = 0.2$ (BAIL1). Reaction conditions: $m_{SILP} = 500$ mg, $P_{total} = 5$ bar ($C_2H_4/CO/Ar = 2:2:1$), $T = 85\,^{\circ}C$, gas flow rate (STP) = 129 mL min^{-1}, GHSV = 9048 h^{-1} (STP), contact time = 0.4 s.

catalyst with P–P/Pd ratios of 20 and 30, respectively (Figure 7). In the latter catalyst system, this activity corresponds to a TON of almost 70 000. Despite the improved stability, some deactivation still occurred during prolonged time on stream, which most likely was linked to Pd black formation as also indicated by the dark coloration of the spent catalysts. Nevertheless, taking the results into account, it is evident that the P–P/Pd ratio and the ligand interactions with the metal center play pivotal roles in the performance of the prepared SILP catalysts.

Conclusions

The supported ionic liquid phase (SILP) technology has been successfully applied for the first time in continuous gas-phase ethylene methoxycarbonylation. Different reaction parameters were studied and their influence on the ethylene methoxycarbonylation provided. A strong correlation of the P–P/Pd ratio with the SILP catalytic activity and stability was found. High ionic liquid loadings (IL) have a negative effect on the catalytic activity owing to mass transfer limitations of the gas transport into the IL phase, and investigations to further increase the stability of the SILP catalysts without hampering the catalytic activity as well as long-term studies are actively undertaken. Furthermore, solid-state NMR analysis is utilized to understand the role of the ligand in the studied reaction as well as the decomposition pathways in more detail. In summary, the work shows the applicability of SILP technology for the ethylene methoxycarbonylation reaction, and provides useful directions to which improvements need to be addressed to demonstrate its potential for implementation on an industrial scale.

Experimental Section

Materials

1-Methylimidazole (≥99 %), *p*-toluenesulfonic acid (*p*-TsOH, ≥98.5 %), 1,4-butanesultone (≥99.97 %), methanol (≥99.8 %), cyclohexane (≥99.8 %), palladium acetate (≥99.98 %), 1,2-bis(di-*tert*-butylphosphinomethane)benzene (DTBPMB, ≥98 %) and 1-butyl-3-methylimidazolium methanesulfonate ([BMIM][$MeSO_3$], IL2, Figure 1, ≥95 %) were purchased from Sigma–Aldrich and used without further purification. A $CO/C_2H_4/Ar = 2:2:1$ gas mixture was purchased from AGA and used as received. If required, all manipulations with the chemicals were performed under inert atmosphere by using Schlenk techniques.

Silica gel (63–200 µm, Merck) was used as the porous support for the SILP catalysts. Before usage, the support was sieved to a narrow particle size distribution between 180–200 µm and dried at 100 °C for 24 h. The resulting silica gel was named SiO_2-100. SiO_2-500 was prepared from the sieved SiO_2 by thermal treatment at 500 °C during 12 h in air.

Synthesis of Brønsted acid ionic liquid (BAIL) and SILP catalysts

The BAIL1 (Figure 1) was synthesized from 1-methylimidazole, 1,4-butanesultone and *p*-TsOH in two reaction steps according to previously reported procedures,[20,21] and the identity and purity was confirmed by NMR analysis (see the Supporting Information, Figures S1–S3). The BAIL1 was chosen as a substitute for a mineral acid, as it has previously been shown to perform excellently as biphasic media in ethylene methoxycarbonylation.[20]

The SILP catalysts were prepared by a slightly modified procedure to a previously reported method.[5] In a typical experiment, the required amount of palladium precursor, diphosphine ligand, and IL (IL/Pd ratio approx. 50–100) were dissolved in degassed methanol at room temperature under an Ar atmosphere and stirred for 1 h. Afterwards, SiO_2-100 or SiO_2-500 support was added to the solution and the mixture stirred for 3 h. Finally, the methanol was removed under reduced pressure and the resulting solid dried overnight under vacuum at 60 °C. The obtained solid SILP catalyst was kept under inert conditions prior to use.

