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Preparation and Characterization of Supported Molybdenum and Tungsten Schiff Base Complexes on MCM-41 as Nanocatalysts for the Epoxidation of Olefins

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Abstract

Two new heterogenized epoxidation nanocatalysts based on molybdenum and tungsten compounds were prepared with covalent grafting of MCM-41 with 3-aminoropropyl trimethoxysilane and subsequent reaction with diphenylphosphinobenzaldehyde and complexation with M (Mo, W)O$_2$(acac)$_2$. X-ray diffraction and nitrogen sorption analyses revealed the preservation of the textural properties of the support as well as accessibility of the channel system despite sequential reduction in surface area, pore volume and pore size. Elemental analyses showed the presence of 0.15 mmol molybdenum and 0.09 mmol tungsten per gram of the catalyst, respectively. Epoxidation of olefins in the presence of M (Mo,W)O$_2$dppb@AmpMCM-41 with tert-butyl hydroperoxide (TBHP) and hydrogen peroxide were examined. **2012 JNS All rights reserved**

1. Introduction

In recent years epoxidation of olefins in the presence of high valent molybdenum and tungsten compounds with oxo ligands have attracted considerable academic and industrial interests [1-12]. These compounds are known to catalyze various industrially valuable processes such as asymmetric olefin epoxidation and alcohol oxidation. In contrast to the molybdenum catalysts one of the difficulties encountered in preparation and catalytic application of tungsten catalysts is the poor availability of suitable starting materials. Typical synthetic routes for

preparation of tungsten compounds start from WO_2Cl_2 (DME) and WO_2 (acac) $_2$ which are difficult to prepare and have poor solubilities in common solvents. Thus tungsten-catalyzed oxo-transfer reactions have been rarely studied compared with the related molybdenum chemistry and relatively few examples have been reported [13-19].

On the other hands, despite the various works on preparation and catalytic investigation of homogeneous molybdenum and tungsten catalysts and also heterogeneous molybdenum catalysts there are few works on the immobilization of tungsten complexes on the solid supports. The most previously reported heterogenized tungsten compounds are prepared with immobilization of peroxo and polyoxotungstates on the silica based supports [17, 18]. There is only one report on preparation and investigation of catalytic activity of supported cis- dioxo tungsten (VI) complexes in the epoxidation of olefins [19].

Also, despite some similarities in the chemistry of molybdenum and tungsten in higher oxidation state (VI), their catalytic behavior in the epoxidation of olefins is not so similar.

Thus in the present work we attempt to prepare two heterogenized molybdenum and tungsten nanocatalysts by covalent attachment of homogeneous complexes with iminophosphine ligand onto the surface of MCM-41. Then investigation and comparison of the catalytic activities of the resulted materials in the epoxidation of olefins with *tert*-BuOOH and hydrogen peroxide revealed the difference in the catalytic behavior of two systems.

2. Experimental

2.1 Materials and characterization

Infrared spectra of the materials were recorded using Shimadzu 8400S FT-IR spectrometer. X-ray diffraction (XRD) data were collected with a Philips Analytical XPert MPD diffractometer using Cu Kα radiation. Chemical analyses of the samples were carried out with Shimadzu ICPS-7000 ver.2 atomic absorption spectrometer. Nitrogen sorption studies were performed at liquid nitrogen temperature using Quanta chrome Nova 2200, Version 7.11 Analyzer. Gas chromatograms were recorded using a gas chromatograph (Shimadzu, GC-2010) equipped with a capillary column and a FID detector.

Cyclohexene, cyclooctene, 1-hexene, hydrogen peroxide (30% in water) and tert-butyl hydroperoxide (TBHP, 80% in di-tertiary butyl peroxide) were purchased from Merck Chemical Company. Diphenylphosphinobenzaldehyde was purchased from Across chemical company.

