

On the Possibility of Mo Substitution in Mesoporous Materials - Cluster Model Calculations

Rohit Kumar Rana and B. Viswanathan*

Department of Chemistry

Indian Institute of Technology, Madras 600 036, India.

Abstract

Scattered Wave SCF- $X\alpha$ calculations were carried out on various Mo-containing cluster models in order to find out the possibility of molybdenum incorporation in a zeolitic framework, containing ring systems as secondary building units. Four and six membered ring clusters were found to stabilize molybdenum in their framework compared to that by linear chain models. Comparison of relative stabilization energies for corner and edge shared MoO_4 moiety favoured the formation of the former one. Calculated HOMO-LUMO electronic transition for tetrahedrally coordinated molybdenum in Mo-containing ring clusters showed a shift of 15 nm from that in Mo-containing linear chain clusters. These results were compared with the experimental results obtained from UV-DRS studies on Mo-MCM-41 catalyst.

Introduction

Zeolites containing transition metal ions in their framework exhibit unique catalytic properties in oxidizing organic substrates with peroxides as oxidant [1-4]. The first example of such catalysts was the titanium silicalite-1 (TS-1), developed by Enichem group [5]. TS-1 has been shown to selectively catalyze a variety of organic substrates with 30% hydrogen peroxide under mild conditions provided the molecule could enter the relatively small pores of the zeolite [1, 5-9]. An important development in this field is the synthesis of transition metal-containing mesoporous (M41S) molecular sieves [10-13]. The benefits of the larger pores are manifested in the oxidation of bulkier substrates with hydrogen peroxide as well as the possibility of using hydroperoxides as the oxygen source.

The catalytic properties of transition metal-containing zeolites or related molecular sieves in oxidation reactions are due to the redox properties the metal sites present in a confined microenvironment. A number quantum chemical studies on titanium silicalites have been attempted in order to find out the precise nature, environment and physico-chemical properties of these active metal centers. De Man and Saucer

[14] carried out *ab initio* calculations on titanium silicalite and showed that, structures with edge shared TiO_4 are unstable and the corner shared tetrahedral titanium species are the preferred ones in the silicalite framework. They assigned the typical 960 cm^{-1} vibrational band to Ti-O-Si antisymmetric stretching mode. Sinclair and Catlow [15] have shown from the Density Functional Theory (DFT) calculations that titanyl groups can be formed from hydroxide forms of four coordinated titanium (IV) sites in the presence of small amount of protic solvents and though they are short-lived, may be responsible for the oxidation reactions. Neurock and Manzer [16] studied the mechanism of alkene epoxidation by hydrogen peroxide on titanium silicate, within the framework of non-local DFT calculations. They have shown that the oxygen closest to the titanium site is the active site for alkene activation.

Oxyfunctionalisation of alkanes and alkenes with hydrogen peroxide on titanium and vanadium silicates has been extensively studied in recent years and the current status of this important reaction has been reviewed by Kumar *et al* [2]. Generally molybdenum-containing catalysts are known to promote a variety of hydrogenation, oxidation and metathesis reactions [17-19]. Molybdenum-containing zeolites have been evaluated for the epoxidation of cyclohexene by Dai

*corresponding author. E-mail: bviswanathan@hotmail.com

and Lunsford [20] and the activity and selectivity of these systems have been shown to be comparable to the more active homogeneous catalysts like $\text{MoO}_2(\text{acac})_2$. In our earlier investigation, it has also been shown that molybdenum incorporation in mesoporous MCM-41 results in unique oxidation activity [21,22]. The aim of the present study is (i) to examine the possibility of incorporation of molybdenum into a zeolite framework either by direct synthesis or by subsequent substitution; (ii) to explore the coordination of molybdenum ions in framework and (iii) to explain the nature of the absorption band at 242 nm, observed in the UV DRS spectra of Mo-MCM-41 [22], using SW Xa calculations.

