

Molybdenum containing surface complex for olefin epoxidation

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Silica-supported molybdenum surface complexes were prepared by the reaction between $(N\equiv)Mo(OtBu)_3$ and silica *via* displacement of the *tert*-butoxy ligands for siloxyls from the silica surface. The structure of the surface molybdenum complexes was well defined by *in-situ* FT-IR, elemental analysis, 1H NMR and ^{13}C CP/MAS NMR techniques. The surface complexes could undergo alcoholysis reaction with CD_3OD and CH_3OH in the same way as free $(N\equiv)Mo(OtBu)_3$ and they show high catalytic activity and selectivity in olefin epoxidation. Initial rates up to 24.9 mmol epoxide $(mmol\ Mo)^{-1}\ min^{-1}$ were achieved in the epoxidation of cyclohexene using TBHP as oxidant.

Introduction

Epoxides are important building blocks in organic synthesis. In fine chemical processes, epoxides are still mostly produced from the oxidation of olefins with peracids; these processes usually lead to low selectivities for epoxide due to a variety of secondary nucleophilic ring-opening reactions and they generate large amounts of waste. Direct epoxidation of olefins using more environmentally benign oxidants such as hydrogen peroxide, alkyl hydroperoxide, and oxygen is probably of the most importance in terms of economical processes.¹ Many kinds of catalysts have appeared in this field in the past decades including zeolitic materials substituted with transition metals,² transition-metal containing amorphous materials,³ homogeneous catalysts based on Re or W,⁴ tungsten-based heteropolyacids, *etc.*⁵ Molybdenum-containing catalysts are widely used in the field of selective oxidation, and one of the most famous example is probably the Halcon (homogeneous) process for the industrial manufacture of propylene oxide.⁶ Because of the advantages of heterogeneous catalysts over homogeneous ones, tremendous effort has been directed towards the heterogenization of molybdenum onto different kinds of supports, such as silica, polymers and mesoporous materials.⁷ One problem associated with the heterogenization of the catalyst is the difficulty to obtain a truly well-defined Mo^{VI} center covalently bonded to the support. Surface Organo-Metallic Chemistry (SOMC) can provide in principle an opportunity to construct a uniform distribution of active sites on the surface of the support, and thus help in getting the required structure/activity relationship.⁸ This approach has already been used to study, understand and improve the Shell catalyst,⁹ and also to design an efficient heterogeneous Sharpless epoxidation catalyst.¹⁰ A crucial point in generating a well-defined system is to use a monomeric precursor and try to graft it *via* one or several covalent bonds. Molybdenum alkoxides typically exist as dinuclear compounds, $[Mo_2(OR)_6]$.¹¹ In contrast $[(N\equiv)Mo(OtBu)_3]$ is monomeric in solution, stable, easily prepared and possesses alkoxy ligands which may potentially be substituted by surface siloxyl ligands.¹² Therefore its grafting onto SiO_2 and MCM-41 and the reactivity of the

material thus formed were investigated as disclosed herein. The catalytic activity of the surface complexes obtained was tested by olefin epoxidation using TBHP as oxidant, and an initial rate as high as 24.9 mmol epoxide $(mmol\ Mo)^{-1}\ min^{-1}$ was achieved.

Experimental

General procedure

All experiments were carried out in the strict absence of oxygen and water. Standard Schlenk techniques under Ar were used for organometallic syntheses. Pentane was distilled over Na/K amalgam and stored under Ar over Na. The $(N\equiv)Mo(OtBu)_3$ complex and the MCM-41 were prepared according to a literature procedure.¹³ Silica (Aerosil[®] Degussa, $200\ m^2\ g^{-1}$) was calcined at $500^\circ C$ in air for 2 h, treated at $500^\circ C$ under vacuum (10^{-5} mmHg) for 12 h (support referred to as SiO_2 -500) and then at $700^\circ C$ for 4 h (support referred to as SiO_2 -700). MCM-41 ($1000\ m^2\ g^{-1}$) was treated at $500^\circ C$ under vacuum (10^{-5} mmHg) after removing the template at $550^\circ C$ (support referred to as MCM-41-500). For the catalytic tests, all substrates were purchased from Aldrich and distilled under Ar before use. TBHP (5.5 M in decane, Aldrich) was degassed and stored over $MgSO_4$. GC analyses were performed on a HP6890 equipped with an HP-1 column (25 m, 0.32 mm).

