MCM-41 Supported Water-soluble TPPTS–Rh Complex in Ionic Liquids: A New Robust Catalyst for Olefin Hydroformylation

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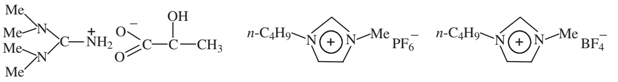
MCM-41 mesoporous silicas-supported water-soluble TPPTS–Rh complex in the ionic liquid TMGL exhibited high performance and stability for the hydroformylation of 1-hexene, and the catalyst system could be reused many times without reducing the activity and selectivity.

In recent years, the ionic liquids (ILs) have been considered as new media for biphasic catalysis to achieve improved catalyst performance and easy catalyst–product separation.[1] However, such catalysis system usually requires considerable amount of ILs.[2] The reduction of IL amount in the reaction processes is inevitably desirable from the viewpoints of economic criteria and possible toxicological concerns. The concept of supported ionic liquid phase catalyst (SILPC) is fulfilled such a demand.[3–5] The exigent need to develop new SILPC that is active, selective, stable, reusable, and clean for olefin hydroformylation is highly acknowledged.[4,5] A SILPC through immobilization of homogenous Rh complexes in ILs onto SiO_2 has been reported by Mehnert et al.[4] They found that such SILPC system showed rather good performance in the hydrogenation and hydroformylation with respect to the IL–organic biphsic catalysis. Riisager et al. found that it was possible to use SiO_2-supported IL-phase Rh–phosphine catalysts for the hydroformylation of propene and 1-octene in a fixed-bed reactor and that the specially designed phosphine ligand was required in order to obtain better aldehyde n/i ratio and higher catalytic stability.[5] Herein, we show, for the first time, that the higher active and aldehyde n/i ratio may be achieved by using MCM-41 to immobilize the conventional water-soluble TPPTS (trisulfonated triphenylphosphine)–Rh complex dissolved in a simple and halogen free IL 1,1,3,3-tetramethylguanidinium lactate (TMGL, Scheme 1) for the hydroformylation of 1-hexene. The results indicated that the SILPC with the TMGL could be reused many times without reducing the activity and selectivity.



TMGL BMI·PF_6 BMI·BF_4

Scheme 1. The structure of ILs.

The preparation of MCM-41-SILPC was referred to the methods described in literature.[5–9] The conversion and selectivity with various catalysts are listed in Table 1. A biphasic catalysis system composed of IL phase and organic phase was formed after the water-soluble TPPTS–Rh complex was dissolved in the IL phase.[10] In such a system, the catalytic activity was dependent of the type of ILs (Table 1). This was mainly ascribed to the property of ILs, which affected the solubility of the TPPTS

Table 1. The evaluation of the different catalysts on 1-hexene hydroformylation[a]

Catalyst	ILs Loading /wt %	α^b	SSA[c] /$m^2\,g^{-1}$	$V_{p\,tot}$[d] /$cm^3\,g^{-1}$	d_{BJH}[e] /nm	Conv. /%	Heptanal n/i	TOF /h^{-1}	TOF /$h^{-1}\,S_{BET}^{-1}$
TMGL–Rh[f]	—	—	—	—	—	5.0	3.2	32	—
$BMIPF_6$–Rh[f]	—	—	—	—	—	3.7	2.4	23	—
$BMIBF_4$–Rh[f]	—	—	—	—	—	3.4	2.2	22	—
TMGL–TPPTS–Rh[f]	—	—	—	—	—	13.0	3.8	82	—
$BMIPF_6$–TPPTS–Rh[f]	—	—	—	—	—	8.0	2.5	50	—
$BMIBF_4$–TPPTS–Rh[f]	—	—	—	—	—	43.4	2.3	271	—
TGML–TPPTS–Rh/MCM-41	0	0	990	0.586	2.8	55.0	0.7	322	0.325
	5	0.038	574	0.493	2.7	55.6	2.7	348	0.606
	10	0.079	469	0.385	2.5	53.2	2.6	330	0.704
	15	0.126	402	0.344	2.6	56.5	3.0	389	0.968
	25	0.237	250	0.233	2.3	36.0	3.5	270	1.080
	50	0.711	153	0.173	2.1	27.9	2.5	197	1.288
TMGL–TPPTS–Rh/SiO_2	15	0.554	108	0.057	2.9	12.6	2.1	87	0.806
$BMIPF_6$–TPPTS–Rh/MCM-41	15	0.098	493	0.224	2.6	48.5	1.7	334	0.667
$BMIBF_4$–TPPTS–Rh/MCM-41	10	0.072	316	0.338	2.9	50.2	1.6	500	1.582