Methodology and model

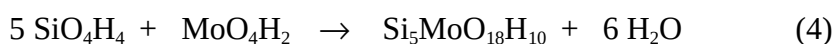
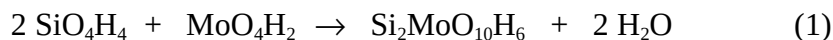
The utility of SCF-Xa method for rapid and bigger cluster calculations of the electronic structure of various complex molecules is well known in the literature [23-26]. In SW Xa method, the molecule or cluster is geometrically divided into three regions: spherical region I surrounding each atom, in the interstitial region II between the spheres and the region III outside a large sphere enclosing the entire molecule. This assumption of muffin-tin potentials allows one to introduce a rapidly convergent partial-wave representation of the molecular orbital wave functions. Though this method makes it inadequate to describe finite molecules, it is found to be useful for the estimation of one-electron spectroscopic properties [27], especially for condensed systems. Therefore, the SW Xa method has been extensively used for the prediction of the electrical, optical and magnetic properties of complex molecules and materials, especially those containing transition elements [28-30].

Spin-restricted Scattered Wave SCF-Xa method was employed for various calculations presented in this communication within the framework of cluster model approximation. Norman overlapping sphere concept was used; the exchange parameters for various elements were taken from Schwarz table [31] and that of outer sphere as a weighted average. Ring systems, which are known to be the building blocks for zeolitic systems, were chosen for cluster models (Fig. 1). In all the clusters the dangling bonds were terminated by hydroxyl groups. Si-O bond distance is taken as 0.161 nm, O-H distance as 0.098 nm and O-T-O (T represents Si or Mo) angle was kept in-between 140-170° depending on the model. In molybdenum containing systems Mo-O bond distance is kept at 0.19 and 0.17 nm for single and double bond respectively for tetrahedrally coordinated sites and 0.19 nm for octahedrally coordinated sites. Radii of all the atomic spheres were optimized to satisfy the Virial theorem. It should be pointed out that the numerical results reported in this communication can best be regarded as indicative of main trend that can be considered in terms of MO perturbations and of their relative magnitudes.

Results and discussion

Energies and relative stabilities

Energies of all the clusters shown in Fig. 1 were calculated and are given in Table 1. Relative stability of molybdenum in various cluster models was evaluated from the energy of formation of the models from corresponding monomeric species. For this purpose the following type of reactions were considered.



Formation energies of the models containing molybdenum were compared with that of pure siliceous systems. Negative values of formation energies comparable to that of pure siliceous system show the possibility of molybdenum incorporation. These energy

changes may be interpreted in terms of the internal energy changes for the above hypothetical processes. If the entropy factor is neglected [32], the order of interaction between molecules in the above processes should provide a minimum energy for the resulting lattice.

