Lengthening alkyl spacers to increase SBA-15-anchored Rh–P complex activities in 1-octene hydroformylation†

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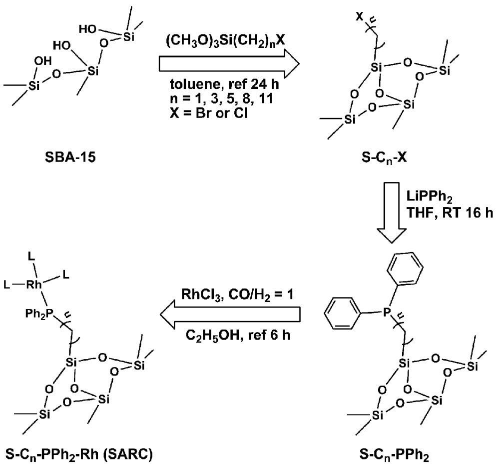
The alkyl spacer was lengthened in heterogenizing a Rh–P complex into mesoporous silicate SBA-15 to increase the immobilized catalyst activities in 1-octene hydroformylation.

Heterogenization[1] of organometallic catalysts into mesoporous molecular sieves has been so far extensively studied. In traditional immobilized catalysts, the metal is stiffly anchored to the support through short organic groups[2,3] as *spacers*.[4] Although the difficulty in catalyst separation has been hence overcome, the immobilized catalysts usually reveal decreased activities than homogeneous counterparts.[2,3] In heterogeneous cases, active sites are localized; reactant molecules are supposed to approach to the solid surface, to be adsorbed by the active site, and then to be activated. Mass transfer thus greatly affects the reaction efficiency. The inner diffusion of substrates in the pores will influence the catalyst activities. Employing immobilized ionic liquid where catalytic complex is dissolved[5] may help to construct a homogenous-like surroundings. The active species leaching is however significant, since the catalyst is actually not bonded.

The present work is motivated by observing the differences between a pinwheel and a flying kite. Imagine that the vane or the kite is the anchored catalyst, and the stick or the rope is the spacer. A bird is imagined as the substrate. In case of the pinwheel, the vanes are immobile owing to the rigid stick. The bird has to fly to it in a specific direction. However, when a kite is flown in the sky through a long rope, the kite is relatively free on account of the flexibility of the rope. The kite has various orientations and covers a wider range, which offers more possibilities for the bird to contact it. Enlightened by this, we took advantage of the flexibility of alkyl spacers to anchor the Rh–P complex into mesoporous SBA-15. *n*-Alkyl chains with different length (C_1, C_3, C_5, C_8 and C_{11}) were used as the spacer functions and the SBA-15-anchored Rh–P complexes (hereafter SARC) catalysts were employed in 1-octene hydroformylation[6] to produce nonyl aldehydes.

As shown in Scheme 1, synthesis of SBA-15, haloalkylation, phosphine ligand connection, and Rh coordination were sequentially carried out to prepare SARC catalysts using precursor $RhCl_3$ (see ESI† for details).



Scheme 1 Preparation of the SARC catalysts.

TEM micrographs of the parent SBA-15 showed very ordered honeycomb-like pores (Fig. E2, ESI†). XRD patterns (Fig. E3, ESI†) reveal that all SARC catalysts have typical hexagonal SBA-15 symmetry. The support structure was preserved.

The catalyst preparation was evidenced by IR.[7] Fig. 1 shows the IR spectra of samples with spacer C_8. Bands ν_{as}(C–H) at 2933 cm^{-1}, ν_s(C–H) at 2878 cm^{-1} and ρ(–CH_n–) at 1457, 1375, 1350, 1296 cm^{-1} in P123-bearing SBA-15 (a) disappeared after calcination (b), indicating the template removal. These C–H absorptions reappeared in chlorooctylated SBA-15 (c). In addition, ν(C–Si) at 725 and 687 cm^{-1}, ν(C–Cl) at 658 cm^{-1} were observed. The peak at 955 cm^{-1} was obviously weakened after the grafting of silane, implying the modifiable silanols[8] were decreased. After the connection of diphenyl phosphine ligands (d), ν(C–Cl) disappeared, and ν(C–Si) intensity was increased. ν(C–P) was observed at 741 cm^{-1}. A broad band characteristic of ν(Ar C=C), which might be composed of several peaks, was observed at 1512 cm^{-1} with p–π conjunction amplifying this band. A tiny absorption was found at 3073 cm^{-1}, which could be assigned to the overtone contributed by ν(Ar C–H) and ν(Ar C=C) of single-substituted benzene. After the anchoring of $RhCl_3$ (e), the ν(Ar C=C) was weakened due to the electron-withdrawing nature of the cation whereas ν(Ar C–H) was enhanced and observed. This indicates the interaction between phosphine ligands and rhodium; ν(C=O) was found at 1969 cm^{-1} (see inset). The stretching of Si–O–Si in the range 1290–996 cm^{-1} and δ(Si–O–Si) at 467 cm^{-1} were unchanged through the SARC catalyst preparation, indicating the SBA-15 framework was not affected. SARC catalysts prepared by other alkyl spacers revealed similar IR spectra.

