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Short Communication

Self-metathesis of methyl oleate on silica-supported Hoveyda–Grubbs catalysts

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ABSTRACT

The self-metathesis of methyl oleate (MO) to yield 9-octadecene and 9-octadecene-1,18-dioate (9-OD) was studied in liquid-phase on silica-supported Hoveyda–Grubbs complex catalysts (HG/SiO_2) containing 0.43–6.0 wt.% HG. The reaction was carried out in a batch reactor at 303–343 K and 101.3 kPa, using cyclohexane as solvent. HG/SiO_2 catalysts were active and highly selective for the MO metathesis reaction; equilibrium values of MO conversion and 9-OD yield were reached in 80 min. No catalyst leaching took place in cyclohexane. Catalysts containing HG >0.87 wt.% showed no significant deactivation after two consecutive catalytic tests.

1. Introduction

Fatty acid methyl esters (FAME) are usually obtained from the transesterification of natural oils and fats with a lower alcohol. Most of oleochemical reactions of FAME are carried out in the carboxy functions, but the synthesis of products formed by reactions of the C C bonds such as epoxidation, metathesis, ozonolisis and hydrogenation is becoming increasingly important at industrial level [1,2]. Olefin metathesis is a very powerful tool for the efficient catalytic formation of carbon–carbon double bonds allowing the synthesis of various useful intermediates and compounds for fine chemistry and for the synthesis of polymers. FAME metathesis has been studied in homogeneous catalysis using mainly Grubbs' Ru complexes [3] as recyclable catalysts. In particular, second generation ruthenium Hoveyda–Grubbs (H-G) catalysts (Fig. 1) present high activity and selectivity, and also exhibit remarkable stability to the presence of moisture and oxygen [4,5]. Nevertheless, only a limited number of industrial processes use homogeneous olefin metathesis because of the high cost of Ru complexes, the difficulties associated with removing ruthenium from the reaction media and the expensive separation/recovery steps required to obtain high-purity products. This situation turns clearly attractive the development of active and stable immobilized supported complexes that would allow straightforward catalyst separation. However, very few papers deal with the use of supported HG catalysts for the metathesis of functionalized substrates. Other than the requirements of high activity and selectivity, suitable solid catalysts for the metathesis of functionalized olefins should tolerate the presence of polar functional groups.

Several methods for immobilization of HG-type complexes have been studied [6–8], but frequently the resulting catalysts suffer from leaching or losses of activity as a result of immobilization. Recently, it has been reported that commercially available Ru–alkylidene complexes immobilized on SiO_2, MCM-41 and SBA supports can be employed without leaching in some solvents or significant activity loss for olefin metathesis reactions (ROMP, RCM, CM) [9–11]. Here, we study the self-metathesis of methyl oleate (MO) on Hoveyda–Grubbs complexes supported on commercial silica to yield 9-octadecene-1,18-dioate (9-OD) and 9-octadecene (Fig. 2). The synthesis of diesters such as 9-OD from the self- and cross-metathesis of FAME was one of the first reactions studied in oleochemistry [12] because unsaturated diesters are valuable intermediates for the production of polymers and fine chemicals [13,14]. The reaction of Fig. 2 has been studied on methyltrioxorhenium (CH_3ReO_3) and $Re_2O_7/SiO_2–Al_2O_3$ promoted with SnBu4 [15,16] but not on HG complex supported on solid supports. Our results in the present study show that silica-supported HG complexes are stable, highly active and selective catalysts for the metathesis of methyl oleate.

2. Experimental

Five HG/SiO_2 samples containing 0.43, 0.87, 1.21, 1.67 and 6.0 wt.% HG (Sigma-Aldrich, 97%) were prepared by impregnating at 298 K a commercial silica (Sigma-Aldrich G62, 230 m^2/g, 200 mesh) previously calcined 2 h at 773 K with a solution of HG in cyclohexane.

