

Molybdenum incorporated silicalite as catalyst for epoxidation of olefins

M. Masteri-Farahani^a, F. Farzaneh^{b,*}, M. Ghandi^a

^a Department of Chemistry, University of Tehran, Tehran, Iran

^b Department of Chemistry, University of Azahra, Tehran, Iran

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Abstract

In this research, synthesis of silicalite containing small amount of molybdenum is described. Characterization of this zeolite was carried out with FT-IR, atomic absorption spectroscopy, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). In order to increase molybdenum content in zeolite structure with grafting method, the prepared silicalite-1 underwent reaction with molybdenum hexacarbonyl at high temperature. The incorporation of molybdenum in the structure was increased to 11%. The modified zeolite catalyzed the epoxidation of olefins (cyclohexene and *trans*-2-hexene-1-ol) with about 90% yield and 98% selectivity.

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1. Introduction

Catalytic oxidation is a major route for industrial synthesis of functionalized hydrocarbons. It is known that compounds of certain transition metals, notably Mo, W, Ti and V catalyze the liquid phase epoxidation of olefins with alkyl hydroperoxides [1–6]. The development of heterogeneous catalytic systems for the epoxidation of olefins is a highly attractive topic in current chemical research [2,7,8]. Among these, heterogeneous molybdenum catalysts are of particular interest and many attempts have been made to prepare them, such as grafting of molybdenum compounds to functionalized polymeric supports [9,10] and preparation of amorphous molybdenum silicate via. the sol–gel method [11,12]. Another preparation

method is the incorporation of molybdenum in the framework of zeolites [13,14].

In this study, we tried to prepare molybdenum silicalite-1 and then modified it by molybdenum hexacarbonyl. The modified zeolite was then used for epoxidation of olefins. Also zeolite Y was prepared and treated with similar procedure. The catalytic activity of resulted zeolite was also investigated in the epoxidation of cyclohexene.

2. Experimental

2.1. Synthesis and characterization of molybdenum containing silicalite-1

The typical procedure for the synthesis of molybdenum containing silicalite-1 is outlined below.

The silica source (sodium silicate, Merck) was introduced into a polyethylene vessel. The molybdenum

* Corresponding author.

E-mail address: farzaneh@azzahra.ac.ir (F. Farzaneh).

source (molybdenum oxide, Merck) and tetrabutyl ammonium hydroxide (prepared in our laboratory from tetrabutyl ammonium bromide and silver oxide, Merck) were added dropwise and the mixture was stirred for 3 days to obtain a homogeneous solution. The contents were then transferred to a stainless steel autoclave and kept at 443 K for 2 days. The synthesized material was separated, washed with distilled water, dried at 383 K and calcined at 813 K for 8 h.

Infrared spectra of as-synthesized and calcined samples were recorded using Shimadzu 4300 FT-IR spectrometer. Powder X-ray diffraction (XRD) data of calcined samples were collected with a Siemens D5000 diffractometer using Cu K α radiation. Chemical analysis of samples was carried out with Perkin-Elmer spectrometer. Scanning electron micrographs (SEM) of the samples were taken with Zeiss-DSM 960A microscope with attached camera.

2.2. Modification of primary silicalite-1 and zeolite Y

Molybdenum hexacarbonyl (264 mg) was dissolved in chloroform (20 ml). To this solution, was added 200 mg of prepared calcined silicalite and stirred overnight. The mixture was dried at 373 K and kept at 773 K for 5 h. White solid was obtained after releasing of bluish vapour. After washing with distilled water and drying, infrared spectra, XRD data, chemical analysis and SEM of samples were collected.

The modification of zeolite Y was also carried out with similar procedure.

2.3. Epoxidation of olefins

Epoxidation of some olefins, such as cyclohexene, *trans*-2-hexene-1-ol and 2-cyclohexene-1-ol was carried out in a flask equipped with a condenser and

a magnetic stirrer. Dichloromethane, cyclohexene and chloroform were used as solvent. Tertiary butyl hydroperoxide (TBHP) was used as oxidant. In a typical procedure, to a mixture of catalyst (0.2 g) and olefin (0.5 ml) in solvent (5 ml) was added TBHP (0.5 ml, 80% in di-tertiary butyl peroxide). The mixture was then refluxed for 15 h. GC-MS of products resulted from epoxidations after filtration and washing with solvent were recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25).