2.2. Preparation of supported ligand dppb@AmpMCM-41

Preparation of mesoporous molecular sieve MCM-41 was done according to the literature method [20]. Modification of the resulted material with aminoropropyl group was performed after calcinations of the as-synthesized MCM-41 as reported earlier [7]. For preparation of dppb@AmpMCM-41, aminoropropyl modified MCM-41 (2 g) was suspended in 30 ml of ethanol and to the resulted mixture was added excess of diphenylphosphinobenzaldehyde (0.3 g, 1 mmol) and refluxed for 24 hours under nitrogen atmosphere. The solid was filtered, dried and then soxhlet extracted with dichloromethane to remove

the excess of unreacted diphenylphosphinobenzaldehyde and dried under vacuum at 373 K.

2.3. Preparation of the nanocatalysts

2.3.1. Preparation of $WO_2(acac)_2$ and $MoO_2(acac)_2$

For the preparation of $WO_2(acac)_2$ with modification of reported method [21] a mixture of 385 mg (0.87 mmol) of $WO_2Cl_2(DMSO)_2$ (Prepared according to literature method [22]) and 15 ml of acetylacetone was refluxed in 30 ml toluene for 24 hours . After cooling the reaction mixture a pale yellow solid was precipitated that was filtered and washed with acetone. $MoO_2(acac)_2$ was prepared according to the literature method [23].

2.3.2. Preparation of M (M = Mo, W)O_2dppb@AmpMCM-41 nanocatalysts

Preparation of M (M = Mo, W)O_2dppb@AmpMCM-41 was performed with modification of reported method for preparation of cis-dioxo tungsten and molybdenum complexes [6, 13]. Excess of M (M=Mo, W)O_2 (acac) $_2$ (1.5 mmol) was dissolved in 30 ml of methanol and to this was added dppb@MCM-41 (1.5 g, dried in vacuum oven at 423 K). The resulted mixture was refluxed for 48 hours under nitrogen atmosphere. After filtration, the solid product was dried and then soxhlet extracted with a mixture of dichloromethane and methanol (1:1) to remove unreacted M (Mo, W)$O_2(acac)_2$. The M(Mo, W)O_2dppb@AmpMCM-41 material was then dried in vacuum oven at 373 K.

2.4. Catalytic epoxidation

Epoxidation of olefins such as 1- hexene, cyclohexene and cyclooctene purchased from Merck was carried out in a 25 ml round bottomed flask equipped with a condenser and a magnetic stirrer. Tert-butylhydroperoxide (TBHP) (obtained from Merck as 80% in di-tertiary butyl peroxide) and hydrogen peroxide (30% in water) were used as oxidants. In a typical procedure, to a mixture of catalyst (100 mg) and olefin (6 mmol) in acetonitrile (10 ml) was added oxidant(1.5 ml) under nitrogen atmosphere and the mixture was refluxed for appropriate time. Analyses of the products were performed using a gas chromatograph. Products were quantified using isooctane (1 g, 8.75 mmol, Merck) as internal standard. The molybdenum and tungsten content of recycled catalysts was measured with atomic absorption spectrometer after dissolution of the solids in hydrogen fluoride solution.

3. Results and discussion

3.1. Preparation of the M (Mo, W)O_2dppb@AmpMCM-41 catalyst

Although useful precursors for preparation of new dioxomolybdenum (VI) complexes are easily available, there are just a few appropriate starting materials for corresponding dioxotungsten (VI) chemistry. M (M=Mo, W)$O_2(acac)_2$ which are moisture-resistant and relatively soluble starting materials have been used in some works [11, 13] and we choose these compounds as precursors for preparation of our catalysts since complexes of acetylacetonato ligand have proven to be useful in ligand exchange reactions. For preparation of supported catalysts based on similar method in literatures [11, 13] replacement of acac ligands with supported bidentate Schiff base ligand