Grafting of $[(N\equiv)Mo(OtBu)_3]$ onto support by gas–solid reaction

This was carried out using standard techniques for the various supports.¹⁴ Typically, the support as a pellet (20 mg) was heated at $500^\circ C$ under vacuum (10^{-5} mmHg) for 12 h and cooled to room temp. The Mo molecular complex was sublimed onto the silica pellet under vacuum, and this support was heated to $80^\circ C$ for 1 h. The excess of molecular complex was removed by reverse sublimation.

Ligand exchange experiment of SiO₂-Mo-500 with alcohol

After sublimation of the [(N≡)Mo(OrBu)₃] onto a silica pellet as described above (pretreated at 500 °C under vacuum at 10⁻⁵ mmHg for 12 h), CD₃OD was introduced into the reactor; after 5 minutes, the reactor was placed under vacuum at 70 °C for 1 h to remove the excess CD₃OD, then CH₃OH was introduced, the reactor was placed under vacuum after 5 minutes to remove the excess CH₃OH at 70 °C for 1 h. This procedure was repeated twice and the ligand exchange reaction was followed by *in-situ* FT-IR spectroscopy.

Grafting of [(N≡)Mo(OrBu)₃] onto support by liquid–solid reaction

Preparation of Mo–Si-500. Grafting was typically carried out by stirring a mixture of [(N≡)Mo(OrBu)₃] (164 mmg, 0.5 mmol) and SiO₂-500 (1.00 g) (pretreated at 500 °C under vacuum at ~10⁻⁵ mmHg for 12 h) in pentane (10 mL) at 20 °C for 3 h. After filtration, the solid was washed three times with pentane and dried under vacuum to yield 1.1 g of a white powder. Elemental analysis: C, 1.09%wt; N, 0.28%wt and Mo, 1.74%wt. Solid state ¹H NMR δ 0.84 ppm. CP/MAS ¹³C NMR δ 29.4 ppm. IR: 2976, 2945, 2902, 2871, 1471, 1451, 1362 cm⁻¹.

Preparation of Mo–Si-700. SiO₂-700 (pretreated at 700 °C under vacuum at ~10⁻⁵ mmHg for 12 h) was used as support, the preparation procedure is similar to that described above. Elemental analysis: C, 2.13%wt; N, 0.30%wt and Mo, 1.90%wt. Solid state ¹H NMR δ 0.74 ppm. CP/MAS ¹³C NMR δ 27.4 ppm. IR: 2976, 2945, 2902, 2871, 1471, 1451, 1362 cm⁻¹.

Preparation of Mo–MCM-41. A mixture of [(N≡)Mo(OrBu)₃] (492 mmg, 1.5 mmol) and MCM-41-500 (1.00 g) (pretreated at 500 °C under vacuum at ~10⁻⁵ mmHg for 12 h) in pentane (15 mL) was stirred at 20 °C for 3 h. After filtration, the solid was washed three times with pentane and dried *in vacuo* to yield 1.4 g of a white powder. Elemental analysis: C, 4.18%wt; N, 1.26%wt and Mo, 6.69%wt. Solid state ¹H NMR δ 1.45. CP/MAS ¹³C NMR δ 29.6. IR: 2977, 2943, 2902, 2871, 1471, 1451, 1361 cm⁻¹.

