

Dynamic Release–Immobilization of a Homogeneous Rhodium Hydroformylation Catalyst by a Polyoxometalate Metal–Organic Framework Composite

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Thermal treatment of phosphotungstic acid (PTA)-MIL-101(Cr) composites in the presence of hydroformylation catalyst RhH(CO)(PPh₃)₃ leads to immobilization of the homogeneous Rh complex within the metal–organic framework (MOF) scaffold by coordination of PTA-Rh. The Rh complex-containing MOFs are tested in the hydroformylation of 1-octene in which PTA competes with CO during ligand association. In the presence of the carbonyl ligand, the Rh complex is released from the MOF and behaves as a homogeneous catalyst. Therefore, the product spectra and selectivities of the Rh complex-containing MOFs are similar to those of RhH(CO)(PPh₃)₃. Upon CO evacuation, Rh recoordinates to PTA, allowing for easy recycling of this new pseudo-heterogeneous catalyst.

The hydroformylation reaction is largely applied in industry to the production of aldehydes and other bulk chemical platforms.^[1] Although the state-of-the-art reaction is homogeneously catalyzed, many attempts have been made to immobilize organometallic complexes for heterogeneous processes. To this end, various organic and inorganic materials (e.g., SiO₂, Al₂O₃, polymers, activated carbon, and zeolites) have been studied and functionalized in many ways.^[2] Although promising examples are reported with respect to catalyst performance and recyclability, metal leaching is a common challenge to overcome in these systems. Moreover, dynamics of the complex in terms of ligand dissociation–association and flexibility may be affected upon immobilization.^[3]

Metal-organic frameworks (MOFs) hold unbeatable internal volumes and adsorption capacities. Moreover, they can be utilized as catalysts by various approaches, one being the use of their empty space, often referred to as encapsulation.^[4] Already, a few examples have been reported in the literature on the utilization of MOFs as hydroformylation catalysts.^[5] Encapsulation is more feasible in cage-type structures such as the

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MIL-101 family.^[6] MIL-101(Cr) is a stable MOF that consists of approximately 30 Å diameter cavities with openings of 12 and 16 Å.^[7] Polyoxometalate MOF composites based on MIL-101 have already been synthesized and used in catalysis.^[6,8]

Polyoxometalates are known to act as mild coordinating ligands in homogeneous catalysis, with a coordination strength lower than that of CO.^[9] Therefore, use of a phosphotungstic acid (PTA)-MOF composite is considered for the dynamic coordination of the RhH(CO)(PPh₃)₃ hydroformylation catalyst. Indeed, the objective of this study, rather than immobilization in its conventional sense, is to utilize MOFs as scaffolds for handling and recycling the Rh-based hydroformylation catalyst and to control its release in the reaction environment by CO coordination: in the absence of CO the catalysts would stay coordinated to the PTA-MOF solid but, at high CO pressure, the homogenous complex would detach from the MOF. Removal of CO from the environment should result in recoordination of the catalyst to the PTA-MOF composite and enable recycling.

MIL-101(Cr) was prepared by hydrothermal synthesis. Two PTA-MIL-101(Cr) composites were synthesized according to the approach reported by Juan-Alcañiz et al. (Table 1).^[8a] 70–75%

Table 1. Textural and chemical properties of MIL-101(Cr) and PTA-MIL- 101(Cr) composites.						
Sample	$S^{[a]}$	<i>V</i> [r	n ³ g ⁻¹]	PTA ^[d]		
	[m ² g ⁻¹]	total ^[b]	micro ^[c]	[wt %]		
MIL-101(Cr)	2750	1.31	1.09	n.a. ^[e]		
15 PTA@MIL-101(Cr)	2100	0.95	0.82	15		
30 PTA@MIL-101(Cr)	1970	0.94	0.76	30		
[a] BET surface area	calculated bet	ween relative	pressures of	of 0.05 and		

0.15; [b] Total pore volume calculated at 0.95 relative pressures of 0.05 and 0.15; [b] Total pore volume calculated at 0.95 relative pressure; [c] Micropore volume obtained from the *t* plot applied to the N₂ isotherm; [d] PTA loading calculated based on wt % W, obtained from inductively coupled plasma optical emission spectrometry; [e] Not applicable.