3. Results

3.1. Synthesis and characterization of silicalite-1 containing small amount of molybdenum

According to the results shown in Table 1, the hydrothermal transformation of gel with molar compositions of run 1 resulted a mixture of silicalite and amorphous phase that its X-ray powder diffraction (XRD) pattern has been shown in Fig. 1(a). By increasing aging and crystallization time (run 2) a pure crystalline phase was obtained and its XRD pattern was similar to that of silicalite-1 (Fig. 1(b)) [15]. By increasing SiO₂/MoO₃ up to 45, no change in product type was observed (run 4). When we used the ratio of 50, a solid obtained which was amorphous. The FT-IR spectrum of the as-synthesized zeolite of run 2 has been given in Fig. 2. This spectrum is similar to that of silicalite-1 [15] and shows the formation of silicalite structure.

On the basis of atomic absorption results, it was found that <0.5% of molybdenum has been incorporated within the zeolite structure. For chemical analysis the zeolite was exchanged with ammonium chloride and then calcined at 813 K and finally washed with distilled water.

Table 1

Typical compositions of the synthesis gel used in the synthesis of molybdenum silicalite

Run no.	SiO ₂ /MoO ₃	TBAOH/MoO ₃	OH ⁻ /SiO ₂	H ₂ O/SiO ₂	Aging time (days)	Crystallization time (h)	Product
1	37	1.5	0.6	352	3	26	Amorphous + silicalite
2	37	1.5	0.6	352	5	48	Silicalite
3	39	1.5	1	197	5	48	Silicalite
4	45	2	1	176	5	48	Silicalite
5	50	1	1	114	5	48	Silicalite

