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Cyclopentadienyl molybdenum complexes grafted on zeolites – synthesis and catalytic application

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η^5-CpMo(CO)$_3$Cl is grafted on H-zeolite-ß (H-ß) and H-zeolite-Y (H-Y) by the reaction of acidic protons with chloro-ligand. The XRD pattern of the zeolites after grafting remains intact and there is no additional peak obtained, indicating the absence of Mo oxide cluster formation during the grafting process. The successful grafting of intact CpMo(CO)$_3$ moieties is evidenced by IR spectroscopy and elemental analysis. Elemental analysis further reveals that H-Y zeolite shows higher Mo complex loading. The obtained heterogeneous materials are found to be efficient and recyclable catalysts for olefin epoxidation.

KEY WORDS: cyclopentadiene; epoxidation; grafting; molybdenum; zeolites.

1. Introduction

Molybdenum based catalysts are known to be versatile catalysts for the oxidation of organic substrates and are applied for the industrial epoxidation of propylene since the late 1960s [1–3]. A detailed understanding of the catalytic reaction mechanisms and the development of new and better catalysts in order to improve both yields and selectivities [4,5] are of continuing interest. Recently, cyclopentadienyl molybdenum complexes of formula Cp′MoO$_2$Cl and Cp′MoO$_2$R (Cp′ = η^5-C$_5$H$_5$ and derivatives, R = aliphatic hydrocarbon ligands) as well as their carbonyl precursor compounds of formula CpMo(CO)$_3$Cl and Cp′Mo(CO)$_3$R were found to be efficient homogeneous catalysts for the epoxidation of alkenes with TBHP as the oxidant [6–8]. However, industrial interest is still to a significant degree focused on heterogeneous catalysis due to its advantages, e.g. easier product/catalyst separation [9]. We and others have successfully heterogenized homogeneous Mo based catalysts and some of mixed metal carbonlyate salts on mesoporous solids by various methodologies and found that the heterogeneous catalysts are active and relatively stable [10–17]. However, some of the products and byproduct molecules formed during the course of the reaction get strongly adsorbed on the amorphous wall surface of the mesoporous materials leading to considerable decrease in catalytic conversions and selectivities when reused repeatedly [10–12]. Furthermore, mesoporous solids are susceptible to hydrothermal and thermal instability [18]. Facile separation of products from the catalysts, enhanced stability and selectivity are important features of hybrid catalysts [19]. In particular, the crystalline channel systems of zeolites are attractive hosts for the designing of hybrid systems since they are structurally much better defined than amorphous and mesoporous supports [19]. Thus, heterogenization of homogeneous Mo based catalysts on highly crystalline zeolite surfaces is an interesting alternative.

In the present investigation η^5-CpMo(CO)$_3$Cl is fixed on the surface of H-ß and H-Y zeolites by the reaction of the chloride ligand with surface protons, and the resulting materials are systematically characterized by XRD, FT-IR and elemental analysis. Furthermore, the obtained systems are tested for epoxidation of cyclooctene using TBHP as the oxidant.

2. Experimental

2.1. Synthetic procedure

Protonated forms of commercial zeolites such as Zeolite-Y (Na-Y) with Si/Al = 2.5, and Zeolite-ß (Na-ß) with Si/Al = 12.5 are obtained by repeated ion-exchange of Na-Y and Na-ß by using 1 M NH$_4$NO$_3$ solution followed by calcination at 823 K under air in a dry oven (Scheme 1). Solvents are dried by standard procedures (THF, toluene with Na/benzophenone ketyl; CH$_2$Cl$_2$% with CaH$_2$), distilled under argon and kept over 4 Å molecular sieves. Grafting experiments (Scheme 1) are carried out using standard Schlenk techniques under argon atmosphere with the following procedure: The H-Y and H-ß zeolites are pre-activated at 523 K under vacuum (10^{-3} mbar) for 6 h to remove physisorbed water. Then the activated zeolites are treated with 8 mmol of η^5-CpMo(CO)$_3$ Cl in 30 ml dry THF under argon atmosphere. The mixture is again stirred for 24 h at 313 K. After the grafting samples are filtered off and the resulting orange solid