of surface area and the pore volume of MIL-101(Cr) were preserved after PTA introduction (Table 1 and Figure S3). XRD analysis confirmed the crystalline structure of MIL-101 (Figure S4). Furthermore, the morphology of all samples was similar, as observed in SEM micrographs (Figure S5). Energy-dispersive X-ray spectroscopic mapping illustrated the homogeneous distribution of W in *n* PTA@MIL-101(Cr) (Figure S6; n = wt% PTA). As demonstrated previously^[8, 10] and in line with these characterization results, the employed synthesis approach led to a molec-



ular distribution of Keggin units within the cavities of *n* PTA@-MIL-101(Cr).

To immobilize RhH(CO)(PPh₃)₃ within the cavities of PTA-containing MIL-101(Cr), 15 PTA@MIL-101(Cr) and 30 PTA@MIL-101(Cr) were heated in solutions of approximately 0.5×10^{-3} and 1.5×10^{-3} M RhH(CO)(PPh₃)₃ in toluene, respectively, at 343 K. After filtration, weakly adsorbed Rh complex was removed from the MOFs by two successive washing steps at the same temperature. The RhH(CO)(PPh₃)₃ solution had a yellowish color, characteristic of a Rh-PPh₃ complex, as shown in Figure S1a. Although heating the solution at 343 K for 18 h did not affect its appearance (not shown), it became colorless after similar treatment in the presence of nPTA@MIL-101(Cr) and filtration (Figure S1b). Inductively coupled plasma optical emission spectrometry revealed 0.25 and 0.88 wt% Rh in Rh-15 PTA@MIL-101(Cr) and Rh-30 PTA@MIL-101(Cr), respectively. These values indicated full uptake from the precursor solutions. The above-mentioned procedure led to 1.10 wt% Rh in Rh@MIL-101(Cr).

Diffuse-reflectance infrared Fourier transform (DRIFT) spectra of MIL-101(Cr), n PTA@MIL-101(Cr), Rh-n PTA@MIL-101(Cr), and RhH(CO)(PPh₃)₃ are shown in Figure 1. Characteristic IR vibra-



Figure 1. DRIFT spectra of MIL-101(Cr) (1), Rh@MIL-101(Cr) (2), 15 PTA@MIL-101(Cr) (3), Rh-15 PTA@MIL-101(Cr) (4), 30 PTA@MIL-101(Cr) (5), Rh-30 PTA@MIL-101(Cr) (6), and RhH(CO)(PPh₃)₃ (7). Samples 1, 3, and 5 were treated at 473 K in a He atmosphere prior to collection of the DRIFT spectra at RT.

tional bands associated with PTA (e.g., 1083 cm^{-1} , assigned to P–O) and the Rh complex (1119 and 1973 cm⁻¹) are clearly visible in samples containing these elements. In the case of Rh-15 PTA@MIL-101(Cr), the band at 1973 cm⁻¹ is hardly visible, attributed to the low Rh loading of this sample. On the other hand, MIL-101(Cr) bands at 1020 and 1163 cm⁻¹, assigned to the Cr–O vibration, are detected for all samples, indicating conservation of the MOF structure.

1-Octene conversion ($X_{1-octene}$) and selectivities towards major reaction products are presented in Figures 2 and S7, Table 2.



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Figure 2. $X_{1-\text{octene}}$ and product selectivities towards olefinic C8 isomers, nonanal (l-aldehyde), and branched (b)-aldehyde(s) vs. reaction time with RhH(CO)(PPh₃)₃ catalyst. Reaction conditions: T=343 K, p=40 bar gauge pressure, H₂/CO molar ratio = 1, $V_{\text{toluene}} = 14 \text{ cm}^3$, $V_{1-\text{octene}} = 6 \text{ cm}^3$, $n_{1-\text{octe-}}$ $_{ne} = 38.2$ mmol, 1-octene/Rh = 9.9×10^3 mol mol⁻¹, and agitation speed = 1000 rpm.

Under the conditions applied to the homogeneous system, $X_{1-\text{octene}}$ reaches 100% after 4 h in absence of the MOF (Figure 2). The major reaction products are olefinic C8 isomers, nonanal, 1-methyloctanal, and other branched C9 aldehydes.

