

Influence of *d*-State Density and Chemistry of Transition Metal Cluster Selenides on Electrocatalysis

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Catalytic studies were carried out on two important electrochemical reaction processes, hydrogen evolution and molecular oxygen reduction in acid medium comparing the transition metal cluster compounds $\text{Mo}_4\text{Ru}_2\text{Se}_8$, $\text{Mo}_2\text{Re}_4\text{Se}_8$, Mo_6Se_8 , and the Mo metal. Our results show that during the hydrogen evolution reaction, in the course of catalytic charge transfer with the cluster, the hydrogen species solely interacts with individual metal atoms. Molecular oxygen, on the other hand, during oxygen reduction interacts with the cluster as a whole. We propose that the important factors involved in such a process are the high density of *d* states and the chemistry of the elements. The former factor can be significantly improved by going from the pure metal to transition metal cluster compounds and mixed transition metal compounds. The second factor can be considered by incorporating adequate transition metal atoms into the cluster. Since less catalytic elements for the reduction of oxygen in acid medium (e.g., Mo, Ru, Re) behave like highly catalytic elements (e.g., Pt, Ir) when incorporated into the cluster structure, these experimental results probably indicate a new route for tailoring efficient catalysts from more abundant transition elements. © 1988 Academic Press, Inc.

INTRODUCTION

In phenomena related to catalysis (1), e.g., hydrogenation, isomerization, ammonia synthesis, and dehydrodesulfurization, much effort has been directed toward understanding how the catalyst works, in order to design improved ones. This has led to several relationships between the catalytic activity of the material and other parameters such as their position in the periodic table, heats of formation of the corresponding compounds, and metal-adsorbate strengths (2, 3). From these studies, it appears that, besides the chemical counterpart, the *d* electron configuration plays a major role in the catalytic behavior of the material and the interaction with the reacting species (3). Similarly, in electrocatalysis, that is in heterogeneous catalytic reactions which involve reactant and product species transferring electrons through a catalyst/electrolyte interface, the catalytic

effect of electrodes has also been correlated with certain parameters. These are heats of adsorption of a reacting molecule (5), work function, percentage of *d* character (6), and distance between neighbors in bimetallic catalyst (7). These research activities also conveyed information as to the importance of 4*d* or 5*d* electron orbitals of transition metals in enhancing catalytic activities frequently encountered in fuel cells (8).

In previous papers, we reported that the transition metal mixed cluster Chevrel phase compounds are able to catalyze the reduction of molecular oxygen in acid medium (9, 10). This led us to focus our efforts on the understanding of *d*-state density vis-à-vis this type of electrochemical process involving a multielectron charge transfer.

In this work, we present experimental evidence of the importance of electronic and chemical factors of these more complex transition metal compounds, with re-

spect to the electrochemical reduction of protons and oxygen in acid medium.

EXPERIMENTAL

The cluster materials were synthesized by solid-state reaction as previously described (11, 12): elements were mixed and fired overnight (1000–1200°C) in an evacuated silica ampoule (residual atmosphere 10^{-2} Torr argon). The powder obtained was reground, cold pressed into pellets, and heated again for 24 h. If necessary a third treatment was used in order to complete the reaction. The single-phased compound was then pressed into pellets to a diameter of ca. 5 mm and a thickness of about 1 mm and sintered for a few hours at the synthesis temperature. The samples were back ohmic contacted with a silver epoxy paste (Scotchcast 3M) and mounted on brass shafts for the rotating disk electrode (RDE) configuration. The epoxy employed to insulate and encapsulate the crystals on Vespel holders was also Scotchcast 3M. The surfaces of the electrodes were washed with acetone and distilled water. Prior to any measurement, the electrodes were systematically subjected to cyclic voltammetric scanning in the region of charging current in well-purged nitrogen solutions for at least 30 min at 0.05 V/s. The electrolyte used was 0.5 M sulfuric acid, pH 0.3 (Merck).

The electrochemical measurements were performed with an EG&G, PAR Model 273 potentiostat, and the recording of the curves on a Philips X-Y recorder. The rotating electrode employed was either a Model EDI from Tacussel or from Pine Instrument. The cell of Pyrex consisted of a single compartment, having a three-electrode configuration.

Platinum ring and saturated Calomel were used as counter and reference electrodes, respectively. The latter was separated from the main compartment through a liquid junction bridge with a ceramic tip of low porosity. In the text, all potentials are quoted with respect to a normal hydrogen electrode (NHE). The experiments were performed, if not otherwise indicated, at room temperature. The Tafel plots reported here were obtained from steady-state measurements.