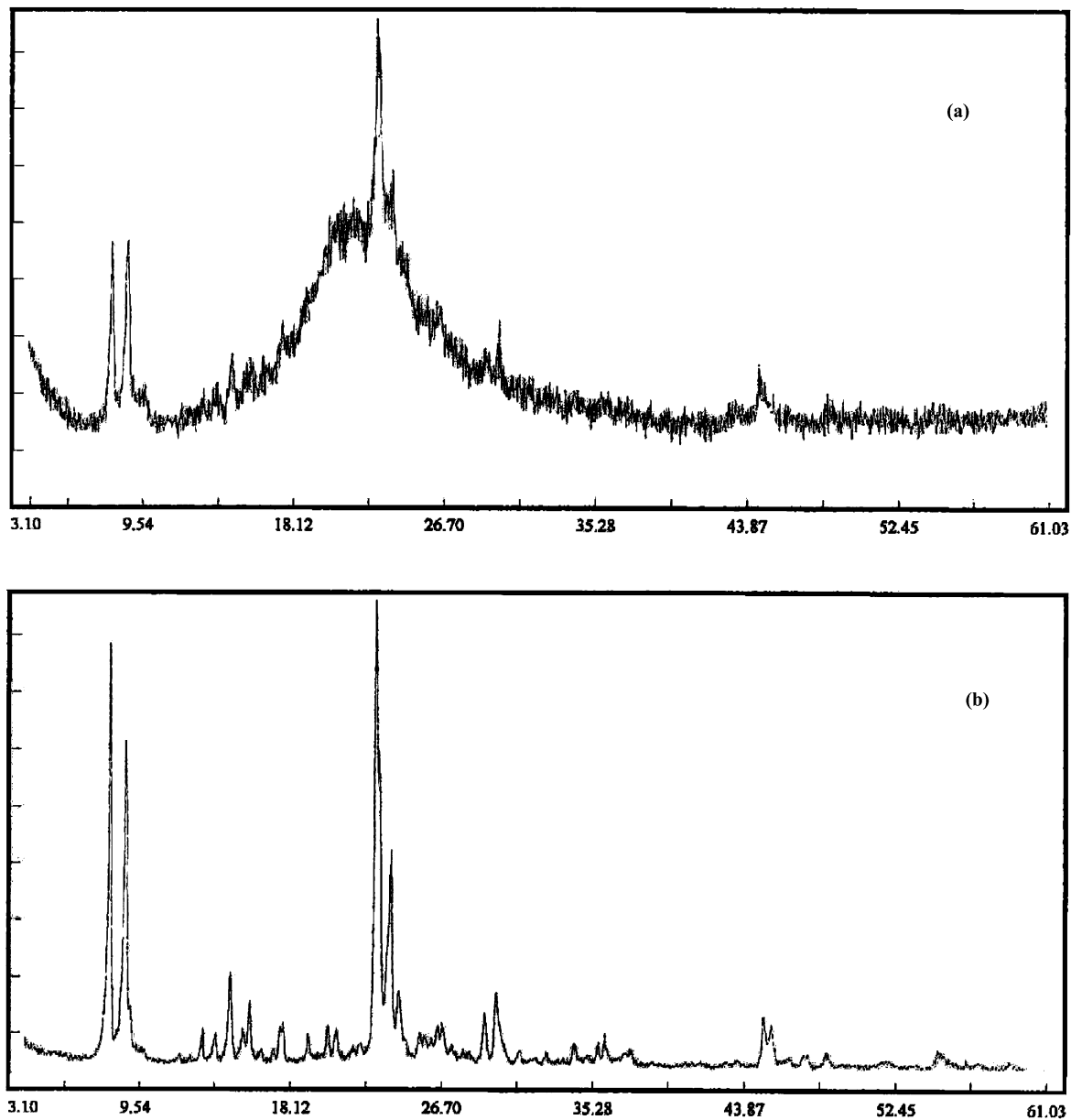


Fig. 1. The XRD patterns of products of: (a) run 1 and (b) run 2.

3.2. Modification and characterization of prepared silicalite-1

Since, the molybdenum content of the zeolite was very low (0.5 wt.%), it was not able to catalyze the epoxidation of olefins efficiently. Thus, the zeolite was

modified in order to increase the amount of molybdenum in its structure.

Modification of prepared zeolite was carried out with solid phase reaction of the hydroxyl groups of zeolite with molybdenum hexacarbonyl at 773 K. During the course of reaction, a bluish solid first forms which

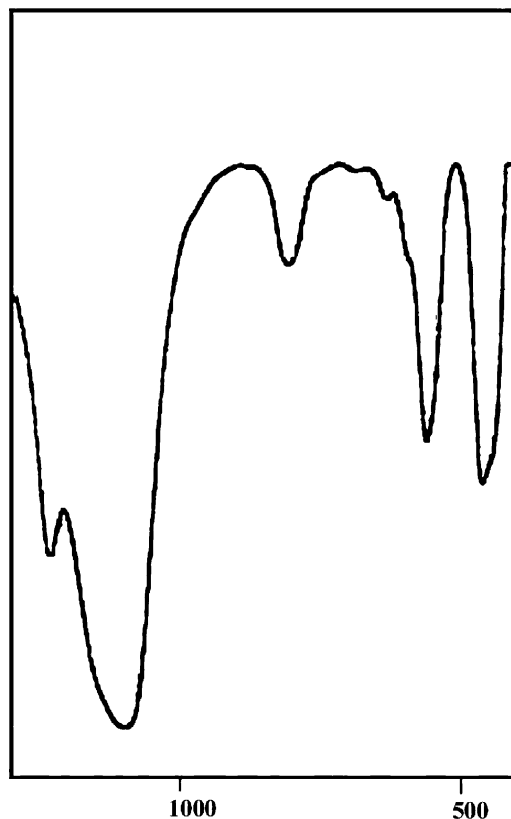


Fig. 2. The FT-IR spectrum of the as-synthesized zeolite.

indicates the production of molybdenum species with oxidation number lower than (+6). As reaction proceeds, the bluish solid turns into a white solid indicating that the molybdenum presents as Mo (+6).

The powder XRD pattern of the product is given in Fig. 3 and shows the formation of silicalite structure. No change in primary structure of zeolite is observed. The FT-IR spectrum of product is shown in Fig. 4. A band at around 989 cm^{-1} which is not present in the spectrum of the silicalite-1 can be assigned to Si–O–Mo asymmetric stretching [13,14]. There is no band in the region of carbonyl group vibration that confirms decomposition of $\text{Mo}(\text{CO})_6$ during the reaction. Atomic absorption studies show 11% incorporation of molybdenum in structure of the zeolite. Fig. 5(a) and (b) show SEMs of primary and modified zeolites, respectively. As observed, the primary crystals of silicalite-1 undergo laminar decomposition during the course of the reaction.

