JOURNAL OF CATALYSIS **119**, 400–414 (1989)

Polyoxometallates as Models for Oxide Catalysts

Part I. An UV–Visible Reflectance Study of Polyoxomolybdates: Influence of Polyhedra Arrangement on the Electronic Transitions and Comparison with Supported Molybdenum Catalysts

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Received November 28, 1988; revised March 15, 1989

Diffuse reflectance spectroscopy is a technique commonly used to determine the symmetry and the environment of transition metal ions in supported oxide catalysts by comparison with reference samples either in solid or liquid state. However, the examination of model polyoxomolybdates with well-established structures such as $Na_2MoO_4 \cdot 2H_2O$, $TBA_2Mo_2O_7$ (TBA = tetrabutylammonium), α-$TBA_4Mo_8O_{26}$, α- and β-$TBA_4SiMo_{12}O_{40}$, $TBA_2Mo_6O_{19}$, $H_8As_4Mo_{12}O_{50}$, α-$TBA_6P_2Mo_{18}O_{62}$, etc., indicates that earlier attributions of the UV–visible bands of supported Mo catalysts may be reconsidered. It is shown that Mo dispersion (Mo cluster size and distance between clusters) or Mo–support interactions have more influence than local Mo symmetry. Indeed, analysis of experimental spectra of polyoxomolybdates indicates that:

—in contrast to an earlier belief, the effect of the local symmetry on the lowest energy transition band of ligand–metal charge transfer is negligible compared to the effect of the more distant environment of the metal.

—a broadening and a red shift of this band are observed when cluster size increases, or when the polarizing effect increases and/or the size of the counter-cation decreases. On the contrary, a narrowing and a blue shift are observed when a polyoxomolybdate is supported, i.e., when its dispersion increases.

—the increasing effects of the different parameters may be classified as follows:

$$\text{local symmetry} < \text{overall symmetry} < \left\{\begin{array}{l}\text{condensation degree (polyanion size)}\\ \text{polarizing effect of the counter-cation}\\ \text{size of the counter-cation}\\ \text{dispersion on a support}\end{array}\right.$$

—UV–visible spectra do not distinguish the effect of strong interaction between Mo (via oxo-bonding Mo–O–Mo) exhibited by the influence of polyanion size from weaker effects such as polyanion interaction (for example, via hydrogen bonding), occurring when the counter-cation is small enough, or from electrostatic effects due to polarization by the counter-cation.

INTRODUCTION

Diffuse reflectance spectroscopy is commonly used to determine the symmetry and the environment of supported transition metal ion catalysts (*1–13*). In the case of catalysts containing Mo, the usual approach consists of the comparison of spectra of catalysts with those of polyoxomolybdate model compounds in the UV–visible range. A number of authors have claimed that the frequency range of the electronic transitions allows determination of the Mo(VI) symmetry (see the literature review below). However, the same spectra

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0021-9517/89 $3.00

TABLE 1

Ligand–Metal Charge Transfer Band Position of Model Molybdate Compounds Generally Used as References

Compounds	Origin and/or treatment	Coordination		UV–Visible spectra band position (nm)				Ref.
		Mo	Ref.					
Na_2MoO_4[a]								
pH 0.5 $H(MoO_4)^-$	BDH Analar	C_{3v}	(*16*)	210	230	260		*17*
pH 1 $H(MoO_4)^-$ or H_2MoO_4	Unknown	C_{3v}	(*16*)	213		280		*12*
pH 9 $(moO_4)^{2-}$	Unknown	Tetra	(*16*)	210	230			*16*
pH 11 $(MoO_4)^{2-}$	BDH Analar	Tetra	(*17*)	210	230			*17*
pH 11 $(MoO_4)^{2-}$	Unknown	Tetra	(*17*)	206	220			*12*
$Na_2MoO_4 \cdot 2H_2O$	BDH Analar	Tetra	(*18*)		225	260		*1*
	Commercial	Tetra	(*18*)		225	260		*5*
	Calcined/500°C	Tetra	(*18*)			270		*3*
$CaMoO_4$	Calcined/500°C	Tetra	(*19*)			270		*3*
$Na_2Mo_2O_7$	Synthesized	Tetra + octa	(*21*)			270–330		*3*
$Mo_4O_{10}(OH)_2$	Synthesized	Sq. pyr.	(*22*)				375	*3*
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	BDH Analar	Octa	(*23, 24*)		225	275	300	*1*
MoO_3	BDH Analar	Octa	(*25*)		220	270	300	*1*
	Commercial	Octa	(*25*)			270	330	*3*
	Calcined/500°C	Octa	(*25*)				320	*4*
	Unknown	Octa	(*25*)			270(sh)	320	*5*

Note. Structures are usually distorted to various extents, depending on the compound.

[a] All the compounds are in solid state except this one.

have often received different assignments, since the model compounds used as references were not always identical.

Since the Mo(VI) ion has a d^0 electronic configuration, the only absorption band which can occur in the UV–visible range of the electronic spectra is due to the ligand–metal charge transfer (LMCT): $O^{2-} \rightarrow Mo^{6+}$. This type of band is usually observed between 200 and 400 nm. The energy of the electronic transitions strongly depends on the ligand field symmetry surrounding the molybdenum center. For oxo-ligands, a more energetic transition is expected for a tetrahedral Mo(VI) than for an octahedral Mo(VI) (*15*).

Israeli (*16*) and Bartecki and Dembicka (*17*) reported the first results concerning the electronic spectroscopy of molybdates in solution, e.g., $Na_2MoO_4 \cdot 2H_2O$. Since then, their spectra (Table 1) have often been used as references in the interpretation of the spectra of solids.

To our knowledge, Ashley and Mitchell (*1, 2*) were the first to employ diffuse reflectance spectroscopy for studying the nature of the molybdenum environment in Mo/Al_2O_3- and $Co–Mo/Al_2O_3$-supported catalysts. Solid model compounds such as sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), molybdenum trioxide (MoO_3), or ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) were used as references (Tables 1 and 2). The authors concluded that the two bands at 225 and 260 nm are characteristic of tetrahedral molybdate and that the additional band at 300 nm is due to octahedral species.

Until 1978, the absorption bands at 260–280 nm were commonly attributed to tetrahedral MoO_4 while the bands at 300–320 nm were assigned to octahedral MoO_6 (*1–9*). Jeziorowski and Knözinger (*10*) were the first to reconsider critically the band attributions, taking into account not only the local symmetry but also the molybdenum environment (see below).