Material Properties

The catalytical properties for hydrogen and oxygen evolution were compared for the following materials: Mo metal, Mo_6Se_8 Chevrel phase, and the mixed cluster Chevrel phases $\text{Mo}_2\text{Re}_4\text{Se}_8$, $\text{Mo}_4\text{Ru}_2\text{Se}_8$. Two differently prepared samples of $\text{Mo}_4\text{Ru}_2\text{Se}_8$ (sample 1 with a preparation technique as described above, sample 2 prepared according to a technique described in Ref. (10)) were used. The structure of the cluster compounds studied is schematized in Fig. 1. While the Mo_6Se_8 phase has metallic properties, the $\text{Mo}_2\text{Re}_4\text{Se}_8$ and $\text{Mo}_4\text{Ru}_2\text{Se}_8$ phases have semiconducting properties. This is a consequence of substituting Mo by Re and Ru which contain higher valency electron numbers thus increasing the valency electron concentration in the cluster from 20 to 24. A filling of the e_g band of the material is obtained. The shifting of the Fermi level within the e_g band from the metallic Mo_6Se_8 phase to the edge of the valence band in the $\text{Mo}_2\text{Re}_4\text{Se}_8$ and $\text{Mo}_4\text{Ru}_2\text{Se}_8$ is shown in Fig. 2. Aside from the total number of states derived from the transition metal and chalcogenide orbitals,

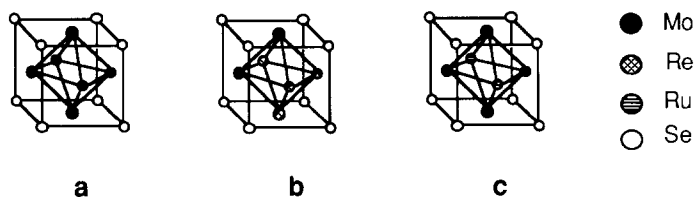


FIG. 1. Schematic unit cell cluster representation of (a) Mo_6Se_8 , (b) $\text{Mo}_2\text{Re}_4\text{Se}_8$, and (c) $\text{Mo}_4\text{Ru}_2\text{Se}_8$. Note that in (b) and (c), a statistical occupancy of Mo and Re or Ru occurs, respectively.

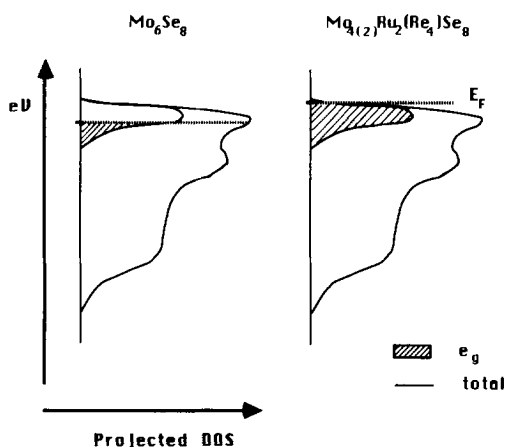


FIG. 2. Band structure scheme (e_g and the total DOS) of the clusters shown in Fig. 1. Schematized according to Ref. (14).

the contribution to the e_g band (valence band) is shown. This latter contributes to the 12 binding orbitals of the transition metal cluster which stem from more than 90% Mo d orbitals (14). The energy gap in these materials has been calculated to range from 1.3 to 1.7 eV (13, 14) and determined to be 1.3 eV for $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$ in a preceding publication (10). It should be emphasized that the cluster volume size decreases from 884.5 to 870 \AA^3 (12) when going from 20 to 24 electrons (15). The deviation of stoichiometry from the 24 e^- count per cluster implies a significant hole density of 10^{20} cm^{-3} , with the consequence that the space charge layer of only 15 \AA is present. This implies that the position of the energy bands is unpinning and changes with the position of the Fermi level and the applied electrode potential or to a position of the redox couple in the electrolyte. The energetic behavior of this electrode is very close to that of a typical metal. The aim of this catalytic study was to compare different Mo-containing compounds in which the concentration of d electrons changes by rising the Fermi level, E_F , when going from the Mo cluster to the substituted ones. The filling up of the e_g valence band was accomplished by substituting Mo for two different transition metals (Re and Ru) to study the chemical effects.