dppb@AmpMCM-41 results in preparation of supported homogeneous catalysts M(Mo,W)O₂dppb@AmpMCM-41 (Scheme 1). For complete complexation of supported bidentate ligands excess of M(Mo,W)O₂(acac)₂ was used and long reaction time (48 h) was chosen. Soxhlet extraction of the products was performed with mixture of dichloromethane and methanol in order to remove the unreacted M(Mo,W)O₂(acac)₂ from the catalysts.
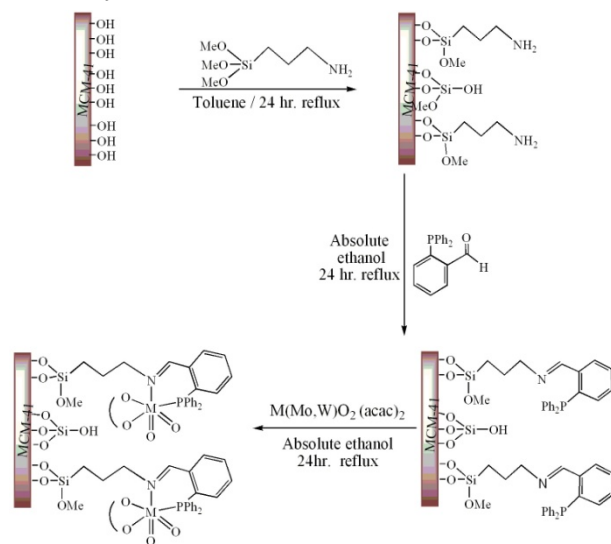
Scheme 1. preparation of supported homogeneous catalysts.

FT-IR spectroscopy provides good evidences for incorporation of the molybdenum and tungsten complexes into the pore structure of the MCM-41. In the FT-IR spectra of the prepared catalysts the C=N stretching vibration bands were shifted to lower wavenumbers with respect to that of uncomplexed materials (Table 1). On the other hand, the observation of two adjacent bands in 900-960 cm⁻¹ range in these materials is characteristic of the presence of cis-dioxotungsten and molybdenum groups as reported earlier [24, 25].

These observations are evidences for the formation of M(Mo,W)O₂dppb@AmpMCM-41 nanocatalyst. Metal content of the prepared materials were determined with ICP-AES chemical analysis (Table 1).

Table 1. Spectroscopic data of the prepared materials

Material	$\upsilon_{W=O}$ (cm⁻¹)	$\upsilon_{C=N}$ (cm⁻¹)	W loading (mmol.g⁻¹)
dppb@AmpMCM-41	-	1650	-
WO₂dppb@AmpMCM-41	920, 958	1608	0.09
MoO₂dppb@AmpMCM-41	906, 944	1617	0.15

3.2. Textural analyses of the prepared nanocatalyst

The powder X-ray diffraction pattern of MCM-41 and M(Mo,W)O₂dppb@AmpMCM-41 materials are shown in Fig. 1a-c. The XRD patterns of the complex grafted MCM-41 materials show a single peak corresponding to the <1 0 0> plane of the hexagonal unit cell. This peak shifts to a lower angle with respect to MCM-41. The absence of higher angle peaks (corresponding to <1 1 0>, <2 0 0> and <2 1 0 > planes) which are present in the parent sample is probably a result of the contrast matching of the silicate framework and organic moieties that are located inside the MCM-41 channels [26].
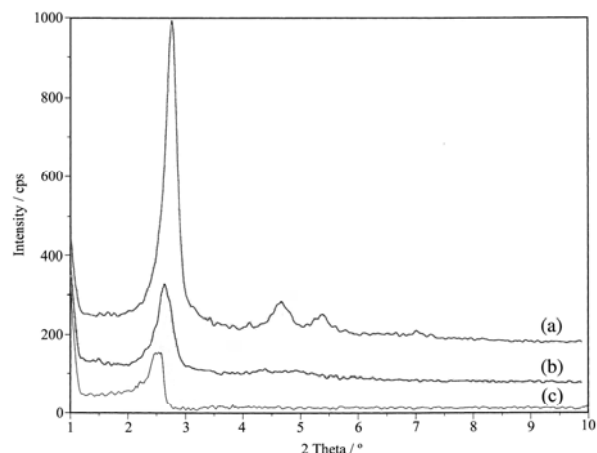
Fig. 1. The XRD patterns of (a) MCM-41, (b) MoO₂dppb@AmpMCM-41 and (c) WO₂dppb @ Amp MCM-41 materials.

The increase in lattice parameter of these materials (Table 2) is an indication of unit cell expansion due to the incorporation of organic groups and metal complexes within the MCM-41.