TABLE 2

Diffuse Reflectance Data and Their Assignments for Some Supported Molybdenum Catalysts

Mo catalysts				UV-visible spectra						Model compounds[b] and Ref.
Ref.	samples	Mo (wt%)	Precursor[a]	Position (nm)					Assignment	
(*1, 2*)	Mo/Al$_2$O$_3$	2	Heptamol.[c]	222		263			Tetra	Na$_2$MoO$_4$[d], MoO$_3$,
		19	MoO$_3$					320	Octa	heptamol.
(*3*)	Bi-Mo	9–48	H$_2$MoO$_4$ or				270		Tetra	Na$_2$MoO$_4$, MoO$_3$,
			heptamol.					333	Octa	heptamol., CaMoO$_4$,
										Na$_2$Mo$_2$O$_7$
(*4*)	Mo/Al$_2$O$_3$	<2	Heptamol.		235		280–295		Tetra	Na$_2$MoO$_4$, MoO$_3$,
		16.7	Heptamol.					320–325	Octa	(MoO$_4$)$^{2-}$, (HMoO$_4$)$^-$
										in solution
	Mo/MgO	0.2–16.7	Heptamol.				265–270		Tetra	(*1, 16, 17*)[e]
(*5*)	Mo/Al$_2$O$_3$	2	Heptamol.	225			260–280		Tetra	Na$_2$MoO$_4$,
		30	Heptamol.	225			260–280		Tetra	(K$_2$O, 2MoO$_4$),
								300–320	Octa	MoO$_3$ (*1, 2, 4*)
(*6, 7*)	Mo/SiO$_2$	0.15–5	MoCl$_5$			250–280			Tetra	
		10	Heptamol.				270–330		Octa	
	Mo/Al$_2$O$_3$	2–12	MoCl$_5$ or			260–270			Tetra	Na$_2$MoO$_4$, MoO$_3$
			heptamol.					300–320	Octa	(*1, 2, 4, 5*)
	Mo/MgO	1–13	MoCl$_5$		235–40			300–310	Octa	
		2–5	Heptamol.				260–280		Tetra	
								300(sh)	Octa	
(*8*)	Mo/SiO$_2$	1.7	Mo(π-C$_3$H$_5$)$_4$				290		Tetra	Na$_2$MoO$_4$, MoO$_3$
	Mo/Al$_2$O$_3$	1.7	Mo(π-C$_3$H$_5$)$_4$				281		Tetra	(*3, 5, 6*)
(*9*)	Mo/SiO$_2$	2–15	Heptamol.					300	Polymol.[f]	Na$_2$MoO$_4$, MoO$_3$,
									Tetra	heptamol.
(*10*)	Mo/Al$_2$O$_3$	1–3	Heptamol.		230–250				Tetra	(Mo$_7$O$_{26}$)$^{6-}$, pH6,
							270–295		Mo–O–Mo	(MoO$_4$)$^{2-}$, pH 8
										(*2, 4, 5, 17*)
(*26*)	Mo/Al$_2$O$_3$	0.8	Heptamol.	225			270		Tetra	Na$_2$MoO$_4$, MoO$_3$,
		6.4–11.3	Heptamol.	220			270	300(sh)	Octa	heptamol.
(*12*)	Mo/Al$_2$O$_3$	3	Heptamol.	210	226				Tetra	(MoO$_4$)$^{2-}$, (HMoO$_4$)$^-$
							290		Polymer	(*16, 17*)
(*13*)	Mo/SiO$_2$	0.17–5	Mo(π-C$_3$H$_5$)$_4$			250–260			Tetra	
							280–290		Dimer, Mo=O	
								320–340	Mo–O–Mo	
										Na$_2$MoO$_4$, MoO$_3$
	Mo/Al$_2$O$_3$	0.67–2	Mo(π-C$_3$H$_5$)$_4$		235				Tetra	(*7*)
							280		Tetra or dimer	
									or telomer	
		5–8	Mo(π-C$_3$H$_5$)$_4$				250–300		Polymer	
(*27*)	Mo/Al$_2$O$_3$	1–10	Heptamol.	210	230				Tetra	
					230		280		Octa	(MoO$_4$)$^{2-}$, (HMoO$_4$)$^-$,
		30–40	Heptamol.		230			320	Distort. octa	Na$_2$MoO$_4$, MoO$_3$
						255			Mo–O–Mo	(*1, 2, 4, 5, 17*)
		>60	Heptamol.					340	Free MoO$_3$	

Note. All the samples are calcined at 500°C in air or oxygen, except in Ref. (*8*).

[a] Precursor for catalysts preparation.

[b] Model compounds used as references.

[c] Heptamol. = (NH$_4$)$_6$Mo$_7$O$_{24}$, 4H$_2$O.

[d] In fact, Na$_2$MoO$_4$, 2H$_2$O.

[e] Model-compounds used as references were taken from the indicated literature.

[f] Polymol. = polyoxomolybdate.

(*1*) *Conflicting Interpretations of Diffuse Reflectance Bands* (*Table 2*)

Instead of attributing the band at 270–295 nm of Mo/Al$_2$O$_3$ to tetrahedral MoO$_4$ as usual (*1–8*), Jeziorowski and Knözinger (*10*) assigned it to a LMCT transition in Mo–O–Mo bridge of polymerized molybdate while Roberge *et al.* (*13*) attributed it either to an oxomolybdenum dimer or to the Mo=O groups of a polymer with a band at 320–340 nm assigned to Mo–O–Mo bridges also present. We can see that the band position attributed to Mo–O–Mo bridges also changes according to the authors: 280–290 nm (*10*) or 320–340 nm (*13*). We also note that the band shifts in the model compounds are of the same order of magnitude as those observed for supported Mo catalysts with different thermal treatments or Mo contents (Tables 1 and 2).

(2) *Validity of the Comparison of Absorption Solution Spectra with Diffuse Reflectance Spectra of Solids*

The use of aqueous or acidified molybdate as reference compounds is very questionable because of the ability of molybdate ions to change their coordination and to polymerize (*28, 29*). For example, in aqueous solution, the monomeric tetrahedral $(MoO_4)^{2-}$ polymerizes, leading to the formation of oligomeric species, especially heptamer $Mo_7O_{24}^{6-}$ (*30a*). At pH 9 and even at pH 11, monomeric tetrahedral $(MoO_4)^{2-}$ cannot exist alone (*30b, 30c*), at variance with some other statements (*16, 17,* Table 1). Furthermore, $(MoO_4)^{2-}$ is protonated in solution and its coordination sphere is solvated by H_2O which leads to an increase in the Mo coordination number (*31*). For most molybdates in solution, the environment of the molybdenum centers may be regarded as a distorted octahedron even if, formally, they possess four oxygen ligands (*32*). Furthermore, it must be noted that the spectrum attributed to $(HMoO_4)^-$ in Ref. (*17*) is more easily explained in terms of a mixture of $(MoO_4)^{2-}$ and of $(Mo_6O_{19})^{2-}$.