TABLE 1

Hydrogen Evolution			
Material	Slope, b (mV/decade)	α	$\log i_0$ (mA cm^{-2})
Mo	63	0.94	-4.84
Mo_6Se_8	73	0.81	-4.35
$\text{Mo}_2\text{Re}_4\text{Se}_8$	146	0.40	-1.70
$\text{Mo}_4\text{Ru}_2\text{Se}_8$	77	0.77	-0.85

RESULTS

Hydrogen Evolution

The Tafel plots of hydrogen evolution currents observed, in 0.5 M H_2SO_4 , using the above-described materials as disks in rotating electrode systems are shown in Fig. 3. It can be seen that the catalytic properties of Mo and the pure Mo cluster compound are clearly inferior to the catalytic behavior of the mixed Ru and Re cluster compounds. In Table 1, Tafel slopes, b , and transfer coefficients, α , values together with values of the exchange current density, i_0 , obtained by extrapolation of the Tafel line to the reversible poten-

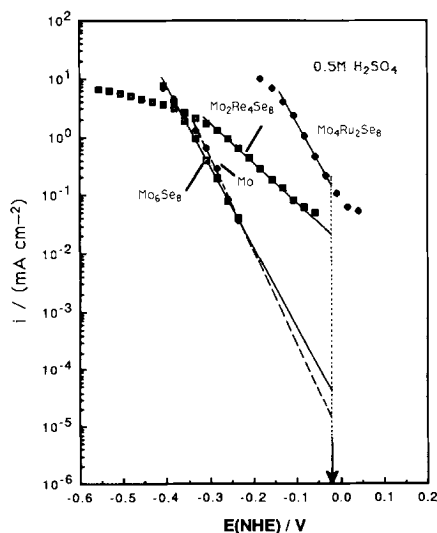


FIG. 3. Tafel plot for the hydrogen evolution at the Mo, Mo_6Se_8 , $\text{Mo}_2\text{Re}_4\text{Se}_8$, and $\text{Mo}_4\text{Ru}_2\text{Se}_8$ electrodes, in 0.5 M H_2SO_4 . The i_0 can be read by intersection of the extrapolated lines with the dotted placed at the thermodynamic potential for H_2 for this medium, pH = 0.3.

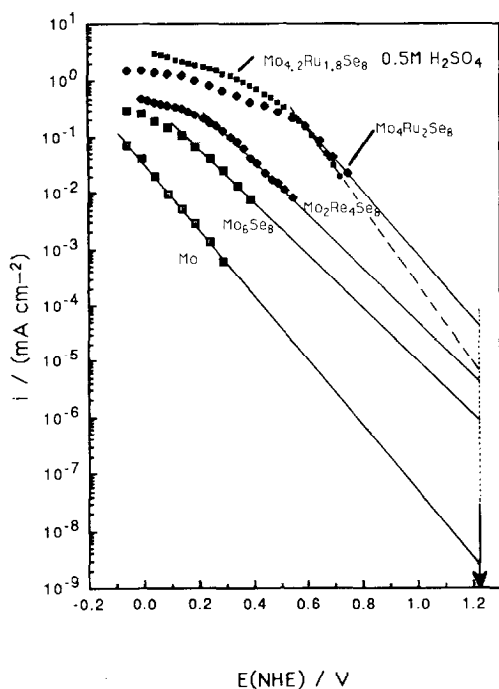


FIG. 4. Corrected mass transfer Tafel plot for molecular oxygen reduction at the Mo, Mo_6Se_8 , $\text{Mo}_2\text{Re}_4\text{Se}_8$, $\text{Mo}_4\text{Ru}_2\text{Se}_8$, and $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$ (sample 2) electrodes, in 0.5 M H_2SO_4 . The data plotted here are those averaged from the varying electrode rotation rates after the mass transfer correction. The i_0 can be read by intersection of the extrapolated lines with the dotted placed at the thermodynamic potential of O_2 for this medium, pH 0.3.

tial are given. With these latter materials a somewhat different behavior can be observed with a negligible overvoltage (at 0.1 mA cm^{-2}) for Ru and a slightly higher one for the Re compound.