The mesoporous structure of the prepared materials can be further confirmed by N_2 adsorption/desorption isotherms (Fig. 2a-e). All of the materials except M(Mo,W)O₂dppb@AmpMCM-41 exhibit type IV isotherms (definition by IUPAC) [27], which is characteristic for mesoporous materials and appearance of hysteresis loop resulted from capillary condensation of nitrogen gas inside the mesopores. The supported metal nanocatalysts exhibited type II isotherm which is characteristic of microporous solids. The dramatic decrease in surface area of these materials is due to incorporation of metal complexes into the pores of the mesoporous material. The specific surface

area, total pore volume and pore diameter (calculated with literature method [28]) of the materials are given in Table 2.
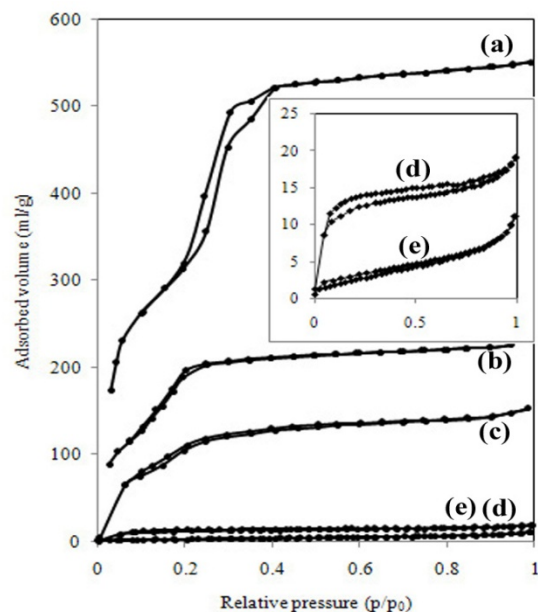
Fig. 2. Nitrogen sorption isotherms of: (a) MCM-41, (b) AmpMCM-41, (c) dppb@AmpMCM-41, (d) WO₂dppb@AmpmCM-41 and (e) MoO₂dppb@AmpMCM-41 materials.

Table 2. Texture parameters of samples taken from XRD and nitrogen sorption studies

Material	Lattice parameter (Å)	BET specific surface area ($m^2.g^{-1}$)	Pore volume ($ml.g^{-1}$)	Average pore diameter (Å)[a]
MCM-41	37.6	1211	0.85	28.2
AmpMCM-41	38.4	753	0.35	19.4
dppb@AmpMCM-41	-	427	0.24	11
WO₂dppb@AmpMCM-41	40.8	40	0.005	10
MoO₂dppb@AmpMCM-41	41.4	11.5	0.005	9.2

[a] The average pore diameter was determined as the ratio of $4V_m$ (pore volume)/S_{BET} (surface area) [28].

3.3. Catalytic epoxidation of olefins

3.3.1. The effect of oxidants on the epoxidation activity

Generally, molybdenum and tungsten compounds catalyze the epoxidation of olefins in the presence of peroxidic reagents such as H_2O_2

and TBHP. The problem in the case of H_2O_2 is the solubility of oxidant (H_2O_2) and substrate (olefin) in the reaction medium. To overcome this problem we conducted the reactions in acetonitrile as the reactants are soluble in this solvent. The results of catalytic epoxidation of cycooctene in the presence of H_2O_2 are given in Table 3. As observed in this

table the tungsten containing nanocatalyst was more active than molybdenum one. This observation is consistent with previously reported behavior of tungsten compounds in the epoxidation of olefins in the presence of H_2O_2 as oxidant [4]. It is concluded that molybdenum compounds are poor nanocatalysts in the epoxidation of olefins in the presence of H_2O_2 as oxidant.

