

# CHAPTER VI

CHAPTER-IV  
X-RAY DIFFRACTION

Binary oxides and alloys of the transition metals are of great interest as catalysts, and their activities are greatly dependent on their electronic structure as also on the method of preparation, controlling their geometric factors.

Direct preparation of the oxides, or alloys system may not be suitable for the preparation of active catalyst with high specific surface area, however, it is possible to prepare the relevant system in a form more suitable for catalytic study or giving much higher activity, through direct decomposing the respective mixed metal oxalates, formates, hydroxides, etc. in air or nitrogen gas atmosphere at lower temperatures. To establish the composition, structure and homogeneity of the mixed system thus prepared, perhaps a most suitable method for the characterization of materials is the X-ray diffraction technique. Valuable information can be obtained from values of lattice spacings alone. Furthermore, as electrons are added across any series, there is a smooth change in metallic radius. Now the interatomic distance or metallic radius may be taken as a measure of the cohesive strength in the sense that the smaller the radius the greater must be the strength of the binding, similarly, as electrons are added through any series by the formation of solid solutions there may be a progressive increase in binding strength, followed by a decrease. Thus, its geometric properties are determined by or related to the electronic constitution.



The study of the catalyst structure as revealed by X-ray diffraction would provide valuable information pertaining to the electronic structure and mechanism of action by metals in the oxides.

X-ray diffraction technique can also be applied for the quantitative chemical analysis of the many component heterogeneous catalysts.

#### PREPARATION OF THE SAMPLES FOR THE STRUCTURAL STUDIES

The oxides of the nickel oxalate and cadmium oxalate and their mixed oxalates were prepared by heating the oxalates in air at 800°C for 6 hours.

The preparation and composition of the individual oxalates and mixed oxalates is as described earlier in TGA.

The oxide samples were stored in a vacuum desiccator and was used for X-ray diffraction analysis.

#### EXPERIMENTAL RESULTS AND DISCUSSION

The pure metal oxalates and mixed oxalates were examined by X-ray diffraction, using Philips-X-ray Diffraction Unit with  $\text{Cu K}_\alpha$  - radiation.

The rate of the scanning of the diffractometer was kept at the 2°/min. The results were recorded on the charts as 2θ Vs.

peak intensity.

Precise measurements were made for the calculation of d-values or the interplaner spacings. The results of the d-values with regard to each composition are listed in Tables-IX and X.

The slight variation in the 'd' values (Table-IX) on passing from nickel oxalate to cadmium oxalate suggests that the mixed oxalates may be either mixed crystals or metastable solid solutions at the grain boundaries.

It is clear from Table-X that the product of decomposition of mixed nickel-cadmium oxalates in air medium are nickel oxide and cadmium oxide.

The literature values (d) of  $\alpha$ -Ni-oxalate and Cd-oxalate and of the oxides NiO and CdO are given in Table-XI.

TABLE-IX  
X-RAY DIFFRACTION DATA

d(A°) VALUES OF NICKEL-CADMIUM OXALATES

Percentage of nickel in mixed Ni-Cd oxalates											
1	2	3	4	5	6	7	8	9	10	11	Physical mixture
100.00	87.84	76.13	67.94	58.60	47.68	39.15	29.95	19.30	9.00		
6.5777	-	-	-	-	-	-	-	-	-	-	-
-	5.3078	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	4.6204	4.7788	4.8117	4.9464	4.8261	
4.6909	4.6211	4.6548	4.6669	4.6710	4.6816	-	-	-	-	-	-
-	-	-	-	-	4.6566	-	4.6242	-	-	4.6523	
-	-	-	-	-	4.5903	4.5856	4.5529	4.5715	-	4.4404	
-	-	-	-	-	4.2011	-	-	-	-	-	-
3.8924	3.8887	3.8748	3.8715	3.8864	3.8864	3.8884	3.8936	3.9832	-	3.8685	
-	-	-	-	-	-	3.7070	3.6776	3.7014	3.7187	3.7069	
3.5991	-	-	-	-	3.5839	3.5880	-	-	3.4106	-	
-	3.1313	-	3.0793	-	-	3.1565	3.1373	3.1550	3.1666	3.1585	
-	2.9464	-	-	2.9530	-	-	2.9807	-	-	-	
2.9359	2.9336	2.9359	2.9297	2.9234	-	-	-	-	-	-	

contd.

TABLE-IX  
contd.

1	2	3	4	5	6	7	8	9	10	11
-	-	-	2.9116	2.9160	2.9145	2.9120	2.8930	2.9093	-	-
-	-	-	-	-	-	-	-	-	2.8266	-
2.7223	-	-	-	-	-	-	2.6905	2.7021	2.7102	2.7041
-	-	-	-	-	2.6630	2.6624	-	-	2.6562	2.6504
-	-	-	-	-	-	2.6494	2.6365	2.6476	-	-
-	-	-	-	-	-	-	-	2.6056	2.6165	2.6108
2.5169	2.5223	-	-	-	-	2.5235	2.5116	2.5201	2.5295	2.5242
-	2.3804	-	-	-	-	2.4292	2.4179	2.4274	2.4348	2.4279
-	2.3804	-	-	-	-	2.3664	2.3535	2.3619	2.3690	2.3652
-	-	-	-	-	-	-	-	-	2.3487	-
-	-	-	-	-	-	2.3000	2.2896	2.2985	2.3059	2.3021
-	-	-	-	-	-	2.2042	-	2.1995	2.2088	2.2011
-	-	-	-	-	-	2.1245	-	2.0997	2.0204	2.0173
2.0551	-	2.0342	-	-	-	2.0111	2.0099	2.0150	-	-
-	-	-	-	-	-	1.9299	1.9229	1.9288	1.9237	1.9311

contd.