Epoxidation of olefins using various surface Mo-complexes

The Mo-containing solid (18 μmol of Mo) was introduced into a two-necked 50 mL glass reactor fitted with a reflux condenser under argon. After addition of the substrate (50 mmol) and CH₂Cl₂ (5 mL), the reaction mixture was heated to reflux and TBHP (17.5 mmol) was added *via* a syringe. The reaction was monitored at certain time intervals by GC analysis using dodecane as an internal standard. The amount of remaining TBHP was measured by iodometric titration at the end of the reaction.

Results and discussion

Preparation and characterization of the surface complexes

The reaction of [(N≡)Mo(OrBu)₃] with SiO₂ partially dehydroxylated at either 500 °C or 700 °C (respectively named Mo–Si-500 and Mo–Si-700) was performed using both gas–solid and liquid–solid reactions.¹⁵ When [(N≡)Mo(OrBu)₃] is sublimed at 85 °C onto a silica disc, the intensity of the ν(Si–OH) band at 3745 cm⁻¹ decreases, while bands in the range of 3000–2860 cm⁻¹ and 1500–1350 cm⁻¹, attributed to ν(C–H) and δ(C–H) respectively, appear (Fig. 1). The evolution of 2,2-dimethylpropanol in the gas phase was detected by IR spectroscopy (Fig. 1 inset). These observations are in

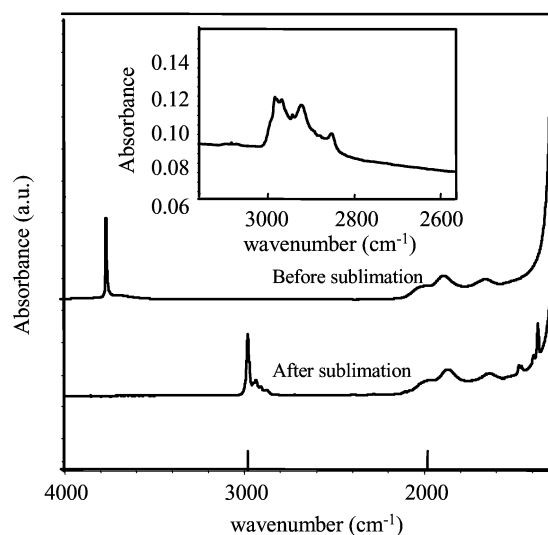


Fig. 1 *In situ* IR spectroscopy before and after sublimation of [(N≡)Mo(OrBu)₃] onto an SiO₂-700 pellet; inset figure is the gas phase evolved during the sublimation.

agreement with a grafting *via* the displacement of the *tert*-butoxy ligands for siloxyls from the silica surface, which is closely related to the alcoholysis reaction reported by Chisholm *et al.*¹¹

Usually, the structure of the product obtained from the reaction of the organometallic compound and triphenylsilanol was a reliable reference to determine the structure of the surface complex. In our previous study of the reaction between [(N≡)Mo(CH₂tBu)₃] and silica, we found that protonation of nitride occurred to give an imido surface complex [(=SiO)–Mo(=NH)(CH₂tBu)₃]. Using triphenylsilanol in place of silica provided the same reactivity and yielded [Ph₃SiO–Mo(=N–H)(CH₂tBu)₃].¹⁶ The reaction of (N≡)Mo(OrBu)₃ with triphenylsilanol gave a mixture of [(Ph₃SiO)_x–Mo(=N)(OrBu)_{3–x}] (observed by liquid ¹H and ¹³C NMR) as in the case of the alcoholysis reaction.¹¹ This result is consistent with the FT-IR data, which support the reaction pathway between [(N≡)Mo(CH₂tBu)₃] and siloxyls of the silica surface. The different reactivity of the two analogous molybdenum complexes with OH groups is probably related to the difference in Mo–N bond strengths, which is 1.66 and 1.72 Å for [(N≡)Mo(OrBu)₃] and [(N≡)Mo(CH₂tBu)₃], respectively.