Oxygen Reduction

The catalytic behavior of the material during oxygen reduction in 0.5 M H_2SO_4 is shown in the Tafel plots reproduced in Fig. 4. Here, a significant improvement is observed in the direction of the Mo metal to Mo_6Se_8 , $\text{Mo}_2\text{Re}_4\text{Se}_8$, and $\text{Mo}_4\text{Ru}_2\text{Se}_8$. The remarkable oxygen reduction properties of $\text{Mo}_4\text{Ru}_2\text{Se}_8$ which has previously been discussed (10) cannot be approached when replacing Ru for Re. This mixed semiconducting cluster compound, however, is still significantly more catalytic

than the pure Mo-containing metallic cluster compound. It is interesting to note that both Ru-mixed clusters behave in a similar manner. Although the Tafel slope is different they are both in the same low current density region. Compare electrochemical data in Table 2.

Temperature Effect on the Oxygen Reduction

The Tafel plots, where the current density is already corrected for mass transfer, in Fig. 5 show that the temperature dependence involves a characteristically different behavior for the Mo_6Se_8 , $\text{Mo}_2\text{Re}_4\text{Se}_8$, and $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$ (sample 2). In the explored potential region there are at least two different processes recognizable, one occurring in the high current density region and one in the low current density region, respectively. The analysis of the temperature dependence of the Tafel slopes in the low current density region for each compound was carried out. From this, the apparent enthalpies of activation, $\Delta H^{\ddagger 0}$, were determined by plotting the reaction rate current density, i_0 , calculated at the reversible electrode potential (corrected for temperature coefficient) versus the inverse of temperature. Electrochemical Arrhenius-type plots were obtained for the substituted cluster compounds, Fig. 6. Very interesting is the increase in the apparent activation energy in the direction of Mo_6Se_8 , $\text{Mo}_2\text{Re}_4\text{Se}_8$, and $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$. For the two latter compounds, the activation energy obtained was 29.2 and 90.6 kJ/mol, respectively (see Table 3). On the other hand, the experimental data for the Mo cluster do not

TABLE 2
Oxygen Reduction

Material	Slope, b (mV/decade)	α	$\log i_0$ (mA cm^{-2})
Mo	170	0.35	-8.57
Mo_6Se_8	210	0.28	-6.02
$\text{Mo}_2\text{Re}_4\text{Se}_8$	206	0.29	-5.34
$\text{Mo}_4\text{Ru}_2\text{Se}_8$	176	0.33	-4.31
$\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$	105	0.56	-5.20

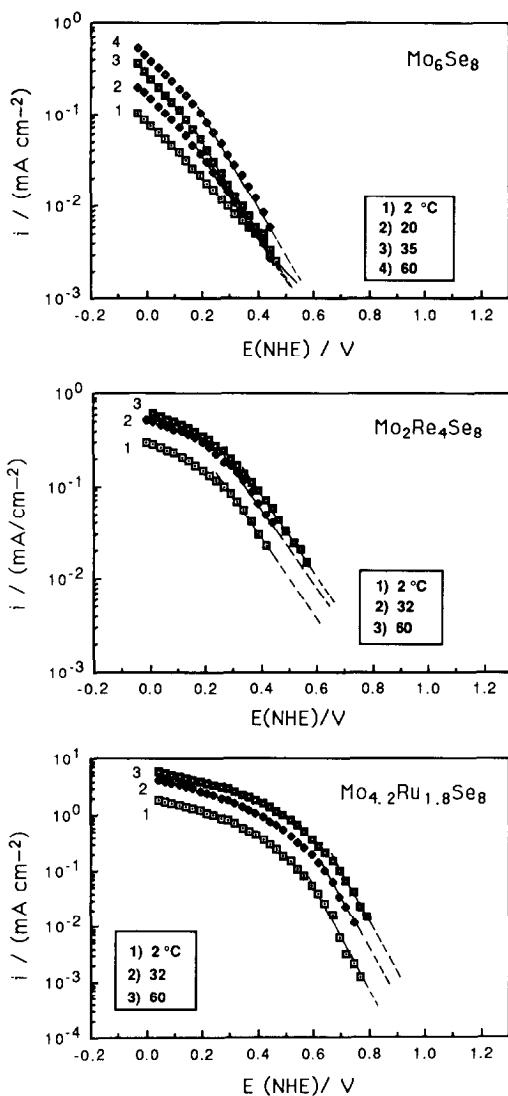


FIG. 5. Corrected mass transfer Tafel plot for molecular oxygen reduction as a function of temperature for Mo_6Se_8 , $\text{Mo}_2\text{Re}_4\text{Se}_8$, and $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$ (sample 2) electrodes in $0.5\text{ M H}_2\text{SO}_4$.

seem to obey the Arrhenius law. A naive explanation for this observation a priori, see discussion below, can be that the increase in surface coverage of the electrode by chemisorbed oxygen and by other, probably formed, strongly bound species lead to a decrease in the number of active sites with high bond energy which are available for the dissociative chemisorption of molecular oxygen. Nevertheless, the apparent activation energy trend for this Mo_6Se_8

TABLE 3

Preexponential Factors and Apparent Activation Energies		
Material	A (mA cm^{-2})	$\Delta H^{\ddagger\circ}$ (kJ mol^{-1})
Mo_6Se_8	—	—
$\text{Mo}_2\text{Re}_4\text{Se}_8$	1.1	29.2
$\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$	1.7×10^9	90.6

cluster compound tends to be smaller than that of the mixed Re and Ru clusters, respectively.