On the other hand, the mean position of the absorption bands may depend on the size of sample particles.

(3) *Validity of the Comparison of the Absorption Band Position of Solid Model Compounds with Different Local and Overall Symmetries*

The solid model compounds used for comparison with supported molybdenum are often $Na_2MoO_4 \cdot 2H_2O$ with tetrahedral Mo(VI) and MoO_3 or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ with octahedral Mo(VI) (Table 2). Both their local and overall symmetries are different. $(MoO_4)^{2-}$ anions in $Na_2MoO_4 \cdot 2H_2O$ may be considered as isolated from each other by Na^+ (Fig. 1a, and 1b). On the contrary, MoO_3 possesses an infinite structure constituted by octahedral Mo(VI) which are joined by sharing edges to form zig-zag-shaped rows; the rows are connected by the vertices of octahedra to form layers (Fig. 1c). The compound $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ is composed of 7 MoO_6 octahedra linked by sharing oxo-edges (Fig. 1d). From Table 1, it can be seen that the energy of the LMCT transition of those last two compounds is slightly different, not only because the Mo local symmetry is not the same, i.e., the octahedral distortion is different, but also because the overall symmetry of the molybdenum environment is not the same.

(4) *Variations in the Band Position of Model Compounds*

The results summarized in Table 2 clearly show that many structural parameters influence light absorption by supported catalysts. The band position of MoO_3, $Na_2MoO_4 \cdot 2H_2O$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ differs according to the authors (Tables 1 and 3) and depends on the origin (commercial or synthetic), on the hydration degree, and on the thermal pretreatment to which the model compounds are subjected. The influence of the hydration degree is clearly shown by the two molybdenum oxides MoO_3 and $MoO_3 \cdot 2H_2O$ (Fig. 2, Table 3). Indeed, water molecules in $MoO_3 \cdot 2H_2O$ are located between the sheets formed by the molybdenum centers without interaction with oxygen atoms and can also act as ligands (*33, 34*). Therefore, the very distorted MoO_6 octahedron in anhydrous MoO_3 becomes a more regular octahedron $MoO_5(OH_2)$ in the dihydrate. On the contrary, the spectrum of sodium molybdate $Na_2MoO_4 \cdot 2H_2O$ does not change when the

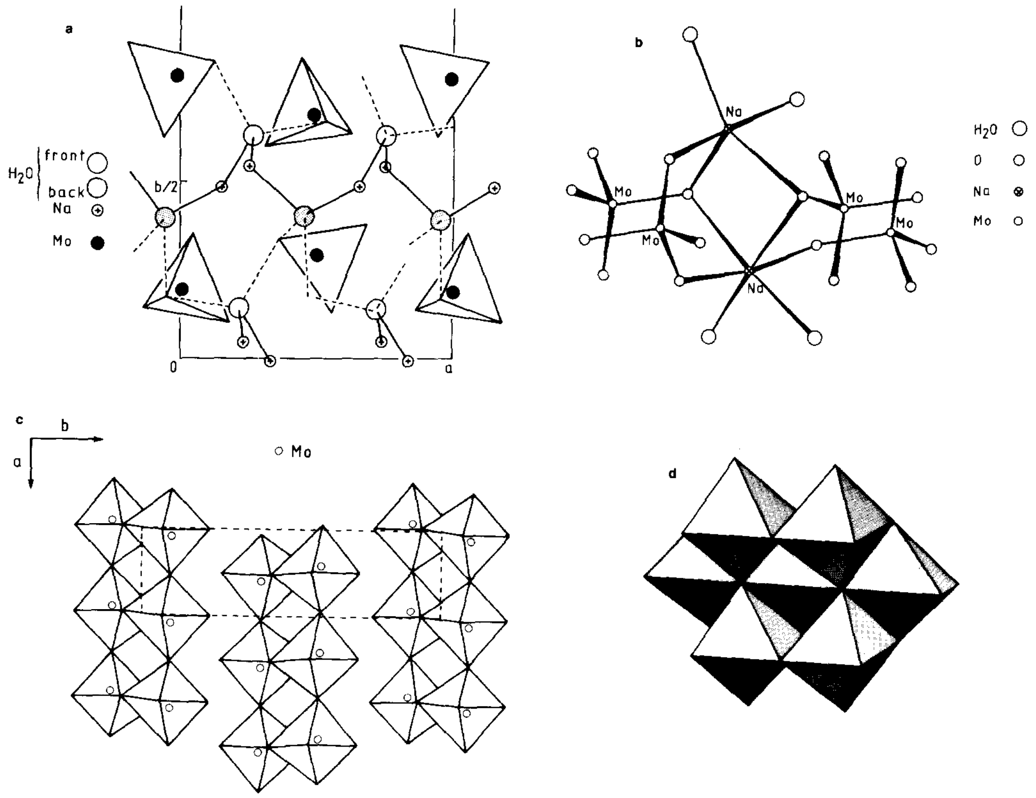

FIG. 1. Structures of: (a) $Na_2MoO_4 \cdot 2H_2O$ viewed along *c* axis (bonds between Na^+ and $(MoO_4)^{2-}$ are omitted as well as Mo–O bonds); (b) $Na_2MoO_4 \cdot 2H_2O$ oxygen coordination around the 2 Na^+ (reproduced from Ref. (*18*)); (c) MoO_3 viewed along [001] axis (the extension of one unit cell is indicated by dashed lines; reproduced from Ref. (*25*)); (d) $(Mo_7O_{24})^{6-}$ in $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, schematically drawn as a regular polyhedron (reproduced from Ref. (*23*)).

compound is hydrated or calcined (Tables 1 and 3). This is probably due to weak interactions between molybdenum centers and water molecules in the hydrated form (Fig. 1a). Indeed, the loss of water is observed at 120°C during TGA.

TABLE 3

Position of the Ligand–Metal Charge Transfer Bands $O^{2-} \rightarrow Mo^{6+}$ of Model Molybdate Compounds (This Work)

Compounds	Origin or treatment	Coordination		Band position (nm)			
		Mo	Ref.				
$Na_2MoO_4 \cdot 2H_2O$	Prolabo	Tetra	(*18*)	260			
	Calcined/500°C	Tetra	(*18*)	260			
$TBA_2Mo_2O_7$	Synthesized (*20*)[a]	Tetra	(*20, 21*)	270			
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Prolabo	Octa	(*23, 24*)		280	305	
MoO_3	Prolabo	Octa	(*15*)	255			350
$MoO_3 \cdot 2H_2O$	Synthesized (*33*)[a]	Octa	(*34, 35*)		280		340

[a] References of the papers where synthesis is described.