The surface complex shows a free ligand exchange property as exhibited by the reaction with CD₃OD and CH₃OH. The FT-IR shows the disappearance of the ν(C–H) vibration associated with the OrBu groups for ν(C–D) vibrations corresponding to CD₃O–M when the surface complex is reacted with CD₃OD (Fig. 2). When it was further reacted with CH₃OH, the ν(C–D) vibration associated with CD₃O–M was replaced by the ν(C–H) vibration of CH₃OH. The same process could be repeated several times. This further corroborates the proposed reaction pathway.

Liquid–solid reaction provides the same material according to IR spectroscopy. The supported surface complexes prepared by liquid–solid reaction were characterized by elemental analysis (Table 1). The results show that the pretreatment temperature of the support has an important effect on the amount of the molybdenum species grafted. With increasing pretreatment temperature, the amount of grafted molybdenum species decreased, this is mainly due to the decrease in the amount of reactive hydroxyl groups when the support was pretreated at higher temperature. Elemental analysis of the supported surface complexes gave C/N/Mo ratios of 5/1/1 and 9/1/1 for the surface complexes obtained with SiO₂-500 and SiO₂-700, respectively. Theoretical values in elemental analysis for a

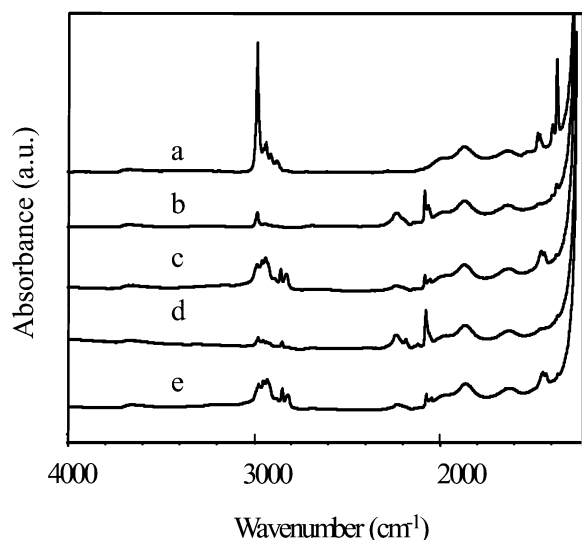


Fig. 2 *In situ* IR spectroscopy. a: Mo-Si-500; b: after reaction with CD₃OD at room temperature and desorption at 70 °C for 1 h; c: further reaction with CH₃OH and desorption at 70 °C for 1 h; d: further reaction with CD₃OD and desorption at 70 °C for 1 h; e: further reaction with CH₃OH and desorption at 70 °C for 1 h.

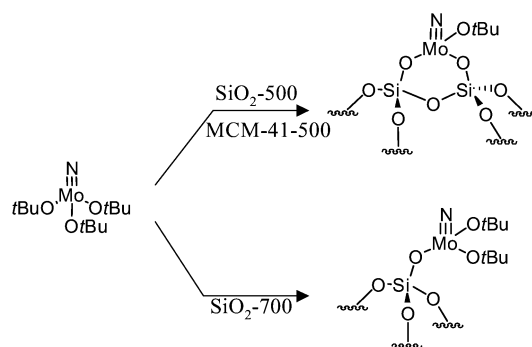
bis-, **1**, or a monografted species, **2**, via reaction of [(N≡)Mo(OrBu)₃] with a silanol group of silica give C/N/Mo ratios of 8/1/1 and 4/1/1, respectively (Scheme 1). This supports that a monografted species is obtained on a SiO₂-700, while the reaction with a SiO₂-500 gives a bisgrafted species and suggests that the nitrido ligand is retained around the Mo center.