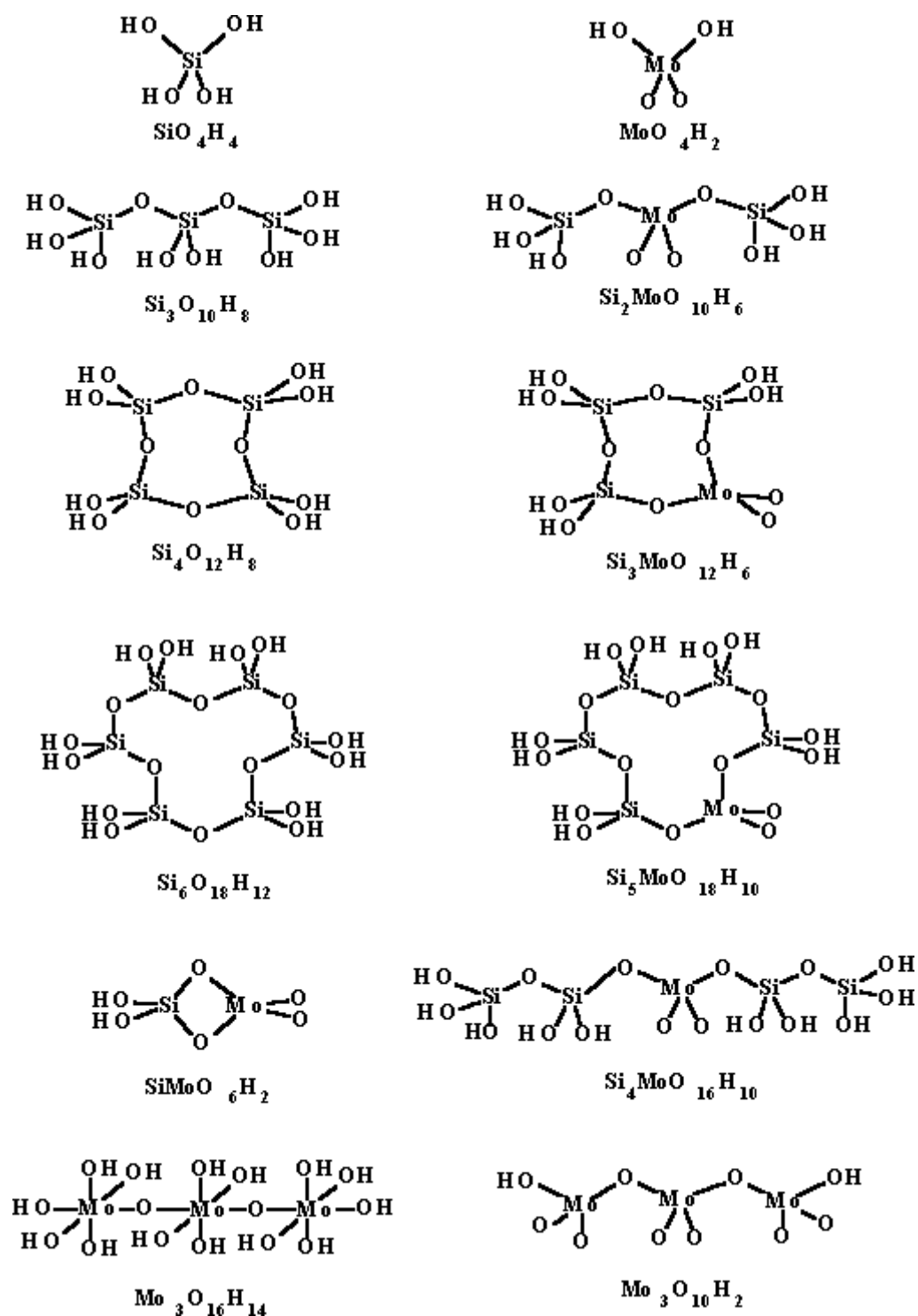


Fig. 1. Schematic representation of various cluster models considered for calculation.

Table 1

Total energies and formation energies of various cluster models.

Model	Geometry	Energy (Ryd.)	Formation Energy ¹ (Ryd.)
SiO ₄ H ₄	Tetrahedron	-1184.6023	-
MoO ₄ H ₂	Tetrahedron	-8554.7468	-
MoO ₆ H ₆	Octahedron	-8858.8402	-
Si ₃ O ₁₀ H ₈	Linear	-3247.4873	-0.767
Si ₂ MoO ₁₀ H ₆	Linear	-10617.994	-1.128
Si ₄ MoO ₁₆ H ₁₀	Linear	-12681.286	-2.303
Si ₄ O ₁₂ H ₈	4-Ring	-4127.352	-3.116
Si ₃ MoO ₁₂ H ₆	4-Ring	-11497.558	-3.177
Si ₆ O ₁₈ H ₁₂	6-Ring	-6191.566	-5.212
Si ₅ MoO ₁₈ H ₁₀	6-Ring	-13561.660	-5.259
SiMoO ₆ H ₂	Bridged	-9432.8365	-0.574
Mo ₃ O ₁₀ H ₂	Linear (Mo in Td.)	-25364.019	-6.865
Mo ₃ O ₁₆ H ₁₄	Linear (Mo in Oh.)	-26277.909	-8.475

¹ Formation Energy = [Total Energy of the products - Total Energy of the reactants] for reactions of the type (a) to (d).

Within the approximations employed this is achieved by successive realization of the most energetically favorable interactions. As follows from the Table 1 the most favorable interactions are for the reactions forming ring systems. Considering the formation energy per T-O-T (T represents Si or Mo) linkages formed, which is given in Table 2, can appropriately compare relative stability of different clusters. The formation

energies per T-O-T linkages for molybdenum in ring systems are found to be more negative than that for molybdenum in linear chain systems. This indicates the stabilization of molybdenum centers in ring systems compared to that in linear chain systems. So, a zeolitic material which generally has ring systems in its framework, can provide a better matrix for molybdenum incorporation than that by amorphous silica.

Table 2

Relative stabilization energy.