3.3. Modification of zeolite Y

Modification of zeolite Y was carried out similarly. Chemical analysis showed 5% molybdenum incorporation in zeolite Y.

3.4. Catalytic epoxidations

The modified Mo-silicalite and MoY were used as catalysts for epoxidation of cyclohexene, 2-cyclohexene-1-ol and *trans*-2-hexene-1-ol.

3.4.1. Epoxidation of cyclohexene

Oxidation of cyclohexene with TBHP in CH_2Cl_2 in the presence of modified Mo-silicalite and MoY yielded cyclohexene oxide as the main product. 2-Cyclohexene-1-ol, 2-cyclohexene-1-one and dicyclohexenyl ether were also identified as minor products (Table 2). The oxidation results in the presence of modified Mo-silicalite in chloroform and cyclohexene as solvents are given in Table 3.

3.4.2. Epoxidation of 2-cyclohexene-1-ol and *trans*-2-hexene-1-ol

Epoxidation of 2-cyclohexene-1-ol and *trans*-2-hexene-1-ol were carried out with TBHP in the presence of modified Mo-silicalite in CHCl_3 as solvent. The results are shown in Table 4.

4. Discussion

Table 1 shows our results of incorporating of molybdenum into the structure of silicalite using the hydrothermal synthesis method. As mentioned earlier, it was characterized by atomic absorption studies that up to 0.5% of molybdenum was present in the lattice. In order to increase the molybdenum content in the silicalite lattice, modification was carried out with molybdenum hexacarbonyl. Since, the silicalite type zeolites contain internal silanol groups (as structural defects) [16,17], we thought that grafting of molybdenum with these groups would increase its incorporation in the silicalite lattice (Fig. 6).

On the basis of the atomic absorption studies, it was shown that 11% of molybdenum has been incorporated in the prepared sample. When this procedure was carried out on zeolite Y the molybdenum content

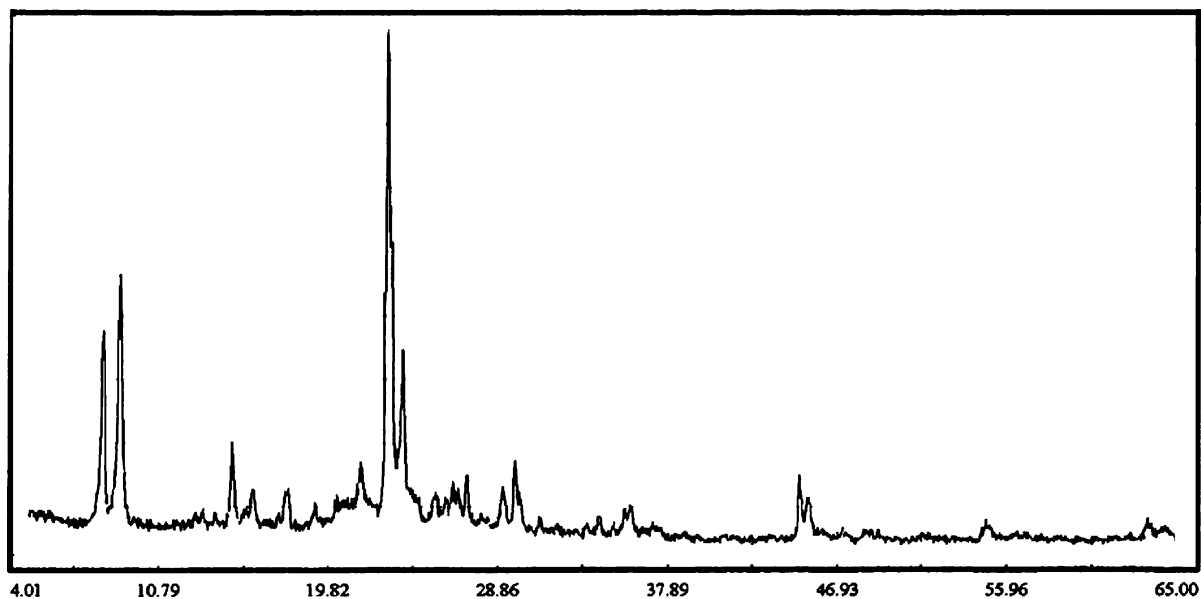


Fig. 3. The XRD pattern of modified molybdenum silicalite.