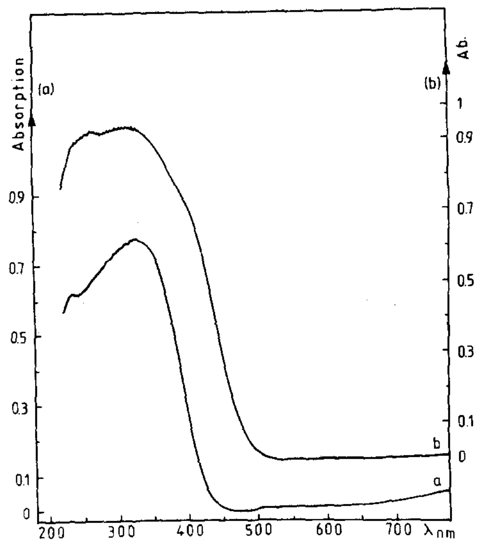

FIG. 2. Diffuse reflectance spectra of: (a) MoO_3, (b) $MoO_3 \cdot 2H_2O$.

(5) *Influence of the Catalyst Support*

Blank experiments with the catalyst support alone are barely mentioned in the papers. For example, the molybdenum absorption bands of Mo/SiO_2 catalysts are found to overlap with that of silica at 260 nm (*36–38*). In consequence, it is impossible to distinguish the Mo bands in that frequency range if the silica band is not subtracted.

All these remarks indicate that comparison of the spectra of supported species with those of known model compounds is not a trivial matter and interpretations must be made with care. We propose to reconsider the interpretations of UV–visible spectra of supported molybdenum catalysts by investigation of the spectra of some polyoxomolybdates with well-known structures. Comparison with these polyoxomolybdates is an intricate problem since two important parameters change from one polyanion to another: the site symmetry of the Mo(VI) centers and the Mo–Mo interactions which depend on the polyanion size. The polyoxomolybdates result from the condensation of molybdate ions in acidic solutions which leads to the formation of bridging oxygens between molybdenum centers. Although the symmetry of the inner coordination sphere of Mo centers, the so-called local symmetry, is formally C_s because it is always slightly distorted, one can consider it to a first approximation as either tetrahedral (MoO_4) or octahedral (MoO_6). In polyoxomolybdates, the molybdenum polyhedra are connected by their vertices, edges, or faces. Some of the molybdenum centers are packed to form intermediate clusters like the trimetallic cluster Mo_3O_{13} with an intermediate symmetry, C_{3v}. These clusters can be arranged by sharing edges or vertices in an overall symmetry T_d, C_{3v}, D_{4h}, etc. It is therefore of interest to study the UV–visible spectra of polyoxomolybdates in order to establish the influence on the band position of the various types of symmetry (local, intermediate, and overall) and of the polyoxomolybdate size.

We have also carried out molecular orbital calculations in Part II of this work (*14*) to support our inferences from the experimentally measured spectra.

EXPERIMENTAL

(*1*) *Sample preparation.* The various polyoxomolybdates used in this study were synthesized according to previous methods (Tables 3 and 4) or purchased from Prolabo, France.

Silica-supported molybdosilicic acid ($H_4SiMo_{12}O_{40} \cdot 14H_2O$) was prepared at room temperature by wet impregnation of silica (Spherosil XOA400, 400 m^2/g, Rhône Poulenc, France) with an aqueous solution of molybdosilicic acid, followed by drying at 100°C. The sample loading is 30% Mo in weight which corresponds to the theoretical loading of the monolayer, on the basis of a close packing arrangement of $(SiMo_{12}O_{40})^{4-}$ (polyanion diameter: 11 Å (*44*, *45*)).

The different counter-cations of the polyanions used in this study were:

—TBA^+: tetrabutylammonium, $(n\text{-}C_4H_9)_4N^+$

TABLE 4

Local, Intermediate, and Overall Symmetry of Some Polyoxomolybdates

Compounds	Ref.[a] (synthesis)	Polyanion	Ref.[b] (structure)	Symmetry			Number of Mo in the isolated cluster
				Local	Intermediate	Overall	
α-$TBA_4SiMo_{12}O_{40}$	(*40*)	α-$(SiMo_{12}O_{40})^{4-}$	(*44, 45*)	*Oh*	*C3v*	*Td*	12
β-$TBA_4SiMo_{12}O_{40}$	(*40*)	β-$(SiMo_{12}O_{40})^{4-}$	(*46*)	*Oh*	*C3v*	*C3v*	12
$H_8As_4Mo_{12}O_{50}$	(*41*)	$(H_4As_4Mo_{12}O_{50})^{4-}$	(*47*)	*Oh*	*C3v*	*Td*	3
$TBA_2Mo_6O_{19}$	(*42*)	$(Mo_6O_{19})^{2-}$	(*48–50*)	*Oh*	*C3v*	*Oh*	6
α-$TBA_6P_2Mo_{18}O_{62}$	(*43*)	α-$(P_2Mo_{18}O_{62})^{6-}$	(*51, 52*)	*Oh*	*C3v*	*D4h*	18

[a] References of the papers where synthesis is described.

[b] References of the papers where the structure was determined.

—Gua$^+$: guanidinium, $C(NH_2)_3^+$

—TODA$^+$: tetraoctadecylammonium, $(n\text{-}C_{18}H_{37})_4N^+$

—TMA$^+$: tetramethylammonium, $(CH_3)_4N^+$

—TriBA$^+$: tributylammonium, $(n\text{-}C_4H_9)_3NH^+$

(*2*) *Equipment*. The samples were characterized by UV–visible reflectance spectroscopy using a Beckman 5270 spectrometer equipped with an integration sphere and a double monochromator.

The samples were ground and put in an aluminium cell covered by a quartz window. Spectra were recorded in air at room temperature in the range 200–600 nm against a $BaSO_4$ reference put in the same type of cell. A band at 210–215 nm was always present in our spectra. It was an artifact due to a defect in the integration sphere and is eliminated from the figures of this paper. Since the diffuse reflectance spectra were not used for quantitative measurements, no attempt was made to use Kubelka–Munk functions. The signal arising from silica at 260 nm was not subtracted from the spectrum of supported molybdosilicic acid. It will be seen in Fig. 9 that the presence of the silica band does not interfere with those observed in the 300–400 nm range.