The crystalline structure of the samples was determined by X-ray diffraction (XRD) using a Shimadzu XD-D1 diffractometer and Ni-filtered

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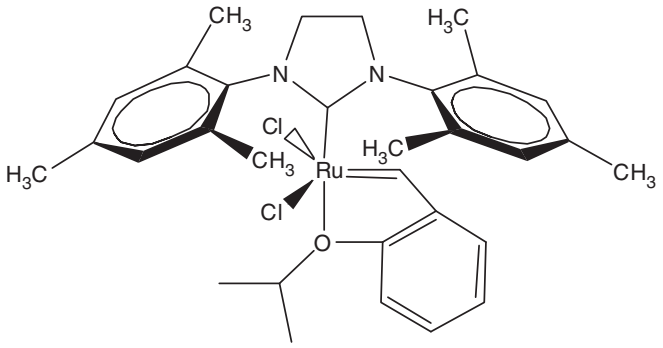

Fig. 1. Second generation ruthenium Hoveyda–Grubbs catalyst.

Cu Kα radiation. The Ru content in HG/SiO_2 samples was determined by measuring by UV–vis spectroscopy (Perkin-Elmer Lambda 20 spectrophotometer) the colorimetric difference of the HG impregnating solution, before and after impregnation.

The thermal stability of HG complex was studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Shimadzu IRPrestige-21 spectrophotometer, equipped with an in-situ high-temperature/high pressure SpectraTech cell and a liquid nitrogen-cooled MCT detector. The sample holder, a ceramic crucible containing a heating resistor and a thermocouple, was placed inside a dome with CaF_2 windows. The spectral resolution was 4 cm^{-1} and 140 scans were added. The DRIFT spectra were collected in Ar (60 ml/min). The HG(6%)/SiO_2 sample was also characterized by DRIFTS at 303 K. The spectrum of silica support was previously collected. The IR spectrum given herein for HG(6%)/SiO_2 is the difference spectrum where the SiO_2 spectrum served as the reference.

The self-metathesis of methyl oleate (Sigma-Aldrich, 99%) was carried out in a glass batch reactor under Ar atmosphere, at 101.3 kPa and temperatures between 303 and 343 K. Cyclohexane (Sigma-Aldrich, anhydrous 99.5%) previously dehydrated in a reflux distillation column was used as solvent. Variable amounts of MO and the catalyst together with cyclohexane (10 ml) and n-dodecane (internal standard) were added to the reactor and agitated with a magnetic stirrer; then the reaction mixture was heated to the reaction temperature in a thermostatic bath. Product concentrations were followed during the reaction by ex-situ gas chromatography using a Agilent 6850 GC chromatograph equipped with flame ionization detector, temperature programmer and a 50 m HP-1 capillary column (50 m × 0.32 mm ID, 1.05 μm film). Product identification was carried out using gas chromatography coupled with mass spectrometry (Varian Saturn 2000) both equipped with a VF5-HT capillary column. Data were collected every 10–20 min for 160–250 min. The only products detected were 9-octadecene and 9-octadecene-1,18-dioate (9-OD).

MO conversion was calculated as $X_{MO} = (C^0_{MO} - C_{MO})/C^0_{MO}$, where C^0_{MO} is the initial concentration of MO and C_{MO} is the concentration of MO at reaction time t. Yields (η_j, mol of product j/mol of MO fed) were calculated as $\eta_j = C_j\nu_{MO}/C^0_{MO}\nu_j$, where ν_{MO} and ν_j are the stoichiometric coefficients of MO and product j, respectively. Selectivities (S_j, mol of product j/mol of MO reacted) were calculated as $S_j = \eta_j/X_{BN}$.

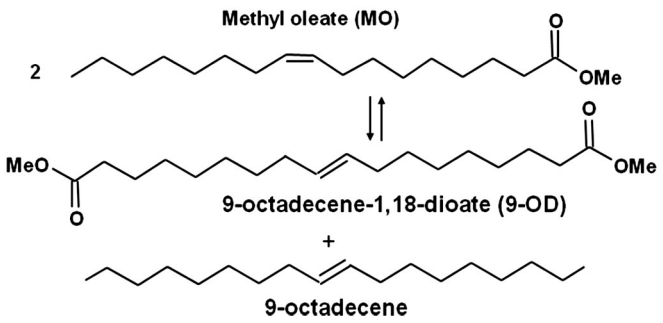

Fig. 2. Self-metathesis of methyl oleate.