Table 2
Epoxidation of cyclohexene in CH_2Cl_2

Run no.	Catalyst	Conversion (%) ^a	Selectivity (%)		
			Epoxide	Alcohol + ketone	Ether
1	Modified Mo-silicalite	36	96	0.4	3.7
2	MoY	20.1	59.6	17.2	23.1

^a Based on the amount of TBHP used in the reaction.Table 3
Epoxidation of cyclohexene in CHCl_3 and cyclohexene

Run no.	Catalyst	Solvent	Conversion (%)	Selectivity (%)		
				Epoxide	Alcohol + ketone	Ether
3	Modified Mo-silicalite	Cyclohexene (C_6H_{10})	86.5	73.5	21.1	5.3
4	Modified Mo-silicalite	CHCl_3	93.1	>98	<1	<0.1

Table 4
Epoxidation of 2-cyclohexene-1-ol and *trans*-2-hexene-1-ol

Run no.	Substrate	Catalyst	Conversion (%)	Selectivity (%)		
				Epoxide	Ketone	Ether
5	2-Cyclohexene-1-ol	Modified Mo-silicalite	40	91	3.8	5
6	<i>trans</i> -2-Hexene-1-ol	Modified Mo-silicalite	91	>97	<2	~1

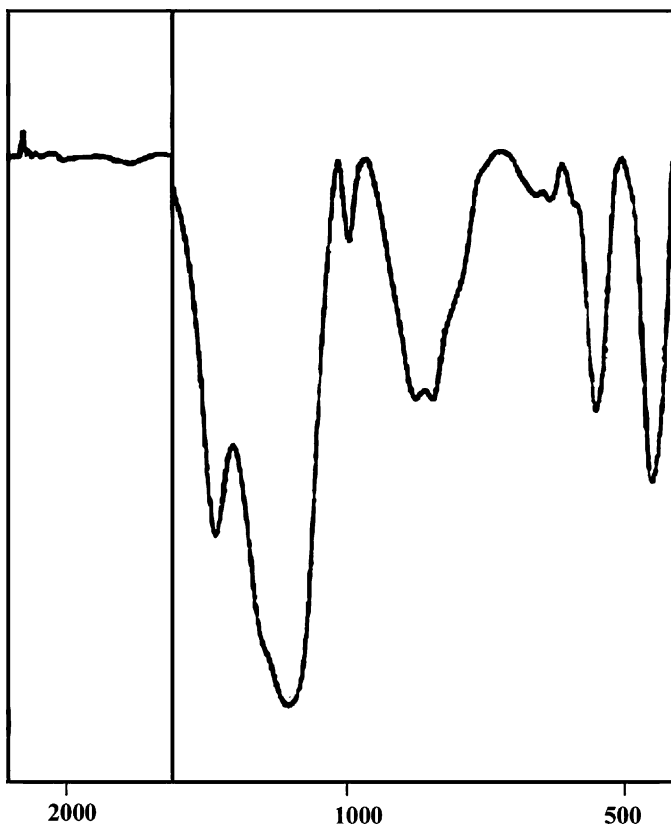


Fig. 4. FT-IR spectrum of modified Mo-silicalite.