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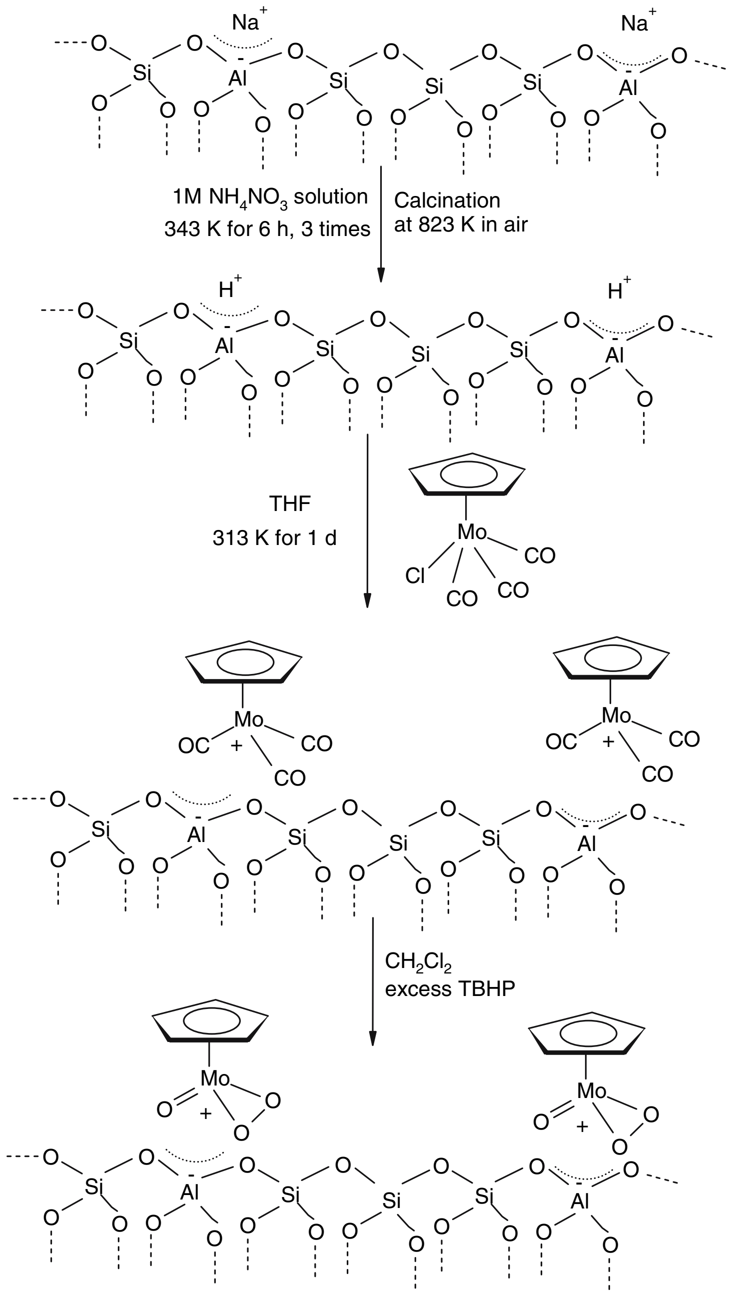

Scheme 1.

is washed repeatedly with CH_2Cl_2 to remove all physisorbed Mo complexes. The washed samples are dried under vacuum at room temperature. The samples synthesized from H-Y and H-ß are designated as H-Y-Mo and H-ß-Mo respectively.

2.2. Characterization methods

Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and co-workers). IR spectra are measured with an Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. Powder XRD data are collected with a Philips X′pert diffractometer using CuK_α radiation filtered by Ni.