3. Results and discussion

3.1. Catalyst characterization

The XRD diffractograms of HG complex [17], silica support and HG(0.87%)/SiO_2 sample are shown in Fig. 3. The diffractogram of HG(0.87%)/SiO_2 presented only the amorphous halo of SiO_2 support. No diffraction peaks attributable to the HG crystalline structure were detected, probably reflecting both the low HG loading and a high dispersion of the HG complex on the support as it has been observed by other authors [9].

The thermal stability of HG complex was studied by DRIFT spectroscopy and the results are presented in Fig. 4. The IR spectrum of HG complex dried at 303 K was similar to those reported by other authors [18]. Several absorption bands appeared in the 1200–1700 cm^{-1} region. The bands at 1651 cm^{-1}, 1454 cm^{-1}, and 1298 cm^{-1} correspond to ν(C C) styrene, ν(C C) aromatic and $\delta(CH_2)$, respectively [18]. Typically, the intensity of the styrene vibration ν(C C) at 1651 cm^{-1} is relatively weak in the HG spectrum due to coordination to Ru. In the 2800–3200 cm^{-1} region the absorption bands at 2945 cm^{-1} and 2976 cm^{-1} are attributable to $\nu(CH_3, CH_2)$ asymmetric and $\nu(CH_3, CH_2)$ symmetric stretches. Essentially the same HG DRIFT spectrum was obtained after heating the HG complex at 373 K but further treatment at 423 K caused the disappearance of several absorption bands, probably reflecting the partial decomposition of the HG complex. The HG(6.0%)/SiO_2 sample dried at 303 K presented the main IR bands characteristics of pure HG complex, thereby indicating that the HG structure was preserved after its deposition on silica.

3.2. Self-metathesis of methyl oleate on HG/SiO_2 samples

Taking into account the results in Fig. 4 on the thermal stability of HG complex, we performed all the catalytic tests for the self-metathesis of methyl oleate at temperatures lower than 373 K. Fig. 5 shows the MO

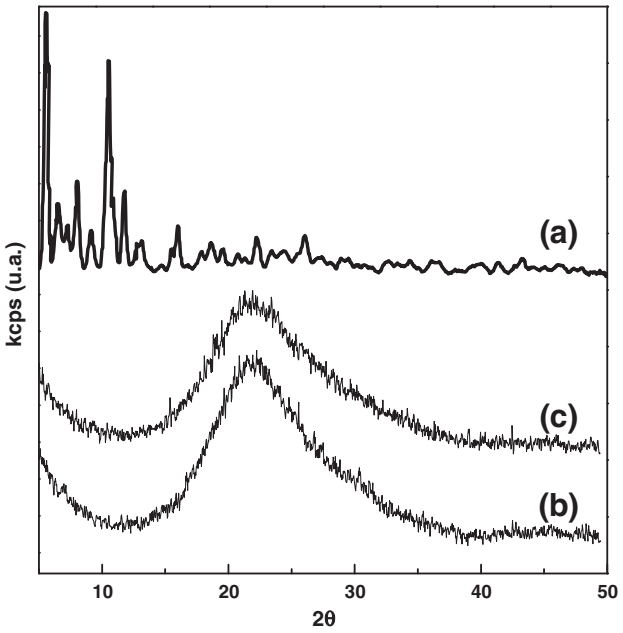

Fig. 3. XRD diffractograms of: (a) HG complex (from 17); (b) SiO_2; (c) HG(0.87%)/SiO_2.