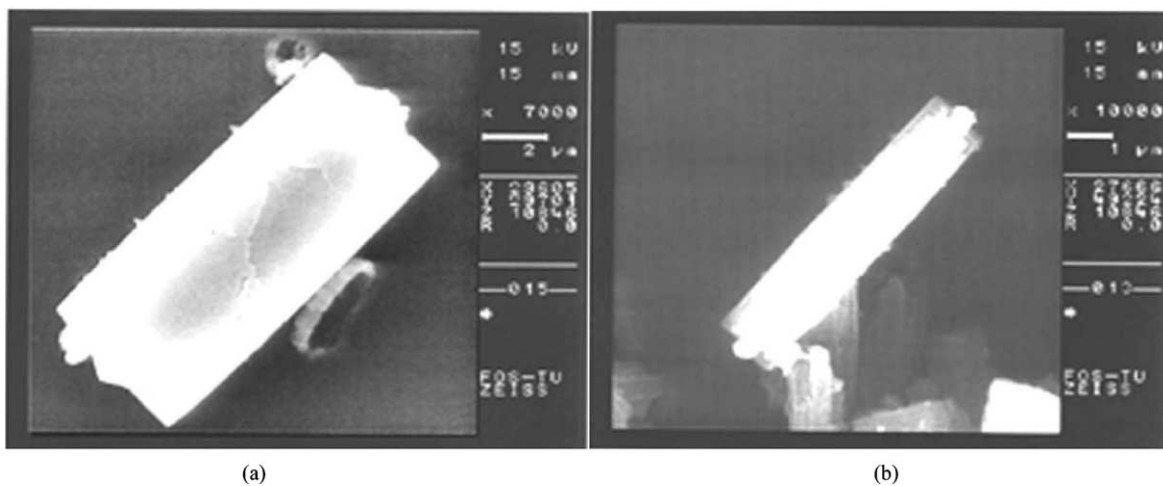


Fig. 5. The SEM of: (a) primary and (b) modified zeolite crystals.

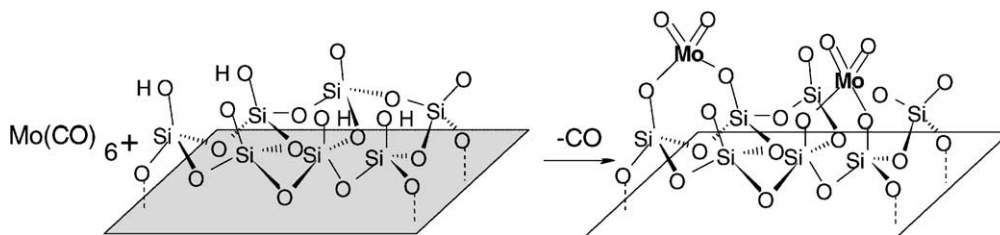


Fig. 6. Grafting of molybdenum into silanol groups of the silicalite.

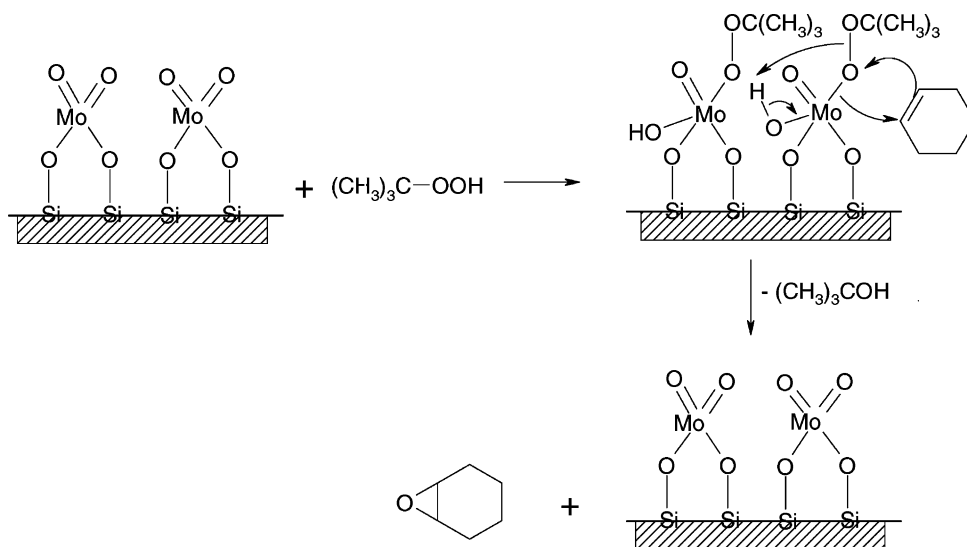


Fig. 7. Mechanism of cyclohexene epoxidation in the presence of modified Mo-silicalite.

was 5%. Therefore, the grafting procedure is recommended whenever the silicalite with defect structure can be treated with transition metal carbonyls. On the basis of results obtained in the oxidation reactions it

can be seen that molybdenum incorporated in silicalite catalyzes the epoxidation of olefins although the efficiency of reaction heavily depends on the percentage of molybdenum incorporated in silicalite (Table 2).