The surface complex obtained by grafting on MCM-41 is structurally similar to those obtained on SiO₂-500 according to elemental analysis and spectroscopic evidence (Fig. 3). The C/N/Mo ratio is 5/1/1, suggesting the formation of bisgrafted species. The mesostructural nature of MCM-41 has a tendency for the formation of multigrafted species because the hexagonal channels in the mesoporous silica could induce strong steric effects. The MCM-41 supported surface complex shows a much higher Mo content in relation to the higher specific surface area and therefore higher silanol contents.¹⁵

Solid state ¹H NMR and CP/MAS ¹³C NMR of all the supported surface species show signals assigned to CH₃ of OrBu groups, which also provide good evidence for the presence of *tert*-butoxy ligands remaining around the metal center in all cases (Fig. 4).

Epoxidation of olefins using TBHP as oxidant

Epoxidation of cyclohexene using various supported surface complexes. With these isolated heterogenized Mo^{VI} centers on various supports in hand, their catalytic activity was tested in the epoxidation of cyclohexene using TBHP as oxidant (Table 2). All supported surface complexes exhibited high selectivities and activities as expected, which were greater



Scheme 1 Proposed reaction pathway between [(N≡)Mo(OrBu)₃] and silica.

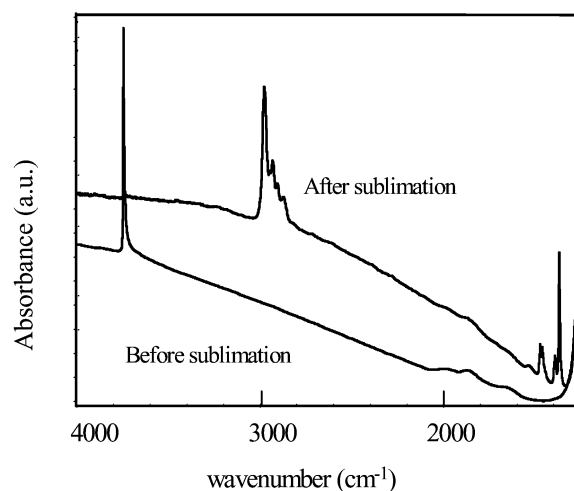


Fig. 3 *In situ* IR spectroscopy before and after sublimation of [(N≡)Mo(OrBu)₃] onto MCM-41.

than 99% and 20 mol epo (mol Mo)⁻¹ min⁻¹ (initial rate), respectively. In contrast, the molecular precursor showed a much lower initial rate as well as a poor selectivity for epoxide; this is probably associated with its rapid transformation under reaction conditions. The high activity and selectivity of the surface complex could be attributed to the isolated molybdenum site.

Epoxidation of various olefins on Mo-Si-700. The epoxidation of representative olefins was then performed using Mo-Si-700 as catalyst (Table 3). Methylcyclohexene and cyclohexene have the highest reactivities followed by styrene. Terminal olefins like 1-hexene or 1-octene showed much slower reactivities, and *trans* olefins do not seem to react under the reaction conditions. *Cis* olefins however are converted with initial rates of 6 to 14 mol epo (mol Mo)⁻¹ min⁻¹ depending on how sterically crowded the double bond is. The data show

Table 1 Elemental analysis for the surface complexes obtained by liquid–solid reaction of [(N≡)Mo(OrBu)₃] with partially dehydroxylated silica and MCM-41

Support	wt% Mo on support	wt% C on support	wt% N on support	C/Mo ^a	N//Mo ^a	mmol Mo/g of support
Mo-Si-500	1.74	1.09	0.28	5.0 (4.0)	1.1 (1.0)	0.18
Mo-Si-700	1.90	2.13	0.30	8.9 (8.0)	1.3 (1.0)	0.20
Mo-MCM-41	6.69	4.18	1.26	5.0 (4.0)	1.3 (1.0)	0.70

^a The number in parentheses (italic) represents the corresponding theoretical numbers (see Scheme 1).