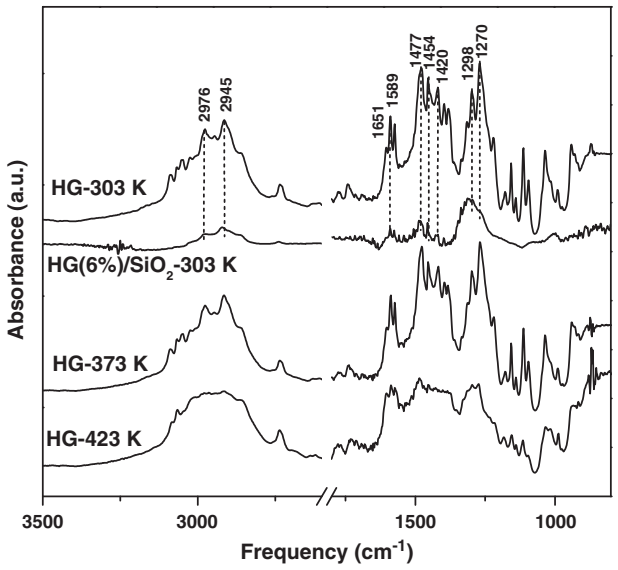

Fig. 4. DRIFT spectra of HG complex treated at increasing temperatures and of HG(6%)/SiO_2.

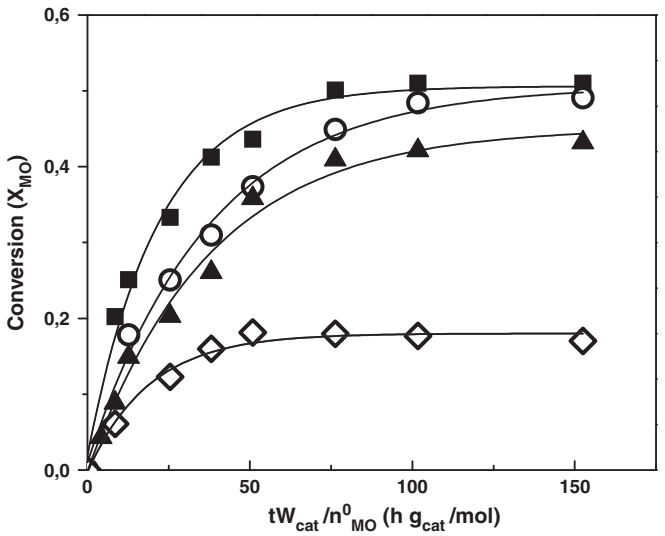

Fig. 6. Self-metathesis of methyl oleate on HG/SiO_2: Effect of %HG. 1.67 %HG (■); 1.21 %HG (○); 0.87 %HG (▲); 0.43 %HG (◊) [$T = 303$ K, solvent: cyclohexane, $C^0_{MO} = 0.059$ M; $W_{cat} = 30$ mg].

conversion (X_{MO}) and yields (η_i) as a function of time obtained at 323 K on HG(0.87%)/SiO_2 and typically illustrates the catalyst behavior during the reaction. The only products detected were 9-octadecene and 9-octadecene-1,18-dioate (9-OD) that reached yields of about 50% for $X_{MO} = 0.5$ after 90 min of reaction. The fact that X_{MO} remained constant after reaching a value of 0.5 is in agreement with previous work reporting that the MO equilibrium conversion for the self-metathesis of MO at 323 K is 50% [16]. In order to verify that our results in Fig. 5 reflect the approach to equilibrium we introduced to the reactor an additional amount of 30 mg of HG(0.87%)/SiO_2 after 130 min of reaction and we effectively observed that X_{MO} was not modified by the addition of catalyst (Fig. 5).

In Fig. 6 we have represented X_{MO} as a function of parameter tW/n^0_{MO} for all the catalysts used in this work, where t is the reaction time, W is the catalyst weight, and n^0_{MO} are the initial moles of MO. The local slope of each curve in Fig. 6 gives the MO conversion rate at a specific value of MO conversion and reaction time. Thus, we determined the initial MO conversion rates (r^0_{MO}, mol/h g_{cat}) by calculating the initial slopes of the curves in Fig. 6. Results are given in Table 1 (entries 1 to 4) and as expected we observed that r^0_{MO} increased with the HG loading on the catalyst. We also determined the initial MO conversion turnover rates (TOF, mol MO/mol HG min) obtaining a value of TOF ≅ 13.8 mol MO/mol HG min for all the catalysts of Fig. 6. This result showed that the HG complex deposited on silica in the 0.43%–1.67% range was in all the cases entirely accessible and active for carrying out the catalytic reaction. It is significant noting that the HG monolayer on our silica support is about 11.6%. We determined this value by successively adding small amounts of the HG complex to 100 mg of SiO_2 placed in 3 ml of cyclohexane into a beaker. We analyzed the supernatant solution following every HG addition until detecting the presence of the HG complex. On the other hand, theoretical calculations using an effective diameter of 1.76 nm for the HG molecule on the support predict a monolayer value of 11.9% HG.