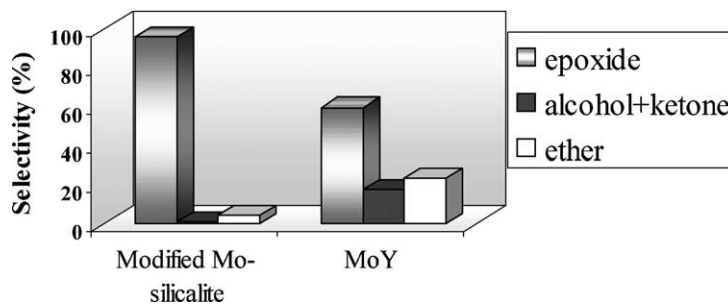


Fig. 8. Results of cyclohexene epoxidation with different catalysts.

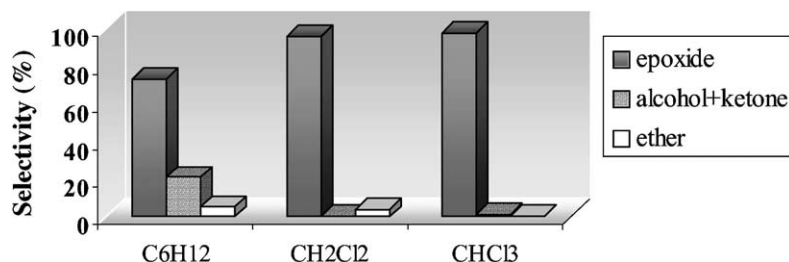


Fig. 9. Effect of solvent change on selectivity of cyclohexene epoxidation.

The observation of moderate to high selectivity of epoxide formation under different conditions represent the moderate oxidation ability of molybdenum and at the same time, its high Lewis acidic character toward the complexation with TBHP in order to transfer the oxidant, oxygen to olefin (Fig. 7) [18]. It is evident that TBHP conversion highly depends on the percentage of molybdenum present in the catalyst. For example, modified Mo-silicalite decomposes TBHP approximately twice faster than Mo-Y (Table 2 and Fig. 8). The observation of lower selectivity in the case of Mo-Y might be attributed to the presence of more Lewis acidic aluminum sites in the catalyst which promote the reaction toward the allylic oxidation [18]. At the same time, its larger cavities allow the easier formation of larger molecules of di(2-cyclohexenyl) ether within the zeolite.

Moreover, the major role of solvent change is observed in TBHP conversion although its minor effect is observed on the selectivity of reaction (Table 3 and Fig. 9). The effect of solvent from the dichloromethane ($\epsilon = 8.9$) to chloroform as less polar solvent ($\epsilon = 4.7$) clearly indicates that the former will occupy the pores and cavities within the period of reaction time more than the latter solvent. This in turn reduces the approach of the substrate and oxidant molecules toward the catalyst active centers inside the cavities.

Table 4 lists the oxidation results of 2-cyclohexene-1-ol and *trans*-2-hexene-1-ol in CHCl_3 . As expected, the TBHP conversion in the case of 2-cyclohexene-1-ol (40%) with more steric demand is lower than *trans*-2-hexene-1-ol (91%) within the same period of time (15 h). The rate enhancement of the latter arises because *trans*-2-hexene-1-ol is linear and can diffuse inside the cavities much more better than the former

and at the same time, the presence of $-\text{OH}$ group binds it better to the cationic center within the cavities.

5. Conclusion

It was shown that treating the silicalite with molybdenum hexacarbonyl could successfully carry out the incorporation of molybdenum in the silicalite lattice. Moreover, the application of this method to zeolite Y showed that molybdenum is incorporated with a lesser extent.

We finally showed that our modified silicalite with 11% of molybdenum could successfully catalyze the epoxidation of the selected olefins with high reactivity and selectivity. Therefore, it is recommended as a suitable catalyst for epoxidation of olefins.

Acknowledgements

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