DISCUSSION

One concept guiding these catalytic studies has been to increase the d electron density near the Fermi level in a series of Mo-containing compounds. When going from the Mo metal to the Mo_6Se_8 cluster compound, the d -state density near the Fermi level should increase because the energy band derived from Mo d states becomes narrower due to the comparatively weak electronic interaction between the clusters. As we can see in Fig. 3 this has no significant influence on hydrogen evolution but already has a significant influence on oxygen reduction. When replacing part of the Mo atoms by Re or Ru to fill up the e_g

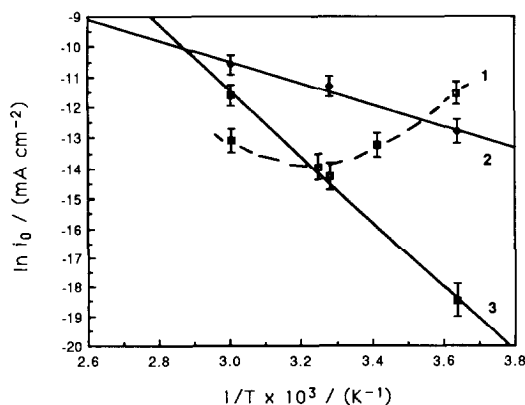
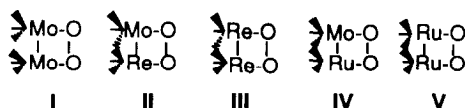


FIG. 6. Electrochemical Arrhenius plot for molecular oxygen reduction on (1) Mo_6Se_8 , (2) $\text{Mo}_2\text{Re}_4\text{Se}_8$, and (3) $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$ (sample 2) electrodes, in $0.5\text{ M H}_2\text{SO}_4$. Plotted data were obtained in the low current density region.

band by shifting the Fermi level slightly above from a high-density region of d states some improvement is obtained for hydrogen and significant improvement for oxygen reduction. At the same time it is learned that a much better catalytic activity is obtained from the Ru-substituted cluster compound than from the Re-substituted one. Since neither Mo, Re, Ru, nor their selenides are catalytically active (in acid medium) to the extent observed in our experiments, a cooperative electronic action of the transition metal atoms in the mixed cluster must be involved. The demonstrated possibility of producing efficient catalysts from poor catalysts just by arranging them in clusters will have implications and applications for catalytic research and should therefore be further examined.

Oxygen-Transition Metal Cluster Interaction Probability

The observed differences obtained in the apparent activation energy and the apparent entropy of activation determining the preexponential factor may be accounted for by the way in which molecular oxygen interacts with the transition metals in the cluster units in order to build a bridge-type complex as shown below. This type of structure on a catalytic surface (16) leads, mainly, to water formation through a four-electron transfer, compared to the formation of hydrogen peroxide (10) which involves a two-electron transfer process. The interaction between the molecular oxygen and the transition metal allows one to consider that on the cluster surface the following complexes of the bridge-type are formed:



Based on the interaction of molecular oxygen with the transition metals in the cluster, the following hypothesis was taken into consideration: If five atom positions on one cluster surface are available (one-half of the

transition metal cluster exposed to the electrolyte), then a total of 15 combinations results. The selenium atoms oriented on this surface should not play a significant role in the catalysis.

From simple statistics, the calculated combinations of the bridge formations resulted to be the following for $\text{Mo}_2\text{Re}_4\text{Se}_8$, **I** (6.7%), **II** (53.3%), and **III** (40%), and for $\text{Mo}_4\text{Ru}_2\text{Se}_8$, **I** (40%), **IV** (53.3%), and **V** (6.7%). Complex **I** can be excluded to be the most active, since Mo_6Se_8 is not active enough; see Fig. 4. Complexes **III** and **V** might be similar to the less active RuO_2 and ReO_2 , as found by Horkans *et al.* (17). Therefore, it is more probable that the complex units depicted as combinations **II** and **IV** play the major role in the electrocatalysis of oxygen reduction. The lower activity obtained for the rhenium-mixed cluster compound compared to that of ruthenium could probably be due to the great stability of compound **III** formed on its surface. In other words, this strongly bound species deactivates the surface by decreasing the number of its active sites. The value of the apparent activation energy obtained accounts for such a process.