RESULTS AND DISCUSSION

Before discussing the influence of structural factors on the diffuse reflectance spectra of various polyoxomolybdates of known structure, let us recall the definitions used here. Local symmetry means the symmetry of the inner coordination sphere of Mo centers; intermediate symmetry refers to the symmetry of the different intermediate clusters which are used as building units to obtain the final polyanion; and overall symmetry refers to the polyanion but not to the salt derived from the arrangement between these polyanions and their corresponding counter-cations.

(*1*) *Influence of the Local Symmetry*

The polyoxomolybdate α-$TBA_4Mo_8O_{26}$ (Fig. 3a) consists of the polyanions $(Mo_8O_{26})^{4-}$ isolated from each other by the counter-ion TBA$^+$. The polyanion possesses two tetrahedral Mo(VI) and six octahedral Mo(VI) and exhibits only one absorption band at around 278 nm. The band position is close to that usually assigned to a tetrahedral Mo(VI) species, although there are three times more octahedra abundant than tetrahedra.

The Mo_2O_7 polymeric structure of $Na_2Mo_2O_7$ (Fig. 3b), whose tetrahedral and octahedral molybdenum centers are alternatively linked by oxo-bridges, only exhibits a

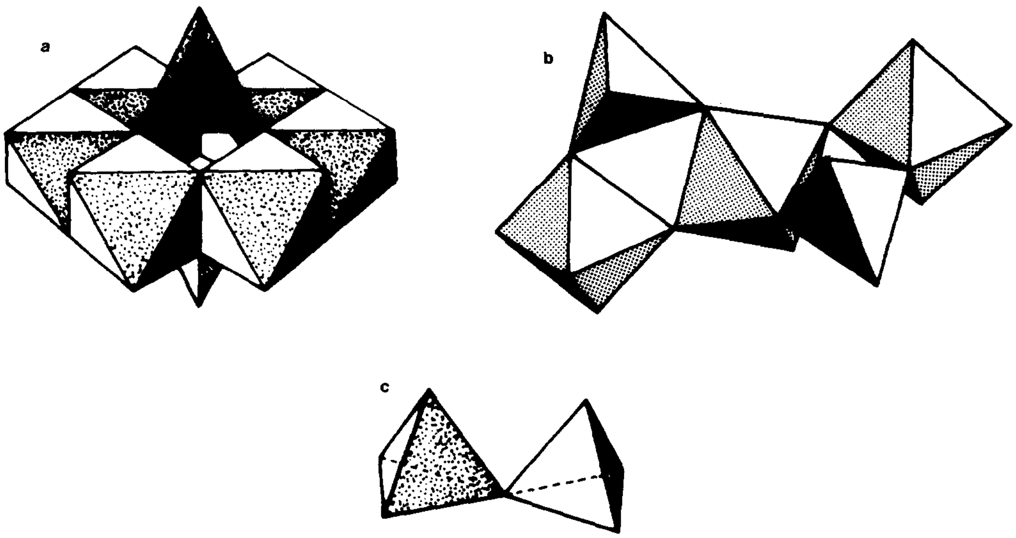

FIG. 3. Structure of the polyanions in: (a) α-$TBA_4Mo_8O_{26}$; (b) $Na_2Mo_2O_7$ (reproduced from Ref. (*39*)); (c) $TBA_2Mo_2O_7$ (TBA^+ = tetrabutylammonium).

very broad line at around 270–330 nm (Table 1). It could be considered as the overlapping of the bands at 260–280 and 300–320 nm, corresponding to pure tetrahedral and octahedral species, respectively. The broadness of the band suggests that it is in fact due rather to the polymeric structure of the compound.

These examples indicate that the band position, i.e., the charge transfer energy, depends less on the local symmetry of the molybdenum than on other structural factors, such as cluster size or overall symmetry. In consequence, the band position does not allow the prediction of the local symmetry of the molybdenum present in the polyanions and, by extension in a supported catalyst. In the following, we will attempt to determine the structural factors which may influence the band position, owing to the examination of polyoxomolybdates spectra.

(2) *Influence of the Polyanion Overall Symmetry*

Two polyanions α-$TBA_4SiMo_{12}O_{40}$ and β-$TBA_4SiMo_{12}O_{40}$ of same condensation degree, same bonding between the intermediate clusters, same counter-cation TBA^+, same hydration degree (anhydrous), but with different overall symmetry, were investigated. The counter-ion TBA^+ is big enough to isolate dimers from each other (*40*). The structure of the polyanions are presented in Fig. 4. Both consist of four groups of three octahedra (Mo_3O_{13} in C_{3v} symmetry). The framework of these four groups differs in such a way that the α-polyanion possesses an overall T_d symmetry (Fig. 4a) whereas that of the β-polyanion is C_{3v} (Fig. 4b, Table 4). Their spectra, presented in Fig. 5, show that their band positions are quite the same: 255 nm (shoulder), 280, and 350 nm. The only difference is in the lowest energy transition band at 350 nm which broadens slightly toward higher wavelengths in the case of the β-polyanion. It may be related to its lower overall symmetry (C_{3v} instead of T_d). It appears therefore that for a given condensation degree and when the molybdenum centers are in strong interaction (oxo-junctions with strong π character), the overall symmetry has a small effect on the number of allowed transitions around the mean one contributing to the bandwidth and a very