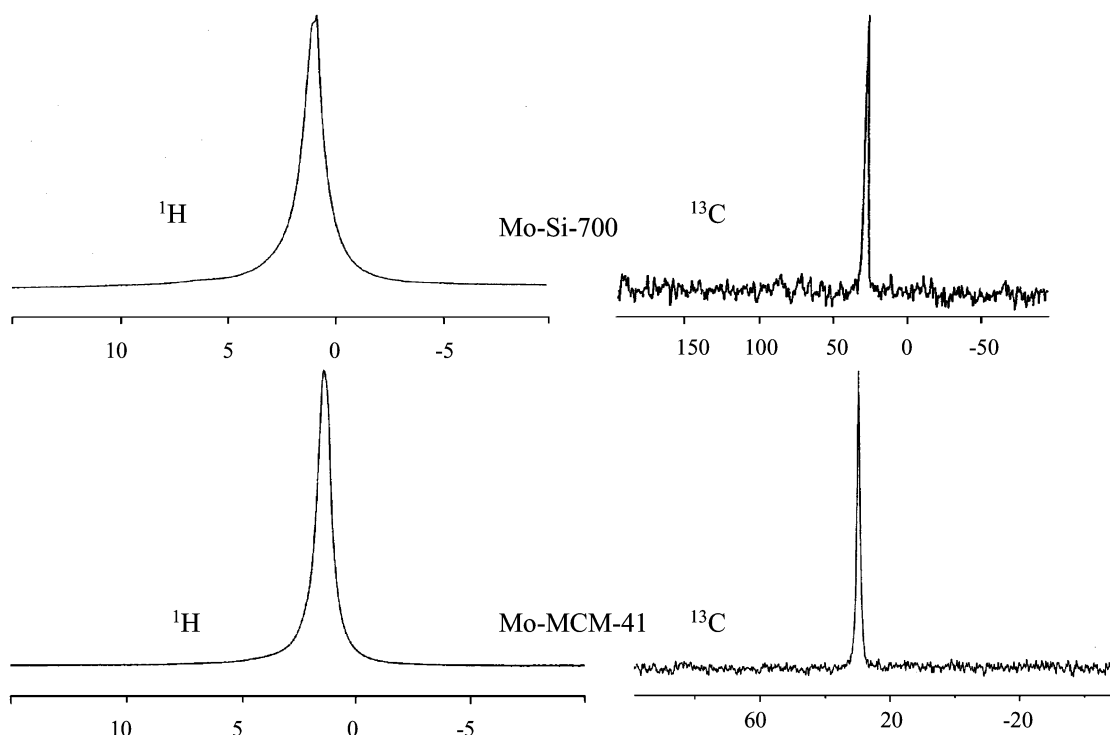


Fig. 4 ^1H and ^{13}C CP/MAS NMR spectra of the supported surface complexes.

Table 2 Epoxidation of cyclohexene on the surface organometallic complexes using TBHP as oxidant^a

Catalyst	Initial rate ^b /mmol epo (mmol Mo) ⁻¹ min ⁻¹	<i>S</i> _{epo} ^c (%)
Mo–SiO ₂ -500	22.8	99.1
Mo–SiO ₂ -700	24.9	99.0
Mo–MCM-41	21.4	96.3
(N≡)Mo(OrBu) ₃	6.6	90.30
Homogeneous Mo ^{vi}	1.5 ^d	—

^a Reaction conditions: Mo (0.018 mmol), cyclohexene (50 mmol), CH₂Cl₂ (5 mL), TBHP 5.5 M in decane (17.5 mmol) heated under reflux in a glass reaction vessel for 2 h. ^b The initial rate is based on the epoxide formation in the first 20 min. ^c The epoxide selectivity corresponds to the formation of epoxide on the oxidant added. ^d See ref. 17.