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† Electronic supplementary information (ESI) available: SARC catalyst preparation, characterization, 1-octene hydroformylation, Rh leaching, and other Rh precursor results. See DOI: 10.1039/b812910j

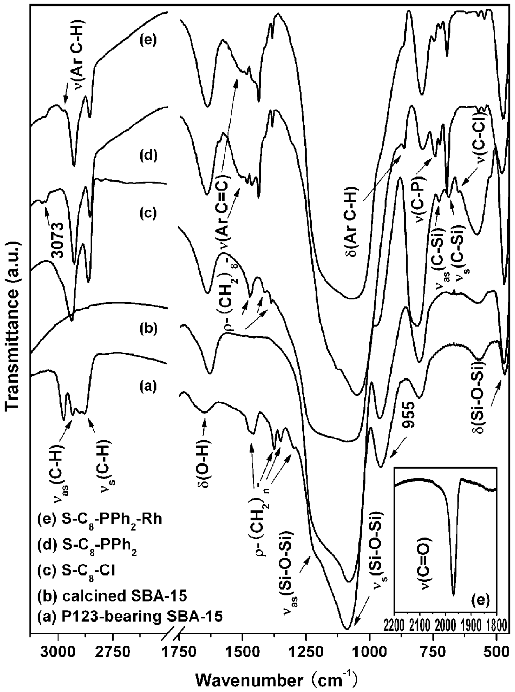


Fig. 1 IR spectra monitoring of SARC catalyst preparation (C_8).

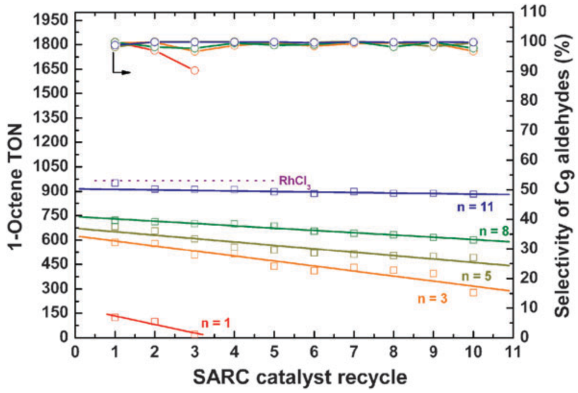


Fig. 2 1-Octene hydroformylation over the SARC catalysts (precursor $RhCl_3$): (☐) 1-octene TON, (○) selectivity of nonyl aldehydes. TON (turnover number) = mol converted 1-octene/immobilized Rh.

N_2 sorption analysis (Fig. E4, ESI†) of the SARC catalysts revealed typical type IV isotherms with H1 hysteresis loop.[9] The pore size distribution was narrow. This indicates all the SARC catalysts maintained ordered mesoporous structure. Textual properties and immobilized Rh contents of SARC catalysts are listed in Table 1.

1-Octene hydroformylation was carried out in an autoclave (reaction temperature 393 K, initial syngas (CO/H_2 = 1) pressure 5 MPa, reaction time 2.5 h, see ESI†). Reaction catalyzed by $RhCl_3$ was also performed. As is shown in Fig. 2, the TON revealed by the SARC catalysts increased with the spacer length. SARC catalyst with spacer C_{11} showed comparable activity to the homogeneous process. SARC catalyst with shortest spacer C_1 showed lowest TON level. All SARC catalysts revealed high selectivity to nonyl aldehydes (>97%). On the contrary, $RhCl_3$ showed a selectivity of only 91%. The high selectivity revealed by SARC catalysts might be attributed to their confining by the mesoporous molecular sieves. By-products (discussed later) were restricted in the pores, and in the liquid they were of low concentration. The ratio of linear and branched nonyl aldehyde is 0.72 (C_1), 0.68 (C_3), 0.57 (C_5), 0.56 (C_8), and 0.53 (C_{11}). Smaller pores seem to favor formation of the linear product. This might because carbonyl is more easily added to the β position of 1-octene owing to the steric hindrance of the adjacent spacers.