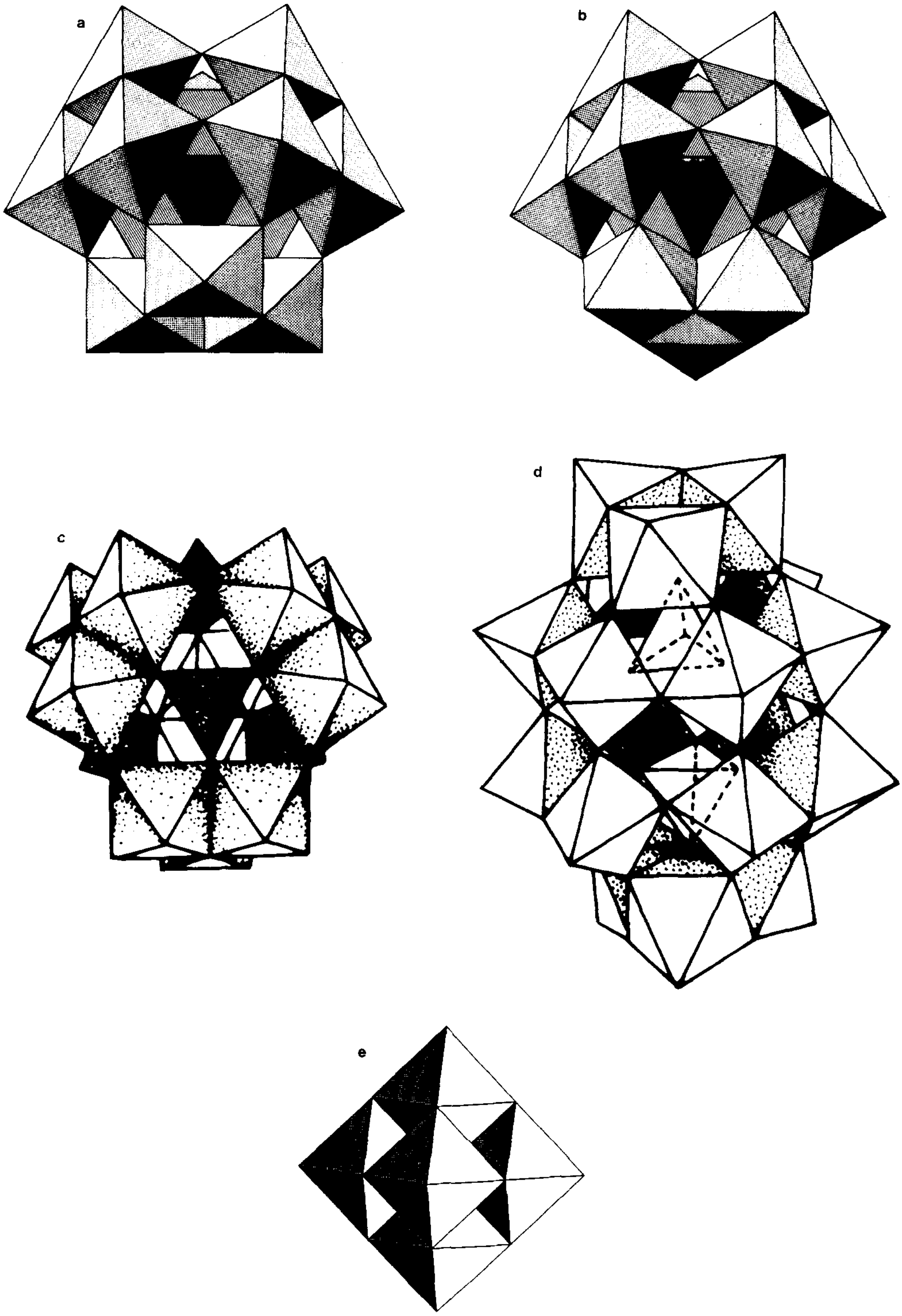

FIG. 4. Structure of the polyanions in: (a) α-TBA$_4$SiMo$_{12}$O$_{40}$ or α-TBA$_3$PMo$_{12}$O$_{40}$; (b) β-TBA$_4$SiMo$_{12}$O$_{40}$; (c) H$_8$As$_4$Mo$_{12}$O$_{50}$ (reproduced from Ref. (*47*)); (d) α-TBA$_6$P$_2$Mo$_{18}$O$_{62}$; (e) TBA$_2$Mo$_6$O$_{19}$ (TBA$^+$ = tetrabutylammonium).

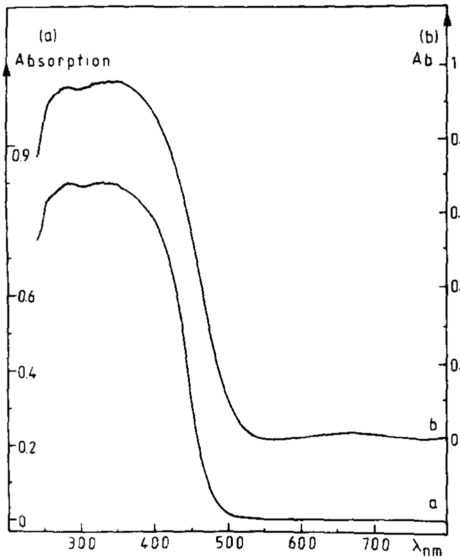

FIG. 5. Diffuse reflectance spectra of: (a) α-$TBA_4Si Mo_{12}O_{40}$; (b) β-$TBA_4SiMo_{12}O_{40}$ (TBA^+ = tetrabutylammonium). *The weak band is due to traces of reduced compound.

slight one on the mean transition energy (band position).

(3) *Influence of the Polyanion Size (Condensation Degree)*

The study of the influence of the condensation degree is not straightforward since a change in the cluster size is often connected to a change in overall symmetry.

The main difference between $Na_2MoO_4 \cdot 2H_2O$ (Fig. 1a and 1b) and $TBA_2Mo_2O_7$ (Fig. 3c), whose Mo is tetrahedral in both compounds, is that in the first case, the Mo centers are isolated from each other by Na^+ ions which are hydrated, whereas in the second case, they are linked by an oxo-bridge to form a dimer; as previously, the counter-ion TBA isolates the polyanions from each other. The wavelength of the lowest energy absorption band is 260 nm for the monomer and 270 nm for the dimer (Fig. 6, Table 3). This first example shows that when the condensation degree increases from one to two molybdenum centers, the lowest energy transition exhibits a bathochromic effect of 10 nm. This effect can be reasonably attributed to the interactions between two MoO_4 units. As the LMCT transition is the result of a ${}^1A \rightarrow {}^1T_2$ transition, the metal–ligand overlap (not the irreducible representation) is of $\pi \rightarrow \pi^*$ type (230 nm for $(MoO_4)^{2-}$ in water (*16*)). That means that the energy of the LMCT transition resulting from the association of two or more MoO_4 units may be calculated using the Hückel model as for unsaturated carbon compounds (*14*).

The reflectance spectra of $TBA_2Mo_6O_{19}$, α-$TBA_3PMo_{12}O_{40}$, $H_8As_4Mo_{12}O_{50}$, and α-$TBA_6P_2Mo_{18}O_{62}$, whose structures are presented in Fig. 4 and Table 4, were investigated. In those compounds, the local symmetry of all Mo(VI) is octahedral and their structures can be described as arrangements of Mo_3O_{13} clusters only, or arrangements of Mo_3O_{13} and Mo_2O_{10} clusters whose octahedral Mo(VI) are connected by μ-oxo-bridges. In α-$(PMo_{12}O_{40})^{3-}$ and $(H_4As_4Mo_{12}O_{50})^{4-}$, Mo centers are assem-

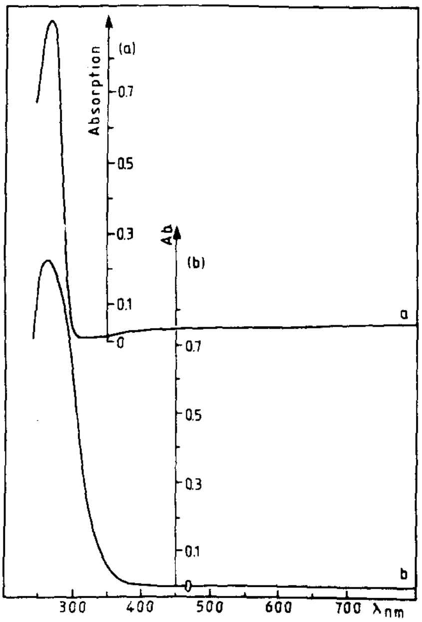

FIG. 6. Diffuse reflectance spectra of: (a) $Na_2Mo O_4 \cdot 2H_2O$; (b) $TBA_2Mo_2O_7$ (TBA^+ = tetrabutylammonium).