TABLE-IX  
contd.

1	2	3	4	5	6	7	8	9	10	11
-	-	-	-	-	-	1.9299	1.9229	1.9288	1.9237	1.9311
-	-	-	-	-	-	1.9221	1.9147	1.9195	1.9194	1.9217
-	-	1.8882	-	-	-	1.8643	-	1.8622	1.8665	1.8641
1.8563	-	-	-	-	-	-	1.8578	-	-	1.8603
-	-	-	-	-	-	1.7813	1.7769	1.7812	1.7852	1.7827
-	-	-	-	-	-	-	-	-	1.7807	1.7788
-	-	-	-	-	-	1.7543	-	1.7528	1.7555	1.7542
-	-	-	-	-	-	-	1.7487	-	1.7521	-
-	-	1.7026	-	-	-	-	-	-	-	-
-	-	-	-	-	-	1.6787	1.6734	1.6773	1.6804	1.6733
-	-	-	-	-	-	-	-	-	1.5604	-
-	-	-	-	-	-	1.6570	-	1.6562	1.6559	1.6564
-	-	-	-	-	-	-	1.6522	1.6232	-	1.6549
-	-	-	-	-	-	-	-	1.6218	1.6225	1.6210
-	-	-	-	-	-	-	-	-	1.5076	1.5360
-	-	-	-	-	-	-	-	-	1.5683	-
-	-	-	-	-	-	-	-	1.5533	-	1.5540
-	-	-	-	-	-	-	-	1.5502	-	1.5513

TABLE-X  
X-RAY DIFFRACTION DATA  
d(A°) VALUES OF OXIDES OF Ni-Cd

		Percentage of Nickel oxide in the sample										
		100.00	87.84	76.13	67.94	58.60	47.68	49.15	29.95	19.30	00.00	Physical mixture
5.5208	-	-	-	-	-	-	-	-	-	-	-	-
5.4801	-	-	-	-	-	-	-	-	-	-	-	-
4.9245	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	2.9644	-	-	-	-	-	-
-	2.6722	2.6872	2.6837	2.6852	2.6824	2.6926	2.6700	2.6829	2.6853	2.6903	-	-
-	-	-	-	-	-	-	-	-	-	-	2.4503	-
-	-	-	-	-	-	-	-	-	-	-	2.4332	-
2.3985	2.3858	2.3967	2.3923	2.3941	2.3918	2.4018	2.3840	2.3931	-	-	2.3957	-
-	-	2.3303	2.3272	2.3283	2.3261	2.3340	-	2.3267	2.3290	2.3310	-	-
-	2.3194	-	-	-	-	-	2.3180	-	-	-	-	-
2.0787	2.0701	2.0779	2.0746	2.0752	2.0735	2.0814	2.0683	2.0744	-	-	2.783	-
-	-	-	-	-	-	-	1.9260	1.9260	-	-	1.9842	-
-	-	1.6520	1.6506	1.6514	1.6502	1.6536	-	1.6503	1.6517	1.6518	-	-
-	1.6468	1.6477	1.6466	-	-	1.6495	1.6463	1.6466	-	-	-	-
-	-	-	-	-	-	-	-	1.6198	-	-	-	-



TABLE-XI

## X-RAY DIFFRACTION LITERATURE DATA

LITERATURE VALUES  $d(A^\circ)$  OF (i)  $NiC_2O_4 \cdot 2H_2O$ , (ii)  $NiO$ ,  
(iii)  $CdC_2O_4$  AND (iv)  $CdO$

$NiC_2O_4 \cdot 2H_2O$		$NiC_2O_4 \cdot 2H_2O$ contd.		$NiO$		$CdC_2O_4$ contd.		$CdC_2O_4$ contd.		$CdO$	
$d(A^\circ)$	$I/I_1$	$d(A^\circ)$	$I/I_1$	$d(A^\circ)$	$I/I_1$	$d(A^\circ)$	$I/I_1$	$d(A^\circ)$	$I/I_1$	$d(A^\circ)$	$I/I_1$
1	2	3	4	5	6	7	8	9	10	11	12
4.77	100	1.965	5	2.09	100	8.0	4	2.41	2	2.71	100
4.14	8	1.925	40	2.41	51	6.5	20	2.33	20	2.35	88
3.94	16	1.763	13	1.48	57	5.7	100			1.66	43
3.57	8	1.720	4			4.69	8				
3.12	1	1.668	8			4.50	30				
3.03	14	1.645	4			3.98	8				
2.959	40	1.625	2			3.70	40				
2.720	2	1.614	6			3.43	16				
2.642	11	1.589	30			3.22	16				

contd.

TABLE-XI  
contd.

	1	2	3	4	5	6	7	8	9	10	11	12
2.528	25	1.559	7				3.08	16				
2.436	5	1.540	3				2.95	40				
2.311	15	1.529	6				2.73	40				
2.169	7	1.518	18				2.65	20				
2.088	30	1.480	20				2.56	8				
2.021	8	1.463	5				2.49	8				