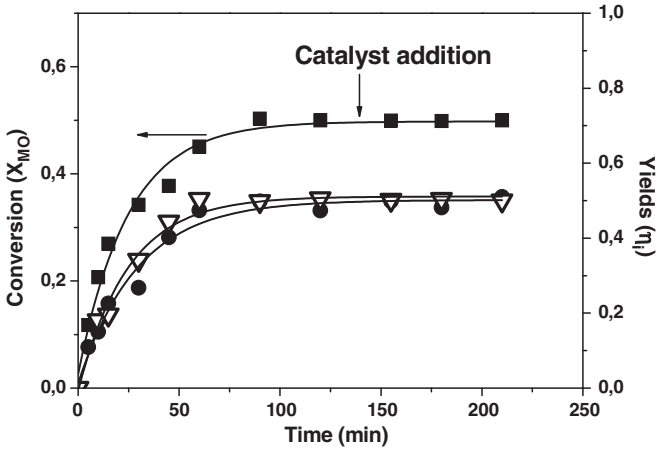

Fig. 5. Catalytic results: MO conversion (X_{MO}) and yields on HG(0.87)/SiO_2. ▽ 9-octadecene, ● 9-OD [$T = 323$ K, $C^0_{MO} = 0.059$ molar; $W_{cat} = 30$ mg, solvent: cyclohexane (10 ml)].

At the end of catalytic runs in Fig. 6, X_{MO}, $\eta_{9\text{-OD}}$, and $\eta_{9\text{-octadecene}}$ reached their equilibrium values on HG(1.67%)/SiO_2 and HG(1.21%)/SiO_2 and were slightly lower on HG(0.87%)/SiO_2 (the $\eta_{9\text{-octadecene}}$ values are not included in Table 1 because they were practically the same than those of $\eta_{9\text{-OD}}$). In contrast, X_{MO} on HG(0.43%)/SiO_2 reached 15% after 50 min reaction and remained constant until the end of the catalytic run. This result strongly suggests that HG/SiO_2 catalysts are deactivated during the MO self-metathesis when containing low HG loadings. The HG loading on HG(0.43%)/SiO_2 sample is only about 3.7% of the HG monolayer value, which would favor a high dispersion of the active species on the support surface. Probably, the isolation of HG molecules on the silica support may facilitate the HG active site deactivation by intermediate species or products formed during the progress of the reaction.

Table 1 also includes data allowing comparison between homogeneous and heterogeneous catalysis for promoting the self-metathesis of MO (entries 5 and 6). Specifically, the initial activity of HG(0.87%)/SiO_2 and dissolved HG complex were determined at 523 K; similar HG amounts were loaded to the reactor in both catalytic runs. The initial MO conversion turnover rate on HG(0.87%)/SiO_2 (29.7 mol MO/mol HG min) was about three times lower as compared to that obtained via homogeneous catalysis (80.5 mol MO/mol HG min).

Finally, it has be noted that the carbon balance for all the samples in Table 1 was higher than 95% showing that HG/SiO_2 catalysts are highly selective for producing 9-octadecene and 9-OD via the self-metathesis of MO.

Table 1
Catalytic results for the self-metathesis of methyl oleate on HG/SiO_2 catalysts.