Model	Formation energy per T-O-T linkages formed ¹ (Ryd.)	Substitution energy ² (Ryd.)
Si ₃ O ₁₀ H ₈	-0.384	—
Si ₂ MoO ₁₀ H ₆	-0.564	-0.361
Si ₄ MoO ₁₆ H ₁₀	-0.576	-0.365
Si ₄ O ₁₂ H ₈	-0.774	—
Si ₃ MoO ₁₂ H ₆	-0.794	-0.061
Si ₆ O ₁₈ H ₁₂	-0.869	—
Si ₅ MoO ₁₈ H ₁₀	-0.877	-0.047

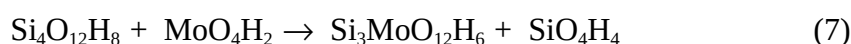
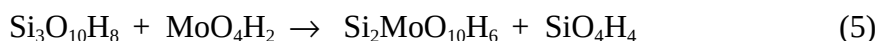
¹ Formation energy (given in Table 1) divided by the number of T-O-T linkages formed in the reactions of the type (a) to (b).

² Substitution Energy = [Total Energy of the products - Total Energy of the reactants] for reactions (e) to (h).

1 Rydberg = 1.31 · 10³ KJ/mole

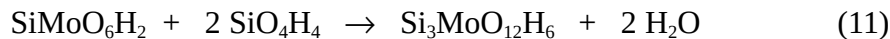
Direct substitution of molybdenum in the silicate matrix is modeled by considering the reaction of MoO_4H_2 with the pure siliceous system to give the corresponding molybdenum-containing system as shown below. It is found that direct substitution is energetically unfavorable for ring systems when

compared to molybdenum in linear chain systems. This can be a proof for the stabilization of molybdenum centers in a silicate matrix through direct synthesis rather than direct substitution in an already prepared silicate matrix of a zeolitic system.



In order to find out the possibility of formation of edge shared molybdenum species instead of corner sharing the following reactions were considered where

the cluster SiMoO_6H_2 having edge shared MoO_4 moiety reacts with SiO_4H_4 to give the corresponding species with corner shared MoO_4 moiety.



The reaction energies for all these cases were found to be negative (Table 3) and it was more so for the ring systems indicating the lower stability of SiMoO_6H_2 cluster. So the edge sharing of MoO_4 moiety is unlikely, which is further supported by the low energy of formation for SiMoO_6H_2 cluster (Table 1). De Man and Sauer have reported similar results for titanium-containing zeolites [14].

Table 3

Stability of edge sharing MoO_4 moiety.

Reaction	Energy of reaction ¹ (Ryd.)
(9)	-0.5552
(10)	-1.7292
(11)	-2.6035
(12)	-4.5575

¹ Energy of reaction = [Total Energy of the products - Total Energy of the reactants] for reactions (9) to (12).

Ground state electronic structure

The SW SCF-Xa computed ground state electronic energy levels of the various molybdenum-containing clusters are represented in Fig. 2. The valence levels can be distinctly grouped into four groups according to the constituent orbitals. Group (1) and (2) comprising of purely Mo 4s and Mo 4p orbitals respectively. Group (3) levels have contributions from Si 3s and O 2s orbitals. The last group (4) constitutes O 2p, Si 3s and Mo 4d bonding and nonbonding orbitals. In group (4) the upper levels are of 2p orbitals of bridged (O_b) and terminal (O_t) oxygens connected to molybdenum and the lower levels are of Si 3p, Mo 4d and O 2p orbitals. The distinct feature of these energy levels is that with increasing cluster size, the valence levels coalesce to form bands.

Table 4 gives the individual atomic orbital contributions to the HOMO and LUMO levels. The atomic orbital distribution indicates that LUMO is mainly constituted of molybdenum 4d orbital, whereas