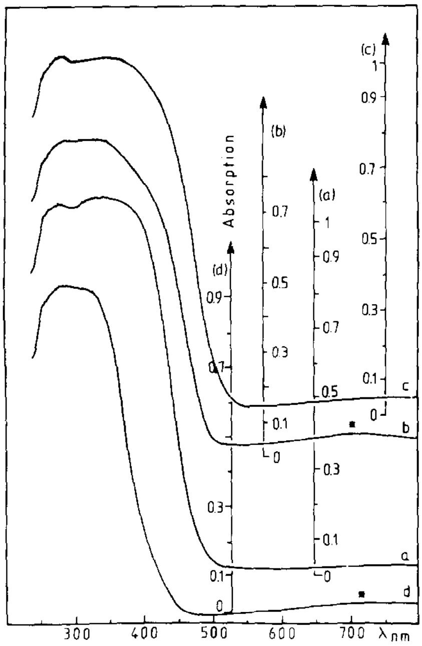

FIG. 7. Diffuse reflectance spectra of: (a) $TBA_2Mo_6O_{19}$; (b) α-$TBA_3PMo_{12}O_{40}$; (c) α-$TBA_6P_2Mo_{18}O_{62}$; (d) $H_8As_4Mo_{12}O_{50}$ (TBA^+ = tetrabutylammonium). *The weak band is due to traces of reduced compound.

bled in four groups of Mo_3O_{13} (C_{3v} symmetry). These groups form a framework with an overall T_d symmetry. The main difference between these two compounds is the assemblage of Mo_3O_{13} clusters. They are isolated from each other by arseniate groups in $(H_4As_4Mo_{12}O_{50})^{4-}$ whereas they are linked together in α-$(PMo_{12}O_{40})^{3-}$. In (α-$P_2Mo_{18}O_{62})^{6-}$, two different types of clusters are present: two terminal Mo_3O_{13} and six Mo_2O_{10} clusters arranged in a double crown, the overall framework having a D_{4h} symmetry. In these three compounds, Mo_3O_{13} and Mo_2O_{10} clusters are connected to each other only by single μ-oxo-bridges (vertices). $(Mo_6O_{19})^{2-}$ is a special case; it can be described as an octahedral assemblage (symmetry O_h) of six octahedra, all the junctions between molybdenum centers being twin μ-oxo-bridge edges. The diffuse reflectance spectra of all the complexes (Fig. 7) contain three distinct bands. Those at 255 nm (shoulder) and at around 280 nm are similar for all the compounds. A third one at higher wavelength shifts toward the red (from 315 to 380 nm) and broadens (from 120 to 240 nm at half height) when the size of the oxomolybdenum cluster increases: 3 Mo in $H_8As_4Mo_{12}O_{50}$, 6 Mo in $TBA_2Mo_6O_{19}$, 12 Mo in α-$TBA_4SiMo_{12}O_{40}$, 18 Mo in α-$TBA_6P_2Mo_{18}O_{62}$.

The cluster size has therefore an important effect on both the band position and the bandwidth. This result is in good agreement with the theoretical calculations of the electronic transitions of polyoxomolybdates (*14*).

It may be noted that the structure of α-$TBA_3PMo_{12}O_{40}$ is the same as that of α-$TBA_4SiMo_{12}O_{40}$, and that their spectra are quite similar (Figs. 5a and 7b). That shows that there is no influence of the central metal ion on the band position.

(*4*) *Influence of the Interactions between Polyanions*

Another factor which may influence the absorption band position is the presence of eventual interactions between polyanions. We studied the case of (α-$SiMo_{12}O_{40})^{4-}$ (Fig. 4a) with different counter-ions of increasing size: $H^+ < Gua^+ < TBA^+ < TODA^+$. Both the local and the overall symmetry of the polyanions are the same; only their interactions are different. For the hydrated molybdosilicic acid ($H_4SiMo_{12}O_{40} \cdot 14H_2O$) and its guanidinium salt, the polyanions are in interaction because of the small size of the counter-ion. By contrast, the polyanions are isolated from each other for the salts of TBA and of TODA (*40*). Their diffuse reflectance spectra, presented in Fig. 8, show that the position of the bands at around 255 and 275 remains unchanged. On the contrary, the lowest energy absorption band shifts toward higher wavelength (from 350 to 420 nm) and broadens when the size of the counter-ion decreases, i.e. when its polarizing power increases and when the relative distance between polyanions decreases.

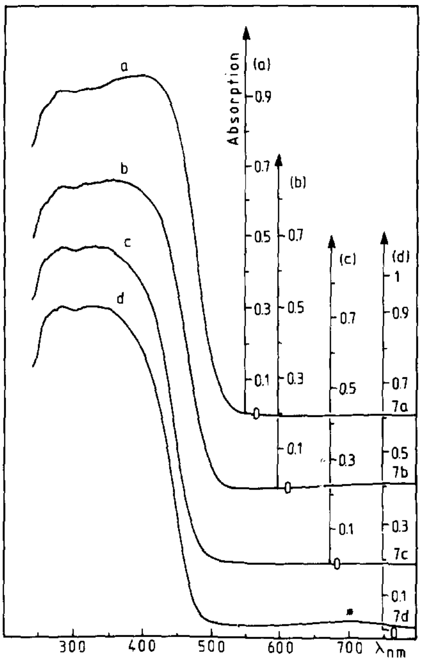

FIG. 8. Diffuse reflectance spectra of: (a) α-H_4Si$Mo_{12}O_{40}$; (b) α-$Gua_4SiMo_{12}O_{40}$; (c) α-$TBA_4SiMO_{12}O_{40}$; (d) α-$TODA_4SiMo_{12}O_{40}$. *The weak band is due to traces of reduced compound (Gua^+ = guanidinium, TBA^+ = tetrabutylammonium, $TODA^+$ = tetraoctadecylammonium).

