estimated. This value was used in the PPP scheme to calculate the ionization potentials of hydrocarbons, and the results are presented in Table 1. Also given are the values obtained with the $\bar{\alpha}$ parameter. It is obvious that striking improvement occurs when $\bar{\alpha}$ is replaced by α. The spectral transitions are of course unaffected by this replacement. Thus we are led to the conclusion that simultaneous agreement in transition energies and ionization potential can be obtained, if a value of coulomb integral is used which is consistent with the basis set assumed in the PPP model.

References

1. HOYLAND, J. R. & GOODMAN, L., *J. chem. Phys.*, **33** (1960), 946; **36** (1962), 12 and 21.
2. FISCHER-HJALMARS, I., *Molecular orbitals in chemistry, physics and biology*, edited by Lowdin & Pullman (Academic Press, New York), 1964, 361.
3. FISCHER-HJALMARS, I., *J. chem. Phys.*, **42** (1965), 1962.
4. LINDERBERG, J., *Chem. Phys. Lett.*, **1** (1967), 39.
5. JUG, K., *Theoret. Chim. Acta (Berl.)*, **16** (1970), 95.
6. WATANABE, K., *J. chem. Phys.*, **26** (1957), 542.
7. Quoted by SKANCKE, P. N., *Acta chem. Scand.*, **18** (1964), 1671.
8. WACKS, M. E. & DIBELER, V. H., *J. chem. Phys.*, **31** (1959), 1557.
9. WACHS, M. E. & DIBELER, V. H., *J. chem. Phys.*, **4** (1964), 1661.
10. BRIEGLAB, G. & CZEKALLA, J., *Z. Electrochem.*, **63** (1959), 6.
11. KURODO, H., *Nature, Lond.*, **201** (1964), 1214.
12. CLARK, L. B., *J. chem. Phys.*, **43** (1965), 2566.
13. FINCH, A. C. M., *J. chem. Soc.*, (1964), 2272.
14. BIRKS, J. B. & SLIFKEN, M. A., *Nature, Lond.*, **191** (1961), 761.
15. MORRISON, J. D. & NICHOLSON, L. C., *J. chem. Phys.*, **20** (1952), 1021.

Physicochemical Properties of Sodium Molybdate Catalyst

P. K. SINHAMAHAPATRA*, S. SINHAMAHAPATRA† & S. K. BHATTACHARYYA

Department of Chemistry, Faculty of Science Banaras Hindu University, Varanasi 221005

Thermal characteristics of sodium molybdate ($Na_2MoO_4.2H_2O$) have been studied and the various transition products characterized by chemical analysis, IR, X-ray diffraction, surface acidities, magnetic susceptibilities and surface area measurements. Sodium molybdate dihydrate undergoes endothermic changes at 150°, 470°, 643° and 689°. The endothermic transitions at 150° are due to dehydration, at 470° and 643° account for crystal transformation and at 689° are due to melting. This compound contains acid sites in the pk_a range, $+6.8$ to -3.0. Medium acid sites ($pk_a = +3.3$) are reduced at 510° whereas weak acid sites ($pk_a \geqslant +5.0$) are increased at 660° and above. The strong acid sites ($pk_a \leqslant +2.0$) however, remain

*Present address: Catalyst Section, Indian Institute of Petroleum, P.O. IIP, Mohkampur, Dehra Dun 248005. To whom correspondence should be addressed.

†Present address: Oil Technology Division, Department of Applied Chemistry, University College of Science and Technology, Calcutta 700009.

almost unchanged till melting. The pure molybdate as well as its thermal transition products are diamagnetic. Surface area of the compounds decreases consistently as a function of calcination temperature. This decrease is suggested to be due to enlargement of micropores formed in individual sodium molybdate crystallites due to sintering.

IT appears from a literature survey that catalytic activity of sodium molybdate[1-6] has some dependence on its calcination temperature. However, the systematic studies on the thermal properties of this molybdate are meagre. The present note deals with the differential thermal analysis (DTA), thermogravimetry (TG), infrared (IR), X-ray diffraction (XRD), surface acidity, magnetic susceptibility and surface area of pure as well as various thermal transition products of sodium molybdate.