SARC catalyst (precursor $RhCl_3$) with spacer C_{11} showed lower activity than $RhCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$ complexes in 1-octene hydroformylation (Table E1, ESI†). However, if these more active Rh precursors are anchored to $S–C_{11}–PPh_2$, the immobilized catalyst also reveals comparable activity to the corresponding homogeneous counterpart. Moreover, the selectivity is higher. If less active precursor $[Rh(Ac)_2]_2$ is employed, the immobilized catalyst showed lower activity as well (Table E1, ESI†).

Fig. E5 (ESI†) showed Rh leaching in the reaction liquid after every SARC catalyst recycle. Sum Rh leaching on

Table 1 Textual properties and Rh contents of SARC catalysts

	a_0[a]/ nm	S_{BET}/ $m^2\ g^{-1}$	D_{BJH}/ nm	V_P/ $cm^3\ g^{-1}$	T_W/ nm	Rh[b] (wt%)
SBA-15	10.96	673	6.2	0.75	4.8	—
$S–C_1–PPh_2–Rh$	10.20	208	5.2	0.33	5.0	0.7
$S–C_3–PPh_2–Rh$	11.21	283	3.7	0.34	7.5	1.5
$S–C_5–PPh_2–Rh$	10.41	242	3.6	0.29	6.8	1.2
$S–C_8–PPh_2–Rh$	10.20	199	3.5	0.30	6.7	1.0
$S–C_{11}–PPh_2–Rh$	10.30	255	3.2	0.32	7.1	0.9

[a] Calculated by $a_0 = (2/\sqrt{3})d_{100}$. S_{BET} = BET specific surface area; D_{BJH} = BJH primary pore diameter; V_P = single-point total pore volume; T_W = hexagonal phase wall thickness ($a_0 - D_{BJH}$). [b] Immobilized Rh contents were determined by ICP-AES analysis.

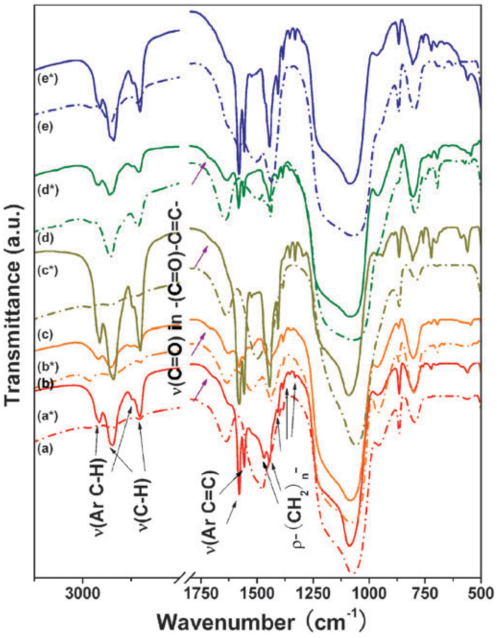
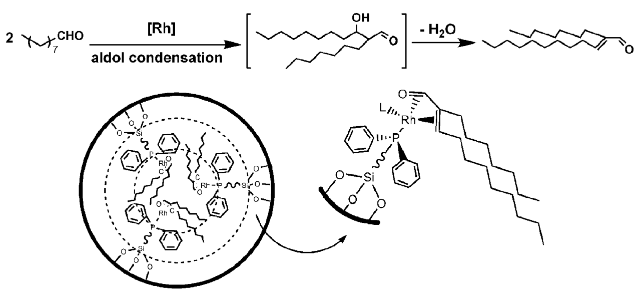


Fig. 3 IR spectra of fresh and recycled SARC catalysts. Spacer n = 1 (a, a*), 3 (b, b*), 5 (c, c*), 8 (d, d*), 11 (e, e*). Fresh catalysts shown as dash-dot lines and recycled ones labeled with asterisks (*).



Scheme 2 The dehydrated product of the aldol condensation adduct coordinates with Rh so as to poison it.

recycling was less than 3% for all catalysts and the leached Rh might originate from the external surface[2] of SBA-15. Fig. 2 reveals that SARC catalyst with shorter alkyl spacers showed more significant activity decrease upon recycling and S–C$_1$–PPh$_2$–Rh was only recycled three times as the third TON sharply decreased to 16% of its initial value. However, S–C$_{11}$–PPh$_2$–Rh revealed a relatively stable activity. The tenth TON was 93% of its initial value. Clearly, Rh leaching does not account for the SARC catalyst activity decrease.