On the contrary, when $H_4SiMo_{12}O_{40} \cdot 14H_2O$ is supported on silica (30% Mo in weight), its lowest energy transition band shifts from 420 (for the bulk compound) to 320 nm (when supported) and becomes narrower (Fig. 9) (even more than for bulk $TODA_4SiMo_{12}O_{40}$ (Fig. 8d)). The structure of the polyanion is preserved on the support (*53*) and theoretical calculations in Part II (*14*) show that the influence of the support on the electronic transitions of isolated octahedral Mo centers is very weak. It may be deduced that the changes observed are due rather to the effect of the support which spreads the polyoxomolybdate even at high Mo loading and thus decreases the interactions between the latter.

To summarize, the existence of interactions between polyanions is equivalent to the formation of a larger polyanion and induces a broadening and a red shift of the lowest energy absorption band toward higher wavelength. This is in agreement with the results found in the previous section.

For supported Mo catalysts, a broadening and a red shift of the lowest energy transition band is therefore expected when the Mo dispersion decreases, i.e., when the Mo content increases. This was indeed observed by Asmolov and Krylov (*4*) and Giordano *et al.* (*5*) on Mo/Al_2O_3 (Table 2), but attributed to a change in local Mo symmetry. In fact, Giordano *et al.* (*5*) observed the development of an IR band at 800 cm^{-1} and the onset of another at 900 cm^{-1} with increasing Mo content. That result suggested to them progressive increase of structures with bridged oxygens in mixed tetra and octahedral Mo(VI) geometries.

(*5*) *Influence of the Counter-Cation Polarizing Effect*

In the examples described above, both the cation size and their polarizing effect changed; it is therefore difficult to distinguish one effect from the other. This last effect is clearly illustrated with the spectra

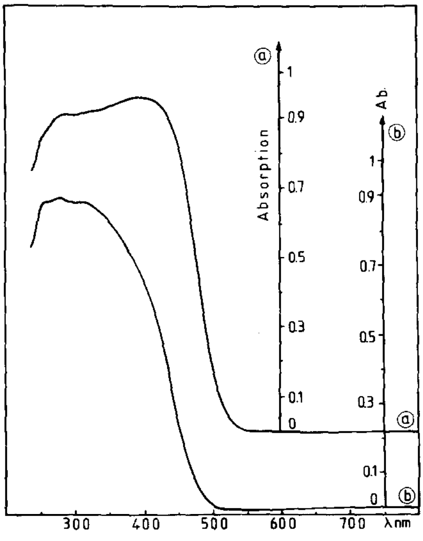

FIG. 9. Diffuse reflectance spectra of: (a) α-H_4Si$Mo_{12}O_{40}$, (b) α-$H_4SiMo_{12}O_{40}$ supported on silica (30 Mo wt%).

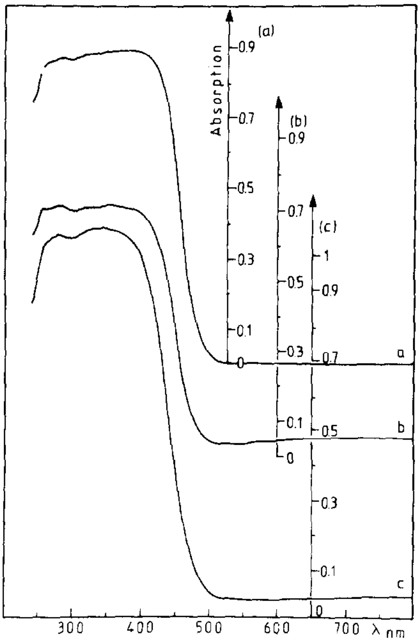

FIG. 10. Diffuse reflectance spectra of: (a) $TMA_2Mo_6O_{19}$, (b) $TriBA_2Mo_6O_{19}$, (c) $TBA_2Mo_6O_{19}$ (TMA^+ = tetramethylammonium, $TriBA^+$ = tributylammonium, TBA^+ = tetrabutylammonium).

of $(Mo_6O_{19})^{2-}$ with two different counter-ions TBA^+ and $TriBA^+$. TBA^+ and $TriBA^+$ have much the same size but the polarizing effect of $TriBA^+$ ($pK_a \approx 11$) is almost similar to H^+ ($pK_e = 14$), i.e., is higher than that of TBA^+ (strong acid). Fig. 10 shows that the bandwidth of the lowest energy transition is larger for TriBA than for TBA. In consequence, the polarizing effect, due to the counter-cation, also has an influence on the lowest energy transition band: when it increases, it induces a band broadening.

CONCLUSION

The examination of the UV–visible spectra of model polyoxomolybdates with well-known structures indicates that the earlier attributions of the UV–visible bands of supported Mo catalysts must be reconsidered. Although definitive assignments on the exact nature of the molybdenum centers cannot be given by this technique, some important conclusions can be drawn from the experimental spectra:

—in contrast to earlier literature, we find that the influence of the local Mo symmetry on the location of the lowest energy transition band of ligand–metal charge transfer is negligible compared to that of the more distant environment of the Mo center.

—a broadening and a red shift of this band are observed when the cluster size increases (this is supported by theoretical calculations (*14*)), or when the polarizing effect increases and/or the size of the counter-cation decreases. The reverse is observed when polyoxomolybdates are supported.

—the increasing effects of the different parameters may be classified as follows:

$$\begin{array}{l} \text{local symmetry} < \\ \text{overall symmetry} < \end{array} \left\{ \begin{array}{l} \text{condensation degree} \\ \quad \text{(polyanion size)} \\ \text{polarizing effect of} \\ \quad \text{the counter-cation} \\ \text{size of the counter-} \\ \quad \text{cation} \\ \text{dispersion on a} \\ \quad \text{support} \end{array} \right.$$

—the analysis of UV–visible spectra does not permit distinguishing the effect of strong interaction between Mo (via oxo-bonding Mo–O–Mo) exhibited by the influence of polyanion size from weaker effects such as polyanion interactions, occurring (for example via hydrogen bonding) when the counter-cation is small enough, or such as electrostatic effects due to the polarizing power of the counter-cation.

— these results indicate that the interpretation of the spectra of supported Mo catalysts is not straightforward: Mo dispersion (Mo cluster size and distance between clusters) appears to have more influence than local Mo symmetry.

This work performed on molybdenum compounds may be extended to other transition metal oxide compounds.

ACKNOWLEDGMENT

This work was supported by Grant A.T.P. 2261 from the Centre National de la Recherche Scientifique (CNRS).

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