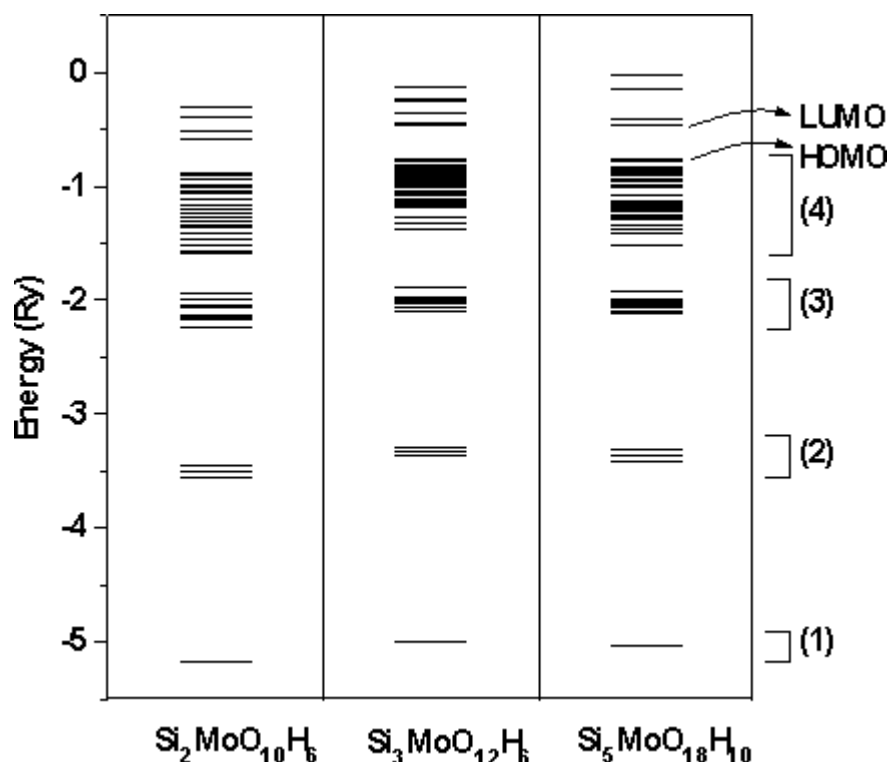


Fig. 2. Molecular orbital energy levels for various molybdenum-containing cluster models.

Table 4
Atomic orbital contributions to HOMO and LUMO.

Model	level	Energy (Ryd.)	atomic orbital contribution		
			Mo ¹ 4d	O2p ² (bridged)	O2p ² (terminal)
Si ₂ MoO ₁₀ H ₆	HOMO	-0.8928	0.0517	0.1421	0.2669
	LUMO	-0.5927	0.5977	0.0309	0.1366
Si ₄ MoO ₁₆ H ₁₀	HOMO	-1.0928	0.0211	0.1564	0.2604
	LUMO	-0.7843	0.5973	0.0171	0.1545
Si ₃ MoO ₁₂ H ₆	HOMO	-0.7684	0.0144	0.0982	0.3124
	LUMO	-0.4629	0.6303	0.0339	0.1004
Si ₅ MoO ₁₈ H ₁₀	HOMO	-0.7556	0.0000	0.0264	0.3560
	LUMO	-0.4695	0.6165	0.0470	0.1073
MoO ₄ H ₂	HOMO	-0.6423	0.0000	0.2776	0.2024
	LUMO	-0.3572	0.6569	0.0291	0.0965
MoO ₆ H ₆	HOMO	-0.5978	0.0000	0.1617	-
	LUMO	-0.3733	0.5956	0.0595	-
Mo ₃ O ₁₀ H ₂	HOMO	-0.7885	0.0017	0.0334	0.4122
	LUMO	-0.5990	0.6242	0.0152	0.0015
Mo ₃ O ₁₆ H ₁₄	HOMO	-0.9529	0.0000	0.0016	0.2437
	LUMO	-0.7654	0.6513	0.0109	0.0052

¹ For Mo₃O₁₀H₂ and Mo₃O₁₆H₁₄, Mo 4d atomic orbital contributions are from all the three molybdenums.

² Atomic orbital contribution from single oxygen atom out of two such equivalent atoms connected to molybdenum (For Mo₃O₁₀H₂, the two terminal oxygens are connected to the central molybdenum and for Mo₃O₁₆H₁₄ there are four such equivalent atoms bridging the central molybdenum and hydrogen).

HOMO has maximum contribution from 2p orbitals of oxygen connected to molybdenum. Considering the type of oxygens contributing to the HOMO and LUMO levels, it reveals that O_t has more contribution than O_b . Thus among the two types of oxygen connected to molybdenum O_t can be the active site during the redox processes. This is in contrast to the results obtained by Taketa *et al.* [33], where their SW SCF-Xa calculations on heteropolyanions of molybdenum show that the bridged oxygen (O_b) is the reactive site. This is because of the octahedral coordination of molybdenum in heteropolyanions. Also it can be seen from the O 2p orbital contributions to HOMO and LUMO of MoO_4H_2 and MoO_6H_6 , where molybdenum is in tetrahedral and octahedral coordination respectively. In case of MoO_4H_4 both HOMO and LUMO have similar contributions from O_b and O_t 2p orbitals and as the hydrogen is substituted by silicate chains (refer to $Si_2MoO_{10}H_6$, $Si_4MoO_{16}H_{10}$, $Si_3MoO_{12}H_6$ and $Si_5MoO_{18}H_{10}$) the contribution from O_b 2p orbital decreases. Whereas,

in case of MoO_6H_6 cluster, both HOMO and LUMO are constituted of purely O_b 2p orbitals.