DTA and TG of sodium molybdate were carried out by the methods reported earlier[7]. For characterization of the thermal transitions sodium molybdate was calcined at 230°, 510°, 660° and 710° in air for 2 hr in each case. IR spectra and XRD patterns of the pure as well as of the calcined samples were obtained at room temperature by the methods described elsewhere[8]. The surface acidic strength distribution in the above samples was measured by indicator-titration method using n-butylamine and indicators of various pk_a values[9]. Magnetic susceptibilities of the samples were determined by Faraday method at 24° using $Hg[Co(NCS)_4]$ as calibrant. Surface areas of the samples were measured by low temperature nitrogen adsorption BET method. The composition of sodium molybdate, as reported is $Na_2MoO_4.2H_2O$.

The DTA curve (not included) records a sharp endothermic peak at 150° followed by three sharp endothermal changes at 470°, 643° and 689°. The TG curve (not included) registers a total weight loss amounting to 15.1% in the temperature range 90-360°. The weight loss (14.3%) in the temperature range 110-60° corresponds to the removal of two molecules of water from the molybdate. Thus, the endothermic peak at 150° is due to the dehydration of sodium molybdate dihydrate. However, after 160°, the weight loss registered in the TG curve is almost negligible (0.8%) which probably accounts for the removal of adsorbed traces of water.

The bands observed in the IR spectrum of pure sample at 3260 and 2220 cm^{-1} are characteristic of symmetric and antisymmetric $\nu O-H$ and $\delta H-O-H$ of lattice water[10-12]. The bands at 900 and 800 cm^{-1} are due to $\nu Mo-O$ characteristic of normal molybdates[13]. The spectrum also reveals the presence of bands at 1800, 1692, 1680 cm^{-1} which are probably due to overtone and combination bands. In the spectra of the samples preheated at 230° and above (up to 700°) a strong band at 830 cm^{-1} is assigned to ν_3 (ref. 14) and that at 1680 cm^{-1} is attributed to first overtone of the band at 830 cm^{-1}. These bands are characteristic of pure Na_2MoO_4 (ref. 14). XRD pattern of the pure sample is reasonably distinct with the characteristic lines having $d = 6.829$, 3.171, 3.050, 3.0, 2.1456, 1.666 Å, etc., which compare excellently with those

TABLE 1 — SURFACE ACIDIC STRENGTH DISTRIBUTION IN
SODIUM MOLYBDATE CATALYST

Sample*	Surface area m²/g	n-Butylamine titre values† for indicators of various pk_a values				
		+6·8	+5·0	+3·3	+2·0	−3·0
SM 230	2·5	0·47	0·12	0·12	0·04	0·04
SM 510	0·7	0·42	0·04	0·04	0·04	0·04
SM 660	0·5	0·69	0·15	0·04	0·04	0·04
SM 700	0·3	0·70	0·16	0·04	0·04	0·04

*The arabic numeral signifies the temperature at which sodium molybdate has been calcined.
†The values are expressed as mmoles/g; accuracy ± 0.01.

reported for $Na_2MoO_4.2H_2O$ (ASTM Card No. 1-0113). Diffraction pattern of the sample heated at 230° is slightly different and shows the presence of a few new strong lines having $d = 5.405$, 3·263, 2·765, 1·865, 1·756, 1·612 Å, etc., resembling closely those reported for standard patterns of Na_2MoO_4 (ASTM Card No. 12-773). Therefore, the endothermic peak at 150° is clearly due to dehydration of the $Na_2MoO_4.2H_2O$. The structure of the dehydrated sample appears to be more crystalline than that of the hydrated one. XRD pattern does not undergo any significant change when the molybdate is calcined at 510° and above. The last endothermic peak at 689° is, however, due to melting. The two peaks at 470° and 643° may be associated with crystal transformation as these changes are not accompanied by any weight change when heated at 470° and above.

Na_2MoO_4 is known to exist[15] in four modifications. The α-form is stable above about 620°; the β-form between 620° and 580°; γ-form between 510° and 410°; and the δ-form below 410°. Thus, the endothermic transitions at 473° and 643° are due to the following transformation:

$$\delta\text{-}Na_2MoO_4 \xrightarrow{470°} \gamma\text{-}Na_2MoO_4 \xrightarrow{643°} \alpha\text{-}Na_2MoO_4$$
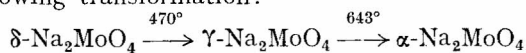
The transition between 620° and 580° could not be observed in the DTA curve and hence it is difficult to show the presence of β-Na_2MoO_4.