Entry	Catalyst	Temperature	Initial reaction rates		MO conversión [a]	Yield[a]	Carbon balance [a]
		(K)	r^0_{MO} (mmol/h g_{cat})	TOF (mol MO/mol HG min)	X_{MO} (%)	$\eta_{9\text{-OD}}$ (%)	(%)
1	HG(0.43%)/SiO_2	303	3.9	13.7	15	14	96
2	HG(0.87%)/SiO_2	303	11.6	13.9	44	43	96
3	HG(1.21%)/SiO_2	303	16.0	13.8	50	49	98
4	HG(1.67%)/SiO_2	303	22.2	13.9	50	50	98
5	HG (dissolved) [b]	323	–	80.5	50	50	99
6	HG(0.87%)/SiO_2	323	24.7	29.7	50	50	100

C^0_{MO} = 0.059 molar; W_{cat} = 30 mg, solvent: cyclohexane (10 ml).
[a] At the end of catalytic runs.
[b] W_{HG} = 0.3 mg.

Taking into account the results in Table 1 (entries 5 and 6) showing that the intrinsic activity of the HG complex for MO conversion was higher when dissolved in the reaction media (homogeneous catalysis), we performed additional tests in order to verify if our results in Table 1 really reflect the activity of the HG complex immobilized on silica; i.e. to exclude the existence of catalyst leaching during the reaction. In this regard, we carried out a standard catalytic test using HG(0.87%)/SiO_2 sample, and after 32% MO conversion, 2 ml (20% vol.) of supernatant solution was transferred into another reactor (Fig. 7). Then, the metathesis reaction continued in both reactors under identical operating conditions. Fig. 7 shows that while X_{MO} continued to increase up to equilibrium in the standard reaction, it remained constant in the reactor containing the removed supernatant solution. Similar qualitative results were obtained using HG(1.21%)/SiO_2 and HG(1.67%)/SiO_2 samples. These results clearly demonstrated that data in Table 1 effectively reflect the activity of immobilized HG complex; in other words, there is not catalyst leaching in cyclohexane.

The effect of temperature on catalyst activity was studied on sample HG(0.87%)/SiO_2. Fig. 8 shows the evolution of X_{MO} as a function of time obtained at 303, 313 and 323 K. From the slopes of the curves in Fig. 8 we determined the initial MO conversion rates for the three temperatures and then we plotted the ln r^0_{MO} values as a function of $1/T$ for calculating the apparent activation energy (E_a) of MO metathesis via an Arrhenius-type function. From the slope of the resulting linear plot, we obtained $E_a = 10 \pm 1$ kcal mol^{-1}.

Finally, we studied the in-situ deactivation of HG(0.87%)/SiO_2 sample by performing two consecutive catalytic tests without stopping the run. The procedure was as follows: after X_{MO} and $\eta_{9\text{-OD}}$ reached their equilibrium values (50%) in a standard run at 323 K, we introduced to the reactor the amount of MO required for reaching again the initial MO concentration, C^0_{MO}, and performed a second consecutive run. Fig. 9 shows the evolution of MO concentration during the two consecutive runs. It is observed that in the second run C_{MO} rapidly decreased from C^0_{MO} to the equilibrium concentration, C^{eq}_{MO}, thereby suggesting that the in situ deactivation of HG(0.87%)/SiO_2 during the first catalytic run was not significant.

4. Conclusions

Second generation Ru Hoveyda–Grubbs complexes supported on silica efficiently promote the self-metathesis of methyl oleate towards 9-octadecene and 9-octadecene-1,18-dioate (9-OD). At 303 K, the methyl oleate equilibrium conversion and the 9-OD and 9-octadene equilibrium yields are rapidly reached on HG/SiO_2 catalysts containing %wt HG higher than 0.87%, being the C balance near 100%. The HG leaching is negligible during the progress of the reaction in cyclohexane reflecting the effective immobilization of the HG complex on the silica surface. The initial MO conversion turnover rate (TOF, mol MO/mol HG min) was almost the same on HG/SiO_2 catalysts containing up to 1.67%HG, thereby suggesting that the HG complex was entirely