After full conversion of the substrate, olefinic C8 isomers convert into branched aldehydes. Therefore, with long reaction times (Figure 2) and/or higher RhH(CO)(PPh₃)₃ concentrations (Figure S7), the linear-to-branched aldehyde ratio decreases. The initial linear-to-branched aldehyde ratio with RhH(CO)(PPh₃)₃ is 2.4–2.5, within the range reported for this catalyst if no excess PPh₃ ligand is added to the reaction mixture.^[9d, 11] The product spectra and selectivities of Rh-nPTA@-MIL-101(Cr) are very similar to those of RhH(CO)(PPh₃)₃ at isoconversion conditions (entries 1 vs. 11 and 3 vs. 13, Table 2, for Rh-30 PTA@MIL-101(Cr) and RhH(CO)(PPh₃)₃, respectively). Recovery of Rh-nPTA@MIL-101(Cr) after the first reaction run and its reuse in a second cycle involves no significant loss of activity or change in selectivity (entries 7 and 8 for Rh-15 PTA@MIL-101(Cr) and entries 11 and 12 for Rh-30PTA@MIL-101(Cr)). However, the reaction mixture, which was initially colorless, turned slightly yellowish after the first run. This color change, in addition to a product spectrum identical to that of RhH(CO)(PPh₃)₃, pointed to leaching of the Rh complex during the course of reaction. To verify this, the filtrate after separation of the used Rh-15 PTA@MIL-101(Cr) (entry 7) was subjected to hydroformylation reaction conditions similar to those in the first run. Such a hot filtration experiment led to further conversion of 1-octene (15%, entry 9).

It is well known that hydroformylation is initiated by ligand dissociation.^[3] In this case, PTA that is primarily coordinated to Rh dissociates from the metal and must compete with CO for ligand association in the reaction cycle. As Rh-carbonyl coordination is stronger, the Rh complex may be released from the MOF after coordination with CO. Once CO is evacuated from the reaction medium, the Rh complex recoordinates to the PTA. This situation is feasible at the process termination step



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Entry Catalytic system 1-octene/Rh [10 ³ mol mol ⁻¹] Reuse [cycle no.] $X_{1-octene}$ [%] 1 RhH(CO)(PPh_3)_3 17.4 - 30 41 36 2 RhH(CO)(PPh_3)_3 9.8 - 58 39 38 3 RhH(CO)(PPh_3)_3 8.7 - 66 40 38 4 RhH(CO)(PPh_3)_3 5.0 - 99 31 41 5 Rh@MIL101(Cr) 4.4 1 37 5 61 6 Pb@MIL101(Cr) 4.4 2 4 n d ^[f] n d ^[f] n d ^[f]	Table 2. Hydroformylation of 1-octene with different catalytic systems. ^[a]							
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	S [%] //							
$ \begin{array}{ c c c c c c c } \hline 1 & RhH(CO)(PPh_3)_3 & 17.4 & - & 30 & 41 & 36 \\ \hline 2 & RhH(CO)(PPh_3)_3 & 9.8 & - & 58 & 39 & 38 \\ \hline 3 & RhH(CO)(PPh_3)_3 & 8.7 & - & 66 & 40 & 38 \\ \hline 4 & RhH(CO)(PPh_3)_3 & 5.0 & - & 99 & 31 & 41 \\ \hline 5 & Rh@MIL101(Cr) & 4.4 & 1 & 37 & 5 & 61 \\ \hline 6 & Rh@MIL101(Cr) & 4.4 & - & a & a & a & a & a & a & a & a & a$	yde ^[c] b-aldehyde(s) ^[d]							
2 RhH(CO)(PPh_3)_3 9.8 - 58 39 38 3 RhH(CO)(PPh_3)_3 8.7 - 66 40 38 4 RhH(CO)(PPh_3)_3 5.0 - 99 31 41 5 Rh@MIL101(Cr) 4.4 1 37 5 61 6 Ph@MIL101(Cr) 4.4 2 4 nd ^{III} nd ^{III}	15 2.5							
3 RhH(CO)(PPh_3)_3 8.7 - 66 40 38 4 RhH(CO)(PPh_3)_3 5.0 - 99 31 41 5 Rh@MIL101(Cr) 4.4 1 37 5 61 6 Pb@MUL101(Cr) 4.4 2 4 ndth ndth	15 2.5							
4 RhH(CO)(PPh_3)_3 5.0 - 99 31 41 5 Rh@MIL101(Cr) 4.4 1 37 5 61 6 Rh@MIL101(Cr) 4.4 2 4 $n d^{ }$ $n d^{ }$	15 2.5							
5 Rh@MIL101(Cr) 4.4 1 37 5 61	19 2.2							
6 Pb@MU101(Cr) 44 2 4 pd ^[f] pd	22 2.7							
6 KINEWILLIUT(CI) 4.4 2 4 H.d. 1.d.	n.d. n.d.							
7 Rh-15 PTA@MIL-101(Cr) 9.7 1 20 40 33	14 2.4							
8 Rh-15 PTA@MIL-101(Cr) 9.7 2 24 43 38	16 2.4							
9 filtrate after 1st run ^(g) n.d. n.a. ^(h) 15 52 40	16 2.4							
10 filtrate after 1st run ⁽ⁱ⁾ n.d. n.a. 3 51 34	14 2.1							
11 Rh-30 PTA@MIL-101(Cr) 5.6 1 34 43 40	17 2.4							
12 Rh-30 PTA@MIL-101(Cr) 5.6 2 32 40 36	15 2.4							
13 Rh-30 PTA@MIL-101(Cr) 2.8 – 70 37 43	17 2.6							
14 Rh-30 PTA@MIL-101(Cr) 2.9 1 69 40 37	15 2.5							
15 Rh-30 PTA@MIL-101(Cr) 2.9 2 70 54 25	11 2.3							
16 Rh-30 PTA@MIL-101(Cr) 2.9 3 71 50 26	11 2.3							
17 Rh-30 PTA@MIL-101(Cr) 2.9 4 67 51 28	12 2.3							
18 Rh-30 PTA@MIL-101(Cr) 2.9 5 63 46 30	13 2.3							
19 Rh-30 PTA@MIL-101(Cr) 2.9 6 65 43 30	13 2.3							