2.3. Catalytic applications

The catalytic behavior of the grafted samples (200 mg; equivalent to 0.025 and 0.056 mmol of Mo for H-ß-Mo and H-Y-Mo) is tested by examining the oxidation of cyclooctene (0.917 g; 9.1 mmol) at 328 K in a liquid phase batch reactor with TBHP (5.5 M in decane; 18.2 mmol) as the oxidizing agent. The samples are analyzed initially at 5 min followed by every 30 min for 4 h and the reaction is terminated after 24 h. The analyses are carried out using a gas chromatograph (HP 5890) equipped with a FID detector.

3. Results and discussion

The powder XRD pattern of parent H-Y and H-ß zeolites as well as the corresponding Mo complex grafted samples are depicted in figure 1. It is clear from the figure that the general XRD pattern is not affected severely by the introduction of the CpMo complex on the surface, however, the overall intensities of the XRD pattern are considerably reduced indicating that the CpMo complexes are present in the channels of the zeolites. FT-IR spectra of parent zeolites and grafted samples are shown in figure 2. The bands at 1206, 1060, and 794 cm^{-1}, can be attributed to stretching vibrations of the aluminosilicate zeolites framework (Si–O–Al). New bands around 2026 and 1985 cm^{-1} are observed on the grafted samples, and can be assigned to terminal carbonyl (CO) group vibrations of the grafted compounds. Additional bands around 3010 cm^{-1} arise from C–H stretching vibrations of the Cp ligand. The presence of these bands after the heterogenization process suggests the presence of intact η^5-$CpMo(CO)_3$ complexes on the channels of the zeolites. In order to transfer the Mo precursor from the formal oxidation state (+II) to the catalytic active species with a formal oxidation state of (+VI) H-ß-Mo and H-Y-Mo are treated with TBHP. After the treatment the bands around 2016 and 1956 cm^{-1} disappear and new bands around 918 and 966 cm^{-1} are formed, indicating the oxidative conversion of the Mo-CO groups into their oxo and peroxo congeners (see Scheme 1) [6,7,10–12,20]. The bands around 3010 cm^{-1} can still be observed after the treatment with TBHP with a similar intensity as before. The oxidative decarbonylation method has already been successfully applied for the oxidation of $Cp'Mo(CO)_3X$ and $Cp'Mo(CO)_3R$ complexes, both in homogeneous [6–8] and in heterogeneous phase with MCM systems [10–12].

Elemental analyses (EAs) of the grafted samples show Mo loadings of 1.25 and 2.82 wt.% for H-ß-Mo and H-Y-Mo materials, respectively. Importantly no detectable amounts of Cl are found in these materials (EA-evidence), thus confirming successful replacement of Cl as shown in Scheme 1. Compared to H-ß-Mo, the H-Y-Mo shows higher Mo loading. The observed higher Mo loading on H-Y-Mo is due to the presence of more aluminium in the H-Y zeolite framework leading to more ionic character of the H-Y bond, in comparison to the H-ß, thus favoring a higher Mo loading. Similar methods of anchoring "single site" bimetallic clusters have been described by Thomas *et al.* [17].

The oxidation of cyclooctene in the presence of the grafted samples as heterogeneous catalysts, yields cyclooctene epoxide as the only significant product. The details concerning the catalytic reaction are given in the experimental part. Blank runs show that no significant amount of epoxide is formed in the absence of catalyst. A catalyst:oxidant:substrate ratio of 1:700:350 and 1:300:150 for H-ß-Mo and H-Y-Mo is used in all experiments unless stated otherwise. The H-ß-Mo and H-Y-Mo catalysts show about 98–100% cyclooctene conversion with ca. 80–100% epoxide selectivity after 24 h reaction time (table 1). The initial activities are somewhat higher for H-Y-Mo than for H-ß-Mo (figure 3). The observed higher activity in case of H-Y-Mo compared to H-ß-Mo may be ascribed to the presence of more aluminium in the framework of H-Y thus enhancing the Lewis activity of the Mo in this system or to the activation of TBHP by the Al sites [15]. The reaction velocity slows down with both systems