Between the Mo metal and the Mo_6 cluster we see no significant difference other than the density of d states near the Fermi level which is higher in the Mo_6 cluster compound because of relatively weak interaction between clusters (the Mo-Mo distance is only 2% larger in the Mo metal). This is sufficient background for concluding that the adsorbate bonding strength is different for the two systems.

The Effect of Temperature on the Tafel Slope and Transfer Coefficient

The data presented in Fig. 5 describe a more complex behavior for the Mo_6Se_8 cluster than that of mixed clusters. This situation is better visualized by plotting the Tafel slope, b , of the low current density region and the corresponding transfer coefficient, α , as shown in Fig. 7. It is evident that the temperature dependence of b (shown as curve 1 for a constant $\alpha = 0.5$)

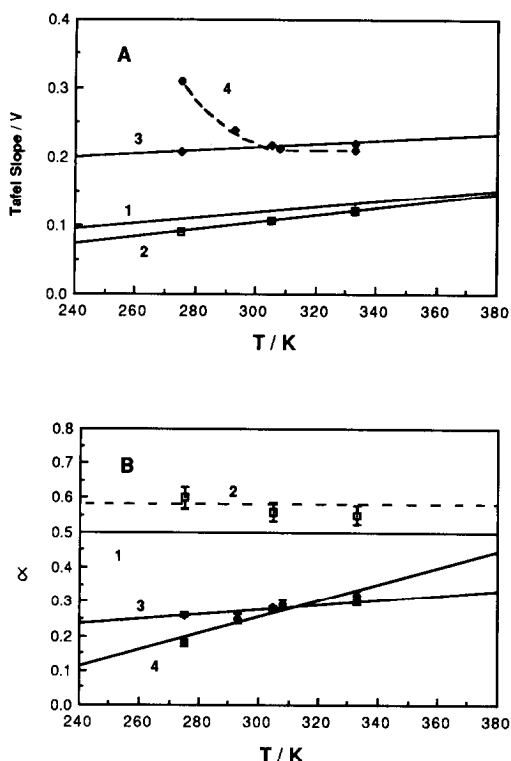


FIG. 7. (A) Tafel slopes, b , and (B) transfer coefficient, α , for the molecular oxygen reduction at the Mo_6Se_8 (4), $\text{Mo}_2\text{Re}_4\text{Se}_8$ (3), and $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$ (2) electrodes, in 0.5 M H_2SO_4 over a range of temperatures. Curve (1) indicates the ideal case; see text.

does not follow the commonly assumed equation $b = (2.3) RT/\alpha F$ (see curves 3 and 4 in Fig. 7A). The complications in the kinetics of the reaction appear to increase from $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$ to $\text{Mo}_2\text{Re}_4\text{Se}_8$ and further to Mo_6Se_8 . Several of the so-called unconventional phenomenologic details of the Tafel slope and the α behavior per se on other catalysts as a function of temperature were discussed by Conway (18). Although this author reports on a series of specific cases, we realize that the behavior of the Mo_6Se_8 cluster does not enter into one of them; see curve 4 in Fig. 7A. Very recently Bockris and Gochev (19) also reviewed the problem. The temperature dependence observed for α , which is stronger for the Mo_6Se_8 than for the $\text{Mo}_2\text{Re}_4\text{Se}_8$ cluster, apparently reflects a direct implication of

the chemistry and physics of the arrangement of atoms in the cluster during the charge transfer to the molecular oxygen in acid medium. We shall not go into mechanistic details, since additional experimental data are lacking. Nevertheless, it is interesting to mention that Agar (20) was the first to point out that a change of entropy is possible when a variation of α with temperature is involved. The entropy involves statistical and structural factors which need further examination.

CONCLUSION

In two important electrochemical processes, oxygen reduction and hydrogen evolution, we observed an improvement in electrocatalysis on going from the Mo metal to a cluster arrangement of the same metal and substituted ones where Re and Ru partially replace Mo. Aside from a specific chemical interaction, with these cluster materials, a factor is the filling up of the $e_g d$ bands which raises the Fermi level.

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