[a] Reaction conditions: T = 343 K, p = 40 bar, t = 2 h, H_2/CO molar ratio = 1, $V_{toluene} = 14$ cm³, $V_{1-octene} = 6$ cm³, $n_{1-octene} = 38.2$ mmol, and agitation speed = 1000 rpm. [b] Olefinic C8 isomers; [c] Nonanal; [d] Branched aldehyde(s); [e] Linear-to-branched aldehyde ratio; [f] Not determined; [g] Before treating the used MOF in the reaction mixture at 343 K for 18 h in an inert atmosphere (see the Experimental Section); [h] Not applicable; [i] After treating the used MOF in the reaction mixture at 343 K for 18 h in an inert atmosphere (see the Experimental Section).

by substitution of syngas with inert gas. Moreover, complex immobilization by nPTA@MIL-101(Cr) can be promoted by reheating the system at 343 K, immediately after the hydroformylation reaction in the same reactor. After such a process termination protocol (see the Experimental Section), the filtrate after catalyst separation becomes colorless and gives negligible conversion upon exposure to hydroformylation reaction conditions (entry 10, Table 2). To further confirm this hypothesis, Rh-30PTA@MIL-101(Cr) catalyst was tested in successive hydroformylation reactions (entries 14-19 and Figure 3). Although the regioselectivity decreased slightly after the first cycle, both conversion and selectivity remained constant after at least six reutilizations of the catalyst. These results indicated that the Rh complex was recoordinated to the PTA after each hydroformylation reaction and CO evacuation, proving the recyclability of this Rh complex-containing MOF.

Heteropolyacids are known to coordinate to Rh by their terminal O atoms and thus can be employed as ligands for hydroformylation catalysts.^[9] To further confirm that PTA acts as an anchoring agent for complex immobilization in the PTA-MOF composite, Rh@MIL-101(Cr) was studied in the hydroformylation reaction.