Atomic charge distributions

The absolute values of Mulliken charges are not well defined in the SW SCF-Xa formalism [34], as it is dependent on the percentage of overlap of the atomic spheres and sphere radii. Therefore the relative trends are only meaningful than the absolute values. Table 5 and 6 give the charges on different atoms in molybdenum-containing and siliceous cluster models respectively. In the monomer the charges are less localized compare to other clusters. Upon molybdenum incorporation a change in the charge distribution is observed similar to the results reported by De Man and Sauer [14] in Mulliken population analyses for titanium incorporation. For molybdenum-containing clusters a decrease in the net charge on molybdenum in linear system from that in monomer is observed. This further decreases from the linear to ring systems though the decrease is smaller. For the bridged

Table 5

Atomic charge distribution in molybdenum-containing cluster models.

Model	net atomic charges			
	Mo	O (bridged)	O (terminal)	Si (nearest neighbor)
MoO_4H_2	1.561	-0.401	-0.481	-
$Si_2MoO_{10}H_6$	1.524	-0.519	-0.361	1.231
$Si_4MoO_{16}H_{10}$	1.530	-0.521	-0.367	1.215
$Si_3MoO_{12}H_6$	1.502	-0.532	-0.318	1.190
$Si_5MoO_{18}H_{10}$	1.503	-0.531	-0.317	1.189

Table 6

Atomic charge distribution in siliceous cluster models.

Model	net atomic charges			
	Si	O (Si-O-Si)	O (Si-O-H)	Si (nearest neighbor)
SiO_4H_4	1.172	-	-0.388	-
$Si_3O_{10}H_8$	1.111	-0.389	-0.298	1.148
$Si_5O_{16}H_{12}$	1.124	-0.399	-0.287	1.155
$Si_4O_{12}H_8$	0.979	-0.393	-0.254	0.979
$Si_6O_{18}H_{12}$	1.019	-0.390	-0.251	1.019

oxygen, connected to molybdenum, there is an increase in the negative charge from monomer to linear and then ring systems. However, for the terminal oxygens, connected to molybdenum, an opposite trend is observed. Net charges on the nearest neighbor silicon atoms are found to decrease from linear to ring systems. Comparison of silicon charges for pure siliceous and molybdenum-containing clusters indicates that upon molybdenum incorporation the charge on silicon increases. As the positive charge on molybdenum and negative charge on the terminal oxygens decrease in the order monomer < linear < ring systems, one should expect an increase in the transition energy for ligand to metal charge transfer transition [35]. This has been discussed in the next section.

HOMO→LUMO electronic transition

From the molecular orbitals, HOMO→LUMO excitation energies were calculated according to the transition state theory [23] for various molybdenum-containing cluster models and are given in Table 6. Atomic orbital contributions from various atoms to the HOMO and LUMO levels are given in Table 4. The atomic orbital distribution indicates that LUMO is mainly constituted of molybdenum 4d orbital, whereas HOMO has maximum contribution from 2p orbitals of oxygen connected to molybdenum. So the HOMO→LUMO excitation is basically ligand-metal charge transfer type. The results thus obtained were compared with the experimental results obtained from UV-DRS studies on Mo-MCM-41.

Though there are other possible transitions, only HOMO→LUMO transition has been considered for comparison purposes. Even if HOMO→LUMO transition were to be symmetry forbidden, there are generally other allowed transitions with almost same energy. The possibility of several transitions with same energy leads to the broadening of the absorption band, which is experimentally observed [20]. It is seen that the LUMO states are mainly contributed by Mo 4d wave functions and to an extent by 2p of terminal oxygens, while the HOMO level is mainly formed from 2p states of oxygen atoms. This type of charge distribution indicates that Mo-O oscillators are involved in the LMCT transition. If the contribution to HOMO were to be pure from oxygen 2p and that of pure Mo 4d then it will give rise to strong LMCT absorption. In view of the poor resolution of the observed absorption spectrum, consideration of an average of the allowed and forbidden transitions may be sufficient for accounting for the observed transitions.