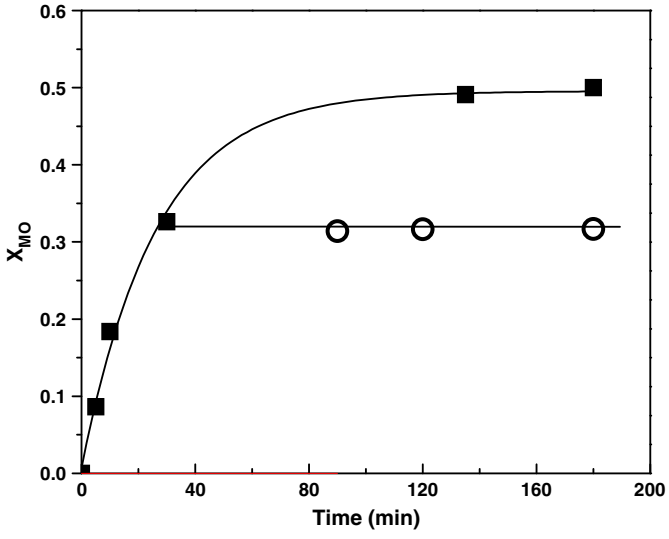

Fig. 7. Split-test for investigating catalyst leaching. Standard catalytic run using HG(0.87%)/SiO_2 (■); removed supernatant (○) [solvent: cyclohexane (10 ml), W_{cat} = 30 mg, T = 323 K, $R_{OM/H\text{-}G}$: 1460, C^0_{MO} = 0.059 M].

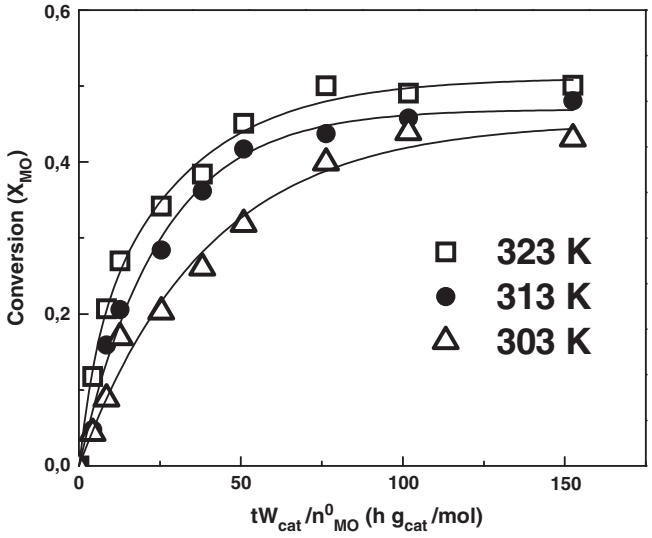

Fig. 8. Effect of temperature on catalyst activity [catalyst: HG(0.87%)/SiO_2, solvent: cyclohexane, C^0_{MO} = 0.059 M; W_{cat} = 30 mg].

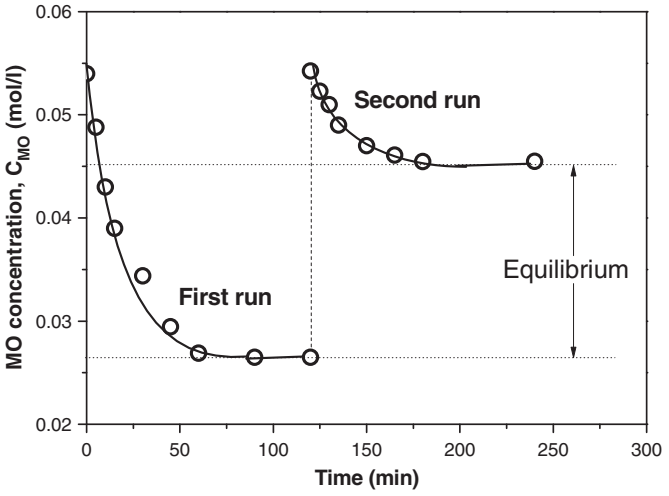

Fig. 9. Consecutive catalytic runs to evaluate in situ catalyst deactivation [catalyst: HG(0.87%)/SiO_2, $T = 323$ K, solvent: cyclohexane, $C^0_{MO} = 0.059$ M; $W_{cat} = 30$ mg].

accessible and active for carrying out the catalytic reaction. Low-loading HG/SiO_2 samples (HG <0.87 wt.%) rapidly deactivate during the reaction but samples containing higher HG loadings maintain their catalytic activity after two consecutive catalytic tests.

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