Table 3 Epoxidation of representative olefins on Mo–Si-700^a

Olefin	Initial rate ^b / mol epo (mol Mo) ⁻¹ min ⁻¹	<i>S</i> _{epo} (mol%) ^c	Conv. TBHP (mol%) ^d
Cyclohexene	24.9	98.9	99.5 (2 h)
1-Methyl-1-cyclohexene	31.4	97.3	95.8 (1 h)
Styrene	18.0	92.1	89.0 (7 h)
1-Octene	3.6	96.7	72.4 (12 h)
1-Hexene	1.5	97.2	73.8 (12 h)
<i>Cis</i> -3-heptene	13.7	97.0	90.1 (3 h)
<i>Cis</i> -4-methyl-2-pentene	6.3	97.8	92.1 (5 h)
2-Ethyl-1-butene	5.7	93.2	90.3 (5 h)

^a Reaction conditions: Mo (0.018 mmol), substrate (119 mmol), CH₂Cl₂ (5 mL), TBHP 5.5 M in decane (17.5 mmol) heated under reflux in a glass reaction vessel. ^b The initial rate is based on the the epoxide formation in the first 20 min. ^c The epoxide selectivity corresponds to the formation of epoxide on the oxidant added. ^d The conversion in TBHP is obtained by its titration by iodometry at the end of the reaction; the number in parentheses corresponds to the reaction time.

that the surface complex catalyzed reaction system is typical of electrophilic epoxidation.

Heterogeneity of the supported surface complex. The heterogeneity of Mo–Si-700 was tested by the epoxidation of cyclohexene. The supported surface complex was reused three times. An obvious loss of activity for each cycle was observed when the supported surface complex was cycled (Fig. 5). However, the filtrate of the reaction mixture of the epoxidation of cyclohexene obtained after one cycle (that is after conversion of 99% of TBHP) was treated with an additional 1000 equiv. of TBHP and showed no or little catalytic activity under

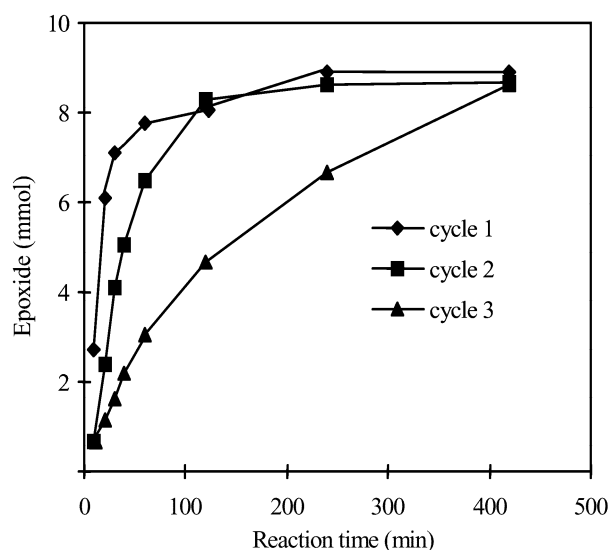


Fig. 5 Different runs of epoxidation of cyclohexene on Mo–Si-700. Reaction conditions for run 1: Mo, 0.018 mmol; cyclohexene, 50 mmol; TBHP, 9 mmol; the reaction mixture is heated under reflux in CH₂Cl₂ (5 mL). The subsequent runs were performed by using the solid after filtration and the same quantities of the various reagents were added.

similar reaction conditions. These data indicate that the high catalytic activity of the surface complexes can probably be attributed to the isolation of molybdenum active sites resulting from controlled grafting on a support. Molybdenum elemental analysis of the supported complex showed that there is about 15 mol% leaching of molybdenum from the catalyst for each cycle. The leaching of molybdenum caused the decrease of the catalytic activity.

Conclusion

In conclusion, silica supported molybdenum containing surface complexes with well-defined structure could be synthesized using the reaction of $[(N\equiv)Mo(OrBu)_3]$ and the hydroxyl group of the silica. The surface complexes with the highly isolated molybdenum centers show high activity and selectivity for the epoxidation of olefins.

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