Calculated wavelengths for HOMO→LUMO transitions in the clusters (MoO_4H_2 , $\text{Mo}_3\text{O}_{10}\text{H}_2$) having molybdenum in tetrahedral coordination are found to be lower than that for molybdenum in octahedral coordination (MoO_6H_6 , $\text{Mo}_3\text{O}_{16}\text{H}_{14}$) [35]. There is a red shift from monomer to trimer in both tetrahedral and octahedral coordinated species. This can be seen from the HOMO and LUMO energy levels, as monomer units are added up, both the levels are stabilized with the LUMO being more stabilized compared to HOMO. This stabilization of the LUMO level could be due to the decrease in its antibonding character as the orbital contributions from oxide ligands are decreased.

There was a shift of around 15 nm towards the lower wavelength for Mo in ring systems from Mo in linear chain systems (Table 7).

Table 7
Calculated wavelengths for HOMO-LUMO electron transition.

Model	Wavelength (nm)
MoO_4H_2	280.3
$\text{Mo}_3\text{O}_{10}\text{H}_2$	326.1
MoO_6H_6	362.6
$\text{Mo}_3\text{O}_{16}\text{H}_{14}$	428.4
$\text{Si}_2\text{MoO}_{10}\text{H}_6$	261.4
$\text{Si}_4\text{MoO}_{16}\text{H}_{10}$	257.1
$\text{Si}_3\text{MoO}_{12}\text{H}_6$	243.5
$\text{Si}_5\text{MoO}_{18}\text{H}_{10}$	239.8

Thus the shift of 10 nm towards lower wavelength for the band due to isolated MoO_4 species, which was observed in the UV-DRS spectrum for Mo-MCM-41 [22] with respect to the spectrum for MoO_3 supported on siliceous MCM-41, can be due to the Mo present in a ring system in case of Mo-MCM-41. It can be seen from Table 7 that the transition wavelength shifts towards the lower side as the number of SiO_4 units increases in the clusters. However, this shift from the linear $\text{Si}_2\text{MoO}_{10}\text{H}_6$ cluster to ring systems ($\text{Si}_3\text{MoO}_{12}\text{H}_6$ and $\text{Si}_5\text{MoO}_{18}\text{H}_{10}$) was higher than that from the same linear $\text{Si}_2\text{MoO}_{10}\text{H}_6$ to linear $\text{Si}_4\text{MoO}_{16}\text{H}_{10}$ cluster. This may be because of the difference in the arrangement of SiO_4 units around MoO_4 unit in the two systems. In case of MoO_3 supported

on siliceous MCM-41 the corresponding band can be due to the Mo present in linear chain since the possibility of direct substitution in linear chain systems is energetically more favorable.

Redox properties

From the energies of HOMO and LUMO for various clusters, given in Table 4, redox properties of the corresponding systems can be evaluated. LUMO for ring systems are found to be destabilized compared to that for linear chain systems. This indicates that molybdenum in linear chain has better capacity for oxidation than molybdenum in ring systems. However, because of lower stability of molybdenum in linear chain than Mo-containing ring systems, the later may prove to be a better system for catalytic use.

Conclusions

Formation energies calculated from the total energies obtained from SW SCF-X α calculations on various cluster models containing molybdenum, show that ring systems are more stable than the linear chain systems. However, when molybdenum is directly substituted in an existing silicate matrix, the system is destabilized for ring systems compared to that for linear chain systems. From this it is inferred that for molybdenum incorporation in a silicate matrix, direct synthesis is preferable rather than direct substitution. Corner shared MoO₄ moiety was found to be energetically favorable compared to the corresponding edge shared species. The shift of the band at lower wavelength, seen in the UV-DRS studies on Mo-MCM-41 and supported molybdena on purely siliceous MCM-41, can be explained from the results obtained from HOMO→LUMO electronic transitions calculated for various molybdenum containing clusters. From the comparison of both relative stability and LUMO energy levels, it is found that molybdenum in a ring system will be a better system than the linear chain systems for catalytic use.