Characterization of SILP catalysts

Thermogravimetric analyses (TGA) of the prepared materials were performed with Mettler Toledo equipment (TGA/DSC1 STARe System) under a nitrogen flow (50 mL$\,$min^{-1}). In a typical experiment, samples were heated from room temperature to 120 °C with a heating rate of 10 °C$\,$min^{-1}. The samples were dried at this temperature for 2 h to eliminate moisture. Then, they were heated from 120 to 600 °C with a ramp of 10 °C$\,$min^{-1}.

The surface area and pore size distribution of the silica supports and the SILP catalysts were obtained from the N_2 adsorption-desorption isotherms performed at −196 °C in a Micromeritics ASAP 2020 volumetric adsorption instrument. Prior to the measurement, samples were degassed under vacuum for 3 h at 120 °C. Specific surface areas (S_{BET}) were calculated by using the Brunauer–Emmett–Teller (BET) method, taking 16.2 nm^2 for the cross-sectional area of the N_2-adsorbed molecule. The total mesopore volume (V_t) was determined by using the de Boer t-plot method.

NH_3 temperature-programmed desorption (TPD) analysis of the silica supports was performed with a Micromeritics Autochem-II instrument. In a typical experiment, 50 mg of dried sample was placed in a quartz reactor and flush with He (50 mL$\,$min^{-1}) at 100 °C for 1 h. Thereafter, the sample was kept under anhydrous NH_3 gas (Air Liquid, 5% NH_3 in He) for 2 h. After NH_3 adsorption, the sample was flushed with He (50 mL$\,$min^{-1}) for 20 min at 100 °C. Finally, the TPD operation was performed by heating the sample from 100 to 700 °C (10 °C$\,$min^{-1}) under a He flow (50 mL$\,$min^{-1}). The NH_3 concentration in the effluent was monitored by a thermal conductivity detector and NH_3 consumption was calculated from calibration experiments.

Continuous gas-phase ethylene methoxycarbonylation in fixed-bed reactor

Gas-phase ethylene methoxycarbonylation was performed in a stainless-steel tubular reactor (30 cm, ID 1.5 cm). The SILP catalyst (500 mg) was loaded in a fixed-bed positioned in the middle of the reactor with a layer of quartz wool above and below the bed to retain the catalyst in place. Premixed $CO/C_2H_4/Ar$ (2:2:1) gas, N_2 (AGA, 5.0), and methanol (with 3.8 wt% cyclohexane as internal standard) were feed to the reactor in the gas-phase through mass-flow controllers connected to a controlled evaporator mixer (CEM) unit (Bronkhorst High-Tech). The experiments were performed at 85 °C, a total pressure of 5 bar, and a constant gas flow rate of 129 NmL$\,$min^{-} (STP). Reaction products were analyzed and the conversion quantified by GC-FID (Agilent 7890A gas chromatograph, non-polar DB-1 column, 30 m).

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Keywords: ionic liquids · carbonylation · fixed-bed technology · palladium · supported ionic liquid phase catalysis

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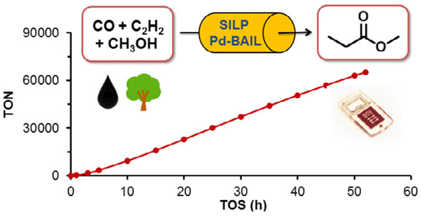
It's all in the ratio: Supported ionic liquid phase (SILP) technology was applied to the Pd-catalyzed continuous, gas-phase methoxycarbonylation of ethylene to selectively produce methyl propanoate in high yields. Studying the influence of catalyst and reaction parameters showed that the SILP catalyst activity and stability was strongly dependent on the ligand to metal ratio.



S. G. Khokarale, E. J. García-Suárez, R. Fehrmann, A. Riisager*

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Highly Selective Continuous Gas-Phase Methoxycarbonylation of Ethylene with Supported Ionic Liquid Phase (SILP) Catalysts