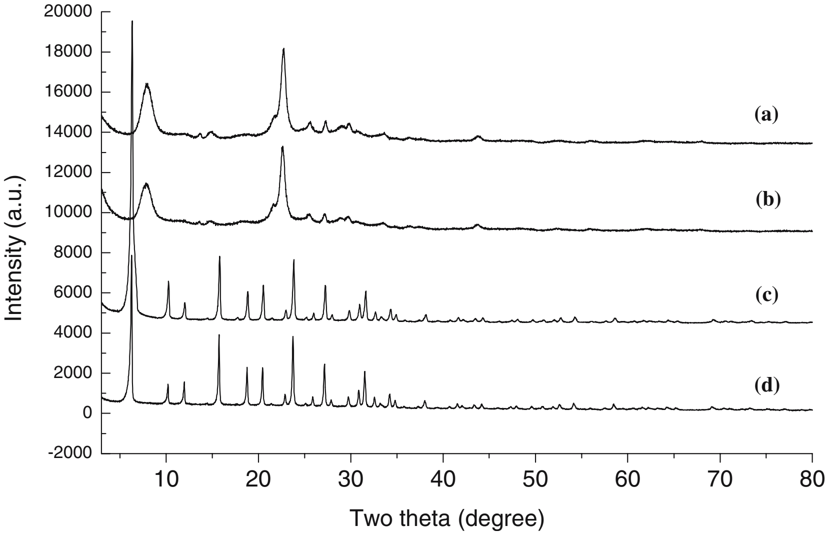

Figure 1. XRD pattern of (a) H-ß, (b) H-ß-Mo, (c) H-Y, and (d) H-Y-Mo.

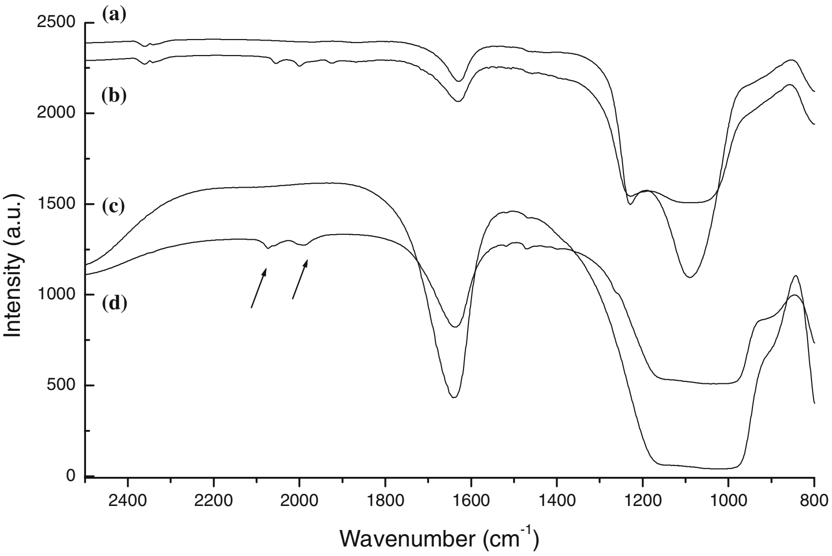

Figure 2. FT-IR spectra of (a) H-ß, (b) H-ß-Mo, (c) H-Y, and (d) H-Y-Mo.