[a] Reaction conditions: TPPTS/Rh = 5 (molar ratio), SILPC = 0.1 g (Rh = 0.8 wt % based on silicas), 1-hexene = 2 mL, toluene = 6 mL, $CO/H_2 = 1$ (V/V), $P(CO/H_2) = 2.0$ MPa, $T = 373$ K, agitation speed = 800 rpm, reaction time = 4 h. [b] pore filling degrees of IL in the support as volume IL/pore volume support. [c] BET specific surface area. [d] Total pore volume. [e] Mean pore diameter determined by BJH method. [f] $Rh(acac)(CO)_2 = 0.0064$ mmol, IL amount = 4.0 mL, others are the same as above. The SSA (m^2g^{-1}) and V_p (cm^3g^{-1}) for MCM-41 and SiO_2 were 1041, 0.789, and 315, 0.179, respectively.

and TPPTS–Rh complex, olefin and syngas.[10,11] With the SILPC, however, it showed much higher activity in the hydroformylation of 1-hexene than that of the corresponding IL–organic biphasic system and the catalytic activity is almost independent of the type of ILs. A higher regio-selectivity in term of heptanal n/i ratio was obtained with either the SILPC or the biphasic system using TMGL in comparison to the one using BMI•PF_6 or BMI•BF_4. The SILPC using SiO_2 as carrier afforded reasonable aldehyde n/i ratio, but it presented much lower conversion of 1-hexene as compared to the SILPC using MCM-41 under identical condition. The 1-hexene conversion and the heptanal n/i ratio were influenced by the TMGL loading weight and the molar ratio of TPPTS/Rh. For instance, in the case of TPPTS/Rh at 5, the heptanal n/i ratio was increased from 0.7 to 3.5 as the TMGL loading increased from 0 to 25 wt % as shown in Table 1. Further increase in the TMGL loading caused decreases in the reaction rate and the heptanal n/i ratio. The highest catalytic activity was obtained with the TMGL loading at 15 wt %.

The hexagonal array of MCM-41 was remained after the treatment at 373 K for 10 h in the TMGL and BMI•BF_4 as evidenced by XRD and N_2-adsorption. The thermogravimetric analysis revealed that the SILPC with TMGL showed a massive weight loss at about 673 K, probably due to the decomposition of the IL. Immobilization of Rh-complex and TMGL onto MCM-41 caused a decrease in the XRD intensity, especially when the TMGL loading higher than 25 wt %. The SAA, pore volume and BJH pore size distributions for the SILPC samples were smaller than that of MCM-41 (Table 1). The results implied that the considerable amounts of IL and Rh-species were essentially located in the inner channel of MCM-41. The SILPC gave the ν_{co} peak at 1984 cm^{-1} and ^{31}P NMR signal at 33.6 ppm, which were probably due to the species likely Rh(acac)(CO)(TPPTS) and/or $HRh(CO)(TPPTS)_2$.[11,12] The lower heptanal n/i ratio with the SILPC suggested that the active species might be the coordinatively unsaturated TPPTS–Rh complexes, which might be similar to those in the supported aqueous-phase Rh catalysts.[13]

The durability of the MCM-41-SILPC with TMGL loading at 10 wt % and TPPTS/Rh = 5 was examined by a series of consecutive runs. The results are shown in Figure 1. After the reaction, the organic phase and the catalyst powder were separated by centrifugation. A colorless organic phase was obtained by decantation and the catalyst powder was reused in the next run. The rhodium content in the organic phase was under detectable level by the AAS (atomic adsorption spectroscopy). The results showed that the SILPC catalyst was active for at least eleven times without significant loss in the catalytic performance.

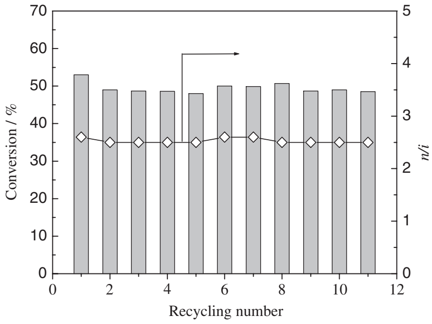


Figure 1. The recycling results of 1-hexene hydroformylation over catalysts TMGL–TPPTS–Rh/MCM-41. TMGL loading = 10 wt %, Rh loading = 0.8 wt % based on silicas, TPPTS/Rh = 5 (molar ratio).

Therefore, the SILPC by immobilization of water-soluble TPPTS–Rh complex dissolved in the TMGL onto MCM-41 showed better hydroformylation performance of 1-hexene, which was ascribed to the combination of the large surface area and uniform mesopore structure of MCM-41, as well as the property of IL. The preparation for the SILPC is relatively simple and the catalyst thus obtained is robust and reusable. The halogen free of TMGL makes it promising in the production of high-valued fine chemicals.

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