Surface acidic strength distribution in sodium molybdate samples is shown in Table 1. It is observed that the medium acid sites ($pk_a = +3.3$) are reduced as the molybdate is calcined at 510°. The strong acid sites ($pk_a \leqslant +2.0$), however, remain almost unchanged up to melting. It is interesting to note that weak acid sites ($pk_a \geqslant +5.0$) increase at 660° and above. The acidic strength of $MoO_3.Fe_2(MoO_4)_3$ at $Ho \leqslant +4.0$ has been reported by Pernicone et al.[16]. They found this molybdate to exhibit varying acid content as a function of calcination temperature. The maximum acidity, 0·06 mmole/g, was found at 500°. Thereafter, a steady decrease was observed up to 700°. At 400°, acidity value at $Ho \leqslant +4.0$ was <0.04. These acidities were found to have a close correlation with catalytic activity of $MoO_3.Fe_2(MoO_4)_3$ in the oxidation of formaldehyde. Sodium molybdate, being oxidation catalyst for many reactions[3,4], may also be expected to use its acidities in the oxidation.

Surface areas of the heat-treated samples of sodium molybdate are given in Table 1. It is seen that when sodium molybdate dihydrate is heated, there is a consistent decrease in the surface area, which may be due to the fact that on heating, the individual sodium molybdate crystals get dehydrated and shrink, thereby increasing the interparticle pores or more appropriately the micropores (dehydration pores) formed in individual sodium molybdate crystallites may enlarge due to sintering, thereby causing a reduction in surface area.

Magnetic measurements reveal that the pure sodium molybdate dehydrate as well as its thermal transition products are diamagnetic.

References

1. SPITALSKII, E. & FUNCK, A., Z. phys. Chem., 126 (1927), 1.
2. Netherland Pat. 413,733 (1965), to Imperial Chemical Industries Ltd.
3. Belg. Pat. 669,981 (1966) to E. I. du Pont.
4. YATSIMIRSKII, K. B. & FILIPPOV, A. P., Zh. neorg. Khim., 9 (1964), 2096.
5. Netherland Pat. 405,089 (1964), to Pennsalt Chemicals Corporation.
6. WILLIAMSON, J. B., Brit. Pat. 1,003,347 (1965).
7. BHATTACHARYYA, S. K., RAMACHANDRAN, V. S. & GHOSH, J. C., Adv. Catalysis, 9 (1957), 114.
8. SINHAMAHAPATRA, P. K. & BHATTACHARYYA, S. K., J. thermal Analysis, 8 (1975), 45; 9 (1976), 279; Chem. Era, XII (3) (1976), 79.
9. HIRSCHLER, A. E. & SCHNEIDER, A., J. chem. engng Data, 6 (1961), 313.
10. GAMO, I., Bull. chem. Soc. Japan, 34 (1961), 760, 765, 1430, 1433.
11. ZECCHINA, A., COLUCCIA, S., GUGLIELMINOTTI, E. & GHIOTTI, G., J. phys. Chem., 75 (1971), 2774.
12. DOUGLAS, R. M., Acta Cryst., 10 (1959), 423.
13. NAKAMOTO, K., Infrared spectra of inorganic and co-ordination compounds (John Wiley, New York), 1963, 159.
14. BUSEY, R. H. & KELLER, O. L. (Jr), J. phys. Chem., 41 (1964), 125.
15. MELLOR, J. W., A comprehensive treatise on inorganic and theoretical chemistry, Vol. 11 (Longmans, London), 1962, 553.
16. PERNICONE, N., LIBERTI, G. & ERSINI, L., Proceedings of 4th international congress on catalysis, Moscow, Reprints of paper No. 21, 1968.

Effect of Triton X-100 on the Kinetics of Irreversible Electrode Processes: Polarographic Behaviour of Ni(II), Co(II), Zn(II) & Mn(II)

SUDHINDRA SWARUP SHARMA, S. K. JHA & MUKHTAR SINGH

Department of Chemistry, Agra College, Agra

Polarographic behaviour of Ni(II), Co(II), Zn(II) and Mn(II) has been studied in 0·1M KNO_3 in the presence of increasing concentrations of Triton X-100 (0·0-0·01%). The values of the kinetic parameters $k^0_{f,h}$ and αn_a) have been calculated by Koutecky's treatment. The well established irreversible electrode processes of Ni(II) and Co(II) become more irreversible with an increase in [Triton X-100]. The quasi-reversible electrode processes of Zn(II) and Mn(II) become totally irreversible with increasing [Triton X-100].