Table 1
Conversion and selectiviies obtained for the heterogeneous materials in repeated runs

No. of runs	H-Y-Mo		H-ß-Mo	
	Conversion (%)	Epoxide selectivity (%)	Conversion (%)	Epoxide selectivity (%)
1st run	100	100	98	79
2nd run	99	92	95	84
3rd run	95	78	85	68

during the course of the reaction. This behavior can be assigned to the interaction of the catalyst with the by-product *tert*-butyl alcohol, [8,10–13] which is formed during the course of the reaction from the spent oxidant TBHP. However, both catalysts show TOFs (370 h^{-1} for H-Y-Mo and 300 h^{-1} for H-ß-Mo respectively) lower than the respective homogeneous catalysts of formula η^5-CpMoR(CO)$_3$) [8] indicating that the reaction is probably diffusion limited. After the first catalytic run the catalysts were washed several times with dichloromethane to remove physisorbed molecules and the catalytic reaction was repeated several times

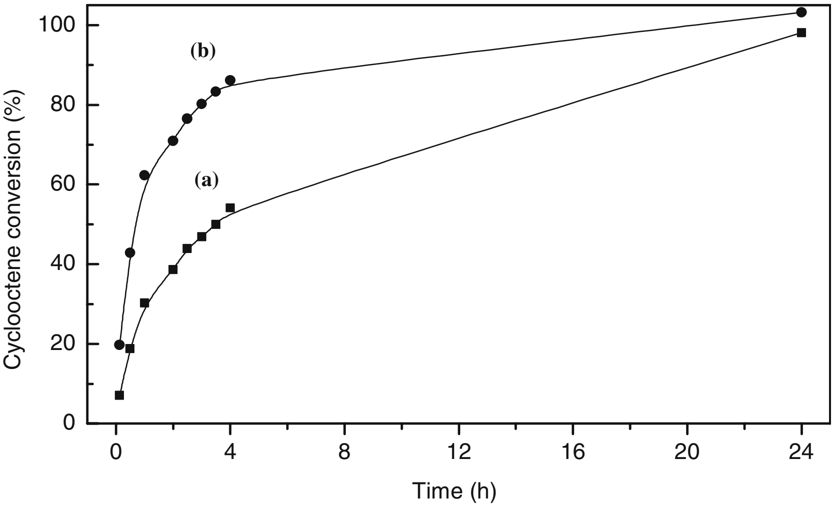

Figure 3. Kinetic profiles of cyclooctene oxidation reactions over (a) H-ß-Mo and (b) H-Y-Mo.

Table 2
Results of the filtration experiments

Samples	Conversion (%) within 24 h	
	Filtrate solution of fresh catalysts	Filtrate solution of recycled catalysts
H-Y-Mo	14.2	3.9
H-ß-Mo	15.4	4.1

(table 1). The catalysts are found to be retaining their activity even after several catalytic runs, however, the catalytic conversion and selectivity decreases somewhat.

The observed activity decrease may be – at least partially – due to the increasing amount of *tert*-butyl alcohol in the close proximity of the catalysts. Concentration gradients are created inside the pores during the catalytic reaction and may be partially maintained despite the washing of the catalysts after each run. Physisorbtion of *tert*-butyl alcohol on the surface material may additional contribute to the observed activity decrease during successive catalytic runs. In contrast to homogeneous reactions the byproduct cannot be removed so easily from the catalyst proximity by simple stirring of the reaction mixture or washing of the catalysts. Leaching seems to be less severe than in some of the previously examined cases. In order to examine the extent of leaching, filtrate experiments were carried out at the reaction temperature, i.e. the reaction mixtures were filtered from the heterogeneous catalysts after 50% of the total conversion was achieved. Then the product formation in the filtrated solution was monitored for another 24 h. The obtained results are summarized in table 2. The filtrate of fresh catalysts shows about 10–15% conversion confirming the leaching of active Mo species being not severe. Furthermore, the filtrated solution of recycled catalysts shows no appreciable conversion (less than 5%). These results indicate that the leaching observed for freshly prepared catalysts is due to weakly bonded Mo complex on the surface. However, after one catalytic cycle the remaining Mo stays on the surface even after several recycle experiments.

4. Conclusion

η^5-CpMo(CO)$_3$Cl is successfully grafted on the surface of zeolites. The grafted samples are active as heterogeneous olefin epoxidation catalysts. The catalysts are comparatively stable to leaching and active even after several applications. The observed activity decrease may originate from remaining *tert*-butyl alcohol inside the pores.

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