References

1. D.R.C. Huybrechts, L. de Bruycker and P.A. Jacobs (1990). *Nature* 345, 240.
2. P. Kumar, R. Kumar and B. Pandey (1990). *Synlett*, 289.
3. M.G. Clerici, G.B. Bellussi and U. Romano (1991). *J. Catal.* 129, 1.
4. A.V. Ramaswamy and S. Sivasanker (1993). *Catal. Lett.* 22, 237.
5. G. Perego, G. Bellussi, C. Como, M. Taramasso, F. Buonomo and A. Esposito in T. Murakami, A. Iijima and J.W. Ward (ed.), *New Developments in Zeolite Science and Technology, Studies in Surface Science and Catalysis* (Elsevier, Amsterdam, 1986), Vol. 28, p. 129.
6. B. Notari in P.J. Grobet, W.J. Mortier, E.F. Vasant and G. Schulz-Ekloff (ed.), *Innovation in Zeolite Material Science, Studies in Surface Science and Catalysis* (Elsevier, Amsterdam, 1988), Vol. 37, p. 413.
7. J.S. Reddy, R. Kumar and P. Ratnasamy (1990). *Appl. Catal.* 58, L1.
8. A. Thangaraj, S. Sivasanker and P. Ratnasamy (1991). *J. Catal.* 131, 394.
9. P.A. Jacobs, Tagungsbericht 9204, *Proceedings of the DGMK Conference, "Selective Oxidations in Petrochemistry"*, Sep. 16-18, 1992, Goslar, Germany, p. 171.
10. A. Corma, M.T. Navarro and J. Perez-Pariente (1994). *J. Chem. Soc., Chem. Commun.*, 147.
11. P.T. Tanev and T.J. Pinnavaia (1995). *Science* 267, 865.
12. K.M. Reddy, I. Moudrakovski and A. Sayari (1994). *J. Chem. Soc., Chem. Commun.*, 1059.
13. W. Zhang, M. Froba, J. Wang, P.T. Tanev, J. Wong and T.J. Pinnavaia (1996). *J. Am. Chem. Soc.* 118, 9164.
14. A.J.M. de Man and J. Sauer (1996). *J. Phys. Chem.* 100, 5025.
15. P.E. Sinclair and C.R.A. Catlow (1997). *J. Chem. Soc., Chem. Commun.*, 1881.
16. M. Neurock and L.E. Manzer (1996). *J. Chem. Soc., Chem. Commun.*, 1133.
17. E.A. Lombardo, M. Lo Jacono and W.K. Hall (1980). *J. Catal.* 64, 50.
18. G.W. Keulks (1970). *J. Catal.* 19, 232.
19. J.J. Rooney and A. Stewart (1977). *Spec. Period. Rep.: Catal.* 1, 277.
20. P.S.E. Dai and J.H. Lunsford (1980). *J. Catal.* 64, 173.
21. R.K. Rana, A.C. Pulikottil and B. Viswanathan in T.S.R. Prasad Rao and G. Murali Dhar (ed.), *Recent Advances in Basic and Applied Aspects of Industrial Catalyst, Studies in Surface Science and Catalysis* (Elsevier, Amsterdam, 1997), Vol. 113, p. 211.
22. R.K. Rana, and B. Viswanathan (1998). *Catal. Lett.* 52, 25.
23. K.H. Jhonson (1973). *Adv. Quantum Chem.* 7, 143.

24. J.C. Slater, Quantum Theory of Molecules and Solids, Vol. 4 (McGraw-Hill, New York, 1974)
25. J.A. Tossell (1975). J. Am. Chem. Soc. 97, 4840.
26. K. Eguchi, T. Seiyama, N. Yamazoe, S. Katsuki and H. Taketa (1988). J. Catal. 111, 336.
27. W. Kohn, A.D. Becke and R.G. Parr (1996). J. Phys. Chem. 100, 12974.
28. K.C. Mishra, I. Osterloh, H. Anton, B. Hannebauer, P.C. Schmidt and K.H. Johnson (1997). J. Mater. Res. 12 (8), 2183.
29. F. Guillot, C. D  zarnaud-Dandine and M. Tronc (1997). Chem. Phys. 224 (2-3), 281.
30. S. Matsubayashi, F. Yakabe, M. Kurimoto, K. Shinagawa, T. Saito and T. Tsushima (1998). J. Magn. Magn. Materials 177-181 (1), 249.
31. K. Schwarz (1972). Phys. Rev. B5, 2466.
32. A.G. Pelmeschikov, G.M. Zhidomorov, S. Beran and J. Tino (1987). J. Phys. Status. Solidi. A 99, 57.
33. H. Taketa, S. Katsuki, K. Eguchi, T. Seiyama and N. Yamazoe (1986). J. Phys. Chem. 90, 2959.
34. D.A. Case and M. Karplus (1977). J. Am. Chem. Soc. 99, 6182.
35. A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd. Ed. (Elsevier, Amsterdam, 1984), p.207.

Received 18 January 2000.