Table 3. Results of catalytic epoxidation of cyclooctene with H_2O_2 in the presence of MO_2 dppb @ AmpMCM-41 nanocatalyst

Catalyst	Time (hours)	Conversion (%)	Selectivity (%)[a]
MoO₂dppb@ AmpMCM-41	3	5	100
	6	21	100
	9	27	100
	21[b]	29	100
WO₂dppb@ AmpMCM-41	3	10	100
	6	67	100
	9	74	100
	21[b]	74	100
No catalyst[c]	12	9	82
MCM-41[d]	12	11	87

Reaction conditions: catalyst (100 mg), olefin (6 mmol), H_2O_2 (1.5 ml), refluxing acetonitrile (10 ml).
[a] Selectivity toward the corresponding epoxide.
[b] Catalytic test after filtration of the catalyst after 9 hours and further refluxing the filtrate for 12 hours.
[c] Reaction was carried out without catalyst.
[d] Reaction was carried out in the presence of MCM-41.

We also investigated the epoxidation of cyclooctene with TBHP as oxidant and the results are given in Table 4. In contrast to the results obtained with H_2O_2, the molybdenum nanocatalyst was more active than tungsten one in the presence of the TBHP as oxidant. This is not surprising as we know from previous literature [1-3] that molybdenum compounds are the best catalysts for the epoxidation of olefins in the presence of TBHP.

On the other hand, epoxidation of cyclohexene and 1-hexene was carried out with H_2O_2 and TBHP in the presence of both nanocatalysts and the results are given in Table 5. As observed again, the tungsten compound was more active catalyst in the presence of H_2O_2 and the molybdenum nanocatalyst was more active in the presence of TBHP.

Table 4. Results of catalytic epoxidation of cyclooctene with TBHP in the presence of MO_2dppb@AmpMCM-41 catalyst

Catalyst	Time (hours)	Conversion (%)	Selectivity (%)[a]
MoO₂dppb@ AmpMCM-41	3	69	100
	6	90	100
	9	99	100
WO₂dppb@ AmpMCM-41	3	10	100
	6	23	100
	9	34	100
No catalyst[b]	12	13	41
MCM-41[c]	12	17	51

Reaction conditions: catalyst (100 mg), olefin (6 mmol), TBHP (1.5 ml), refluxing acetonitrile (10 ml).
[a] Selectivity toward the corresponding epoxide.
[b] Reaction was carried out without catalyst.
[c] Reaction was carried out in the presence of MCM-41.

Comparison of the results of the table 5 with that of Tables 3 and 4 show that cyclooctene was more reactive than cyclohexene and 1-hexene. This is because of the higher electronic density of double bond in the case of cyclooctene, as the mechanism of the epoxidation of olefins in the presence of molybdenum and tungsten compounds are electrophilic oxotransfer [29].

The results with parent MCM-41 and blank (no catalyst) are also included in this Table to clarify the effect of the catalysts.

Stabilities of the prepared metal nanocatalysts were also investigated in separate test in which

epoxidation of cyclooctene was allowed to proceed 9 hours and then reaction mixture was filtered. The filtrate was allowed to further react under the same reaction conditions for another 12 hours. The conversions and selectivities were determined immediately (after 9 h) and also after

21 h (Table 3). It was found that after separation of the nanocatalysts the conversion only slightly increased and then remains constant. Thus, it can be deduced that the catalytic epoxidation is truly heterogeneous in nature.

Table 5. Results of catalytic epoxidation of cyclohexene and 1-hexene with different oxidants in the presence of $MO_2dppb@AmpMCM-41$ nanocatalyst

Catalyst	Olefin	oxidant	Time (hours)	Conversion (%)	Selectivity (%)[a]
$MoO_2dppb@$ AmpMCM-41	cycohexene	TBHP	9	92	98
	1-hexene	TBHP	9	25	99
$WO_2dppb@$ AmpMCM-41	cyclohexene	H_2O_2	9	84	50
	1-hexene	H_2O_2	9	15	97

Reaction conditions: catalyst (100 mg), olefin (6 mmol), oxidant (1.5 ml), refluxing acetonitrile (10 ml).
[a] Selectivity toward the corresponding epoxide. In the case of cyclohexene other products were found to be alcohol, ketone and ether.

4. Conclusion

In this work, we have shown that functionalization of MCM-41 with a bidentate Schiff base ligand and subsequent complexation with molybdenum and tungsten affords truly heterogenized catalysts which are active in catalytic epoxidation of olefins. But it was found that the tungsten compound was more active in the presence of H_2O_2 while the molybdenum compound was more active in the presence of TBHP.

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