Compared to other systems, selectivity towards olefinic C8 isomers over Rh@MIL-101(Cr) is lower by a factor of 10 (entry 5, Table 2). In spite of this improvement, which already points to electronic modifications of Rh, conversion drops dramatically from 37% in the first reaction run to less than 5% on reuse of Rh@MIL-101(Cr) in the second cycle (entries 5 and 6, respectively). Therefore, the Rh complex is not strongly anchored in MIL-101(Cr) if PTA is absent. Notably, 1-octene is converted in blank runs over neither MIL-101(Cr) nor nPTA@MIL-



Figure 3. $X_{1-\text{octene}}$ and product selectivities towards olefinic C8 isomers, nonanal (l-aldehyde), and (b)-branched aldehyde(s) vs. number of cycles with Rh-30 PTA@MIL-101(Cr) catalyst. Reaction conditions: T = 343 K, p = 40 bar, t = 2 h, H₂/CO molar ratio = 1, $n_{1-\text{octene}} = 38.2$ mmol, 1-octene/ Rh = 2.9×10^3 mol mol⁻¹, and agitation speed = 1000 rpm.

101(Cr) (entries 1–3, Table S1). At similar 1-octene/Rh ratios, $X_{1-octene}$ is lower with Rh-*n* PTA@MIL-101(Cr) than with RhH(CO)(PPh₃)₃ (entries 2 and 7, Table 2, respectively).

On the other hand, addition of MIL-101(Cr) or $Cr(NO_3)_3$ to the reaction mixture with RhH(CO)(PPh_3)_3 results in the loss of catalytic activity (the effect of $Cr(NO_3)_3$ addition is much stronger; entries 4 and 5, Table S1 and entry 4, Table 2). Approximately one third of Cr atoms in MIL-101(Cr) are unsaturated. Hence, it is speculated that unsaturated Cr sites are responsible for lowering $X_{1-octene}$ if Rh complex-containing MIL-101 is used. Due to interactions with the W–O moiety, the concentra-



tion of such free Cr sites decreases in PTA-MOF composites. Indeed, the 1-octene turnover number $[mol_{1-octene} mol_{Rh}^{-1}]$ for Rh@MIL-101(Cr) is lower than those obtained for Rh-15PTA@MIL-101(Cr) and Rh-30PTA@MIL-101(Cr) (1.6 vs. 1.9 10³ mol_{1-octene} mol_{Rh}^{-1}, respectively, entries 5, 7, and 11, Table 2). These results further indicate that, although mobile, the Rh complex closely interacts with the MOF structure.

Thermogravimetric analysis shows that both MIL-101(Cr) and PTA-MOF composites are thermally stable up to 600 K (Figure S8), which is much higher than the typical hydroformylation reaction temperatures of 333–473 K. Comparing the XRD pattern of MIL-101(Cr) after 2 h exposure to the reaction environment with that after 24 h shows no changes in the MOF pattern (Figure 4).



Figure 4. XRD patterns (CoK_a) of MIL-101(Cr) and Rh-15 PTA@MIL-101(Cr) after use in hydroformylation experiments for different durations. Reaction conditions: T = 343 K, p = 40 bar gauge pressure (MIL-101(Cr)) or 15 bar gauge pressure (Rh-15 PTA@MIL-101(Cr)), H₂/CO molar ratio = 1, $V_{\text{toluene}} = 14 \text{ cm}^3$, $V_{\text{1-octene}} = 6 \text{ cm}^3$, m = 0.08 g (MIL-101(Cr)) or 0.16 g (Rh-15 PTA@MIL-101(Cr)), and agitation speed = 1000 rpm.

In summary, the phosphotungstic acid-MIL-101(Cr) composite is thermally and chemically stable in a hydroformylation reaction environment. Phosphotungstic acid coordinates to Rh as a ligand and is used as an anchoring agent for complex immobilization in the PTA-MOF composite. In the course of hydroformylation, CO competes with phosphotungstic acid, thus, the Rh complex is released from the metal–organic framework and behaves as a homogeneous catalyst. Once CO is removed from the reaction environment, Rh recoordinates to phosphotungstic acid and reallocates relocates within the metal–organic framework cavities, allowing easy recycling of the homogeneous catalyst. This new approach for the controlled release and immobilization of organometallic complexes allows the full recycling of homogeneous catalysts and enables the use of related composites in other catalytic applications.