To investigate the reasons for catalyst activity decrease, IR was performed on recycled catalysts (S–C$_1$–PPh$_2$–Rh 3 runs; others 10 runs). In Fig. 3, ν(alkyl C–H), ν(Ar C=C), ν(C–Si), and ν(C–P) were obviously enhanced after SARC catalyst recycles. ν(Ar C–H) was found as a shoulder peak on ν(alkyl C–H). In the range 1530–1320 cm^{-1}, a series of absorptions was observed as the fingerprint of oligomeric alkane rocking. No coordinated carbonyl was found. A peak located at *ca.* 1705 cm^{-1} appearing as shoulder peak on δ(O–H), was observed. This peak could be assigned to the ν(C=O) in the –(C=O)–C=C– structure.[7] This means an α,β-unsaturated species existed in the recycled catalyst. The aldol condensation is regarded as the side reaction of olefin hydroformylation.[6] The dehydrated product of the aldol condensation adduct is an acyclic α,β-unsaturated compound. On the basis of the literature and the IR spectra, we assume an 18-carbon α,β-unsaturated aldehyde, the dehydration product of the aldol condensation adduct of nonyl aldehydes, was produced and coordinated with Rh (Scheme 2). It was also detected by GC-MS in the liquid. The phosphorus p electrons, phenyl π electrons, π electrons from C=C and C=O in the α,β-unsaturated aldehyde, and rhodium d electrons together led to a strong conjugation. The conjugation should enhance all the stretching vibrations as observed. The stably coordinated α,β-unsaturated aldehyde was difficult to release during the catalytic process, and thus SARC catalysts were poisoned. All SARC catalysts have mesopores (Table 1), and mass transfer is therefore eliminated. It is shown, however, the dimer of nonyl aldehydes was not efficiently diffused out of the pores. Molecular sieve-based catalysts are superior in polymerization,[10] which is probably attributable to the confining of porous materials and their high adsorption capacity. The by-product coordinated with Rh in SARC catalysts and showed only a low concentration in liquids. When a longer spacer was employed, the pore size was smaller. The terminal active sites (Scheme 2) were confined into a smaller central circle, which disfavored the long linear aldehyde coordination owing to the steric hindrance. SARC catalyst with spacer C$_{11}$ showed no obvious activity decrease during the catalyst recycles, and no ν(C=O) in the –(C=O)–C=C– was observed (Fig. 3e*). However, when a shorter spacer was involved, the active sites were confined within in a larger circle and the immobilized Rh–P complexes maintained a relatively longer distance with each other, which favored the by-product coordination and such complexes were inert towards hydroformylation.

^{13}C CP-MAS NMR spectra (Fig. E6, ESI†, C$_3$ shown for example) of recycled SARC catalysts revealed a carbon signal from C=O in the α,β-unsaturated aldehyde at 185.8 ppm, while the coordinated carbonyl of fresh catalyst gave the signal at 179.9 ppm. The phenyl gave a resonance at 126.8 ppm (fresh) and 129.1 ppm (recycled). This difference may arise from C=C in the unsaturated aldehyde. In addition, the recycled catalyst gave more resonance peaks characteristic of alkyls, indicating the long chain of the dehydrated product.

In conclusion, Rh–P complex (using precursor RhCl$_3$) was anchored to SBA-15 through linear alkyls with different length (C$_1$, C$_3$, C$_5$, C$_8$ and C$_{11}$, respectively) as spacers. The prepared SARC catalysts reveal remarkable selectivity of nonyl aldehydes in 1-octene hydroformylation, satisfying low metal loss, and several catalyst runs. The catalyst activity in 1-octene hydroformylation increases with the increasing length of alkyl spacer. SARC catalyst prepared by longest alkyl C$_{11}$ as connecting spacer shows highest TON comparable to the homogeneous process. SARC catalyst activity can be further promoted by choosing a more active rhodium precursor (*e.g.* RhCl(CO)(PPh$_3$)$_2$ or RhCl(PPh$_3$)$_3$) anchoring through spacer C$_{11}$. Furthermore, SARC catalyst with Rh immobilized through spacer C$_{11}$ reveals stable activity during the catalyst recycling. A 18-carbon α,β-unsaturated aldehyde formed by the dehydration of the aldol condensation adduct may stably chelate with Rh owing to the high degree of conjugation, which is inert towards 1-octene hydroformylation. Longer spacers helped the SARC catalyst maintain the activity since the coordination of the linear long aldehyde was disfavored by steric hindrance.

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