Experimental Section

MIL-101(Cr) was prepared by hydrothermal synthesis: Cr(NO₃)₃·9H₂O (1.63 g) and terephthalic acid (0.7 g) were dissolved in distilled H₂O (20 g) inside an autoclave Teflon liner Teflon-lined autoclave. Acid concentration HF_(aq) (0.15 g) was added to the mixture. (Warning: Special precautions must be taken on handling

HF_(aq); see the MSDS.) The autoclave was then heated to 493 K over 0.75 h and kept at this temperature for 8 h in an oven under rotary conditions. After cooling to RT, the crystallized product was filtered and washed overnight with boiling ethanol (96%) under reflux. The powder was then filtered and dried overnight at 433 K under static air conditions. The synthesis yield was approximately 30%. PTA-MIL-101(Cr) composites were synthesized by following the above procedure, except that PTA (0.2 or 0.4 g) was added to the mixture with Cr(NO₃)₃·9H₂O and terephthalic acid. PTA-MIL-101(Cr) composites were denoted nPTA@MIL-101(Cr), in which n indicates wt% PTA. For the immobilization of the hydroformylation catalyst, RhH(CO)(PPh₃)₃ (0.02 g) and 15 PTA@MIL-101(Cr) (0.5 g) or RhH(CO)(PPh₃)₃ (0.055 g) and 30 PTA@MIL-101(Cr) (0.5 g) were mixed with toluene (40 cm³) inside an autoclave Teflon liner Teflonlined autoclave. The autoclave was heated at 343 K for 18 h in an oven under rotary conditions. The mixture was then filtered through a cannula, mixed with 1-octene/toluene (3:10, 40 cm³) inside the autoclave, and heated at 343 K for 18 h in the rotary oven for washing. The washing step was repeated twice to remove the weakly adsorbed Rh complex, with pure toluene used in the second step (Figure S1). The powder was then filtered and dried at 343 K in an Ar atmosphere. To avoid exposure to air, RhH(CO)(PPh₃)₃-containing samples and solutions were handled in a glove box during the whole procedure unless isolated from the environment by means of a sealed autoclave or flask. Rh complexcontaining MOFs were denoted Rh-nPTA@MIL-101(Cr), in which n indicates wt % PTA in the MOF before complex immobilization. For comparison, the above procedure was repeated with $RhH(CO)(PPh_3)_3$ (0.055 g) and MIL-101(Cr) (0.5 g) and this sample denoted Rh@MIL-101(Cr).

Hydroformylation experiments were performed in a Parr 5000 Multi Reactor Stirrer System under constant syngas pressure (semi-batch conditions). The reaction vessels (autoclaves) had a volume of 45 cm³ and stirring was performed by suspended magnetic bars to avoid grinding the catalyst particles (Figure S2a). Autoclaves were transferred to the glove box and filled with toluene (14 cm³) as solvent, 1-octene (6 cm³) as substrate, and RhH(CO)(PPh₃)₃ or Rh complex-containing MOFs (0.08 or 0.16 g). The reaction medium was isolated from the environment by using a shut-off valve mounted on top of the autoclaves (Figure S2b) when disconnected from the experimental unit.

Before starting the reaction, traces of air in the opened connections were removed by consecutively pressurizing and depressurizing the system with He. Syngas was then introduced to the autoclaves by consecutively pressurizing and depressurizing the system with an equimolar mixture of H₂ and CO. Subsequently, the syngas pressure was stabilized at 40 bar gauge pressure (1 bar = 100 kPa) and autoclaves were heated to 343 K at a heating rate of 2 Kmin⁻¹ and kept at this temperature for a targeted duration. After the reaction time had elapsed, reactors were depressurized immediately, syngas was replaced by consecutively pressurizing and depressurizing the system with He, and the vessels were cooled. The autoclaves were then transferred to the glove box for GC sampling.

After liquid sampling, the autoclaves were resealed, reconnected to the experimental unit, and flushed with He. The used MOF was heated in the reaction mixture at 343 K (2 Kmin⁻¹) for 18 h under a 5 bar gauge pressure of He. Finally, the powder was separated from the solution by using a cannula in the glove box. Occasionally, the filtrate before or after the latter step was subjected to the hydroformylation reaction conditions described above. This allowed for the measurement and comparison of the homogeneous conversion of unreacted substrate before and after the final treat-



ment step. Additionally, the Rh complex-loaded MOFs were recovered and tested in successive cycles.

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