

## Determination of the number of *d* electron states in catalysts†

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**Abstract.** X-ray *K*-absorption edge measurements and metal Auger intensity ratios have been employed to determine the number of *d*-electron states in manganese oxide catalysts; the Auger method appears to be more reliable for the purpose.

**Keywords.** Manganese *K*-absorption edge; x-ray absorption edges of catalysts; Auger spectra of catalysts; *d*-electrons in catalysts.

### 1. Introduction

Metal Auger intensity ratios in transition metal compounds are determined by the number of valence electrons. Accordingly, the *L*VV/*L*MV Auger intensity ratio in first row transition metal compounds varies proportionally with the number of valence electrons (Rao *et al* 1980; Yashonath *et al* 1983). Metal Auger transitions can therefore be employed to investigate surface oxidation of metals. The number of valence electron states in transition metal compounds can also be determined by making x-ray absorption edge measurements since the chemical shifts of absorption edges are determined by the oxidation state or the effective charge of the metal (Sarode *et al* 1979; Sankar *et al* 1983). We considered it most worthwhile to carry out a comparative investigation of the *d*-electron states in MnO<sub>2</sub> and MnO<sub>2</sub>-SiO<sub>2</sub> catalysts by employing both the Auger and x-ray absorption edge measurements. In the x-ray absorption edge study, we have employed the Mn (*1s* → *3d*) transition in the near edge structure besides the chemical shifts of the *K*-absorption edge.

### 2. Experimental

MnO<sub>2</sub> was prepared by the decomposition of the nitrate at 470 K in air. The sample of the MnO<sub>2</sub>-SiO<sub>2</sub> catalyst (Mn content: 55% (W/W)) was prepared by coprecipitation of MnO<sub>2</sub> and SiO<sub>2</sub> from an aqueous solution of KMnO<sub>4</sub> and sodium silicate using starch to reduce KMnO<sub>4</sub> from Mn<sup>7+</sup> to a nominal Mn<sup>4+</sup>. Both MnO<sub>2</sub> and MnO<sub>2</sub>-SiO<sub>2</sub> samples were activated by heating in a stream of dry oxygen at 620 K for 3 hours. These catalysts were deactivated by heating them in air at 970 K. Reduction of the samples was carried out in dry hydrogen at 670 K for 3 hours. Mn metal, MnO, Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub> and KMnO<sub>4</sub> were studied as reference systems.

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X-ray induced Auger electron spectra (AES) were recorded with an ESCA III Mark 2 spectrometer of V.G. Scientific Ltd., U.K. *In situ* activation and reduction of the catalysts could be carried out in the sample preparation chamber of the spectrometer for the Auger studies. AES of these oxides have contributions from both inter and intra-atomic processes (Rao and Sarma 1982). For example, the  $L_{VV}$  transition of MnO would include  $L(Mn)V(Mn)V(Mn)$  as well as  $L(Mn)V(O)V(O)$  transitions. Since we were interested in the intra-atomic process, the interatomic contribution was subtracted out assuming the line shapes of the two transitions to be similar to those of the pure metal.

X-ray  $K$ -absorption spectra were recorded with a bent crystal spectrograph described earlier (Sankar *et al* 1983). The uncertainty in the measurement of the position was  $\pm 0.8$  eV. For the x-ray absorption measurements freshly prepared samples of known thickness were placed between cellophane adhesive tapes.

### 3. Results and discussion

#### 3.1 X-ray absorption edge measurements

Typical x-ray absorption  $K$ -edge spectra of the various catalyst samples are shown in figure 1. Chemical shifts,  $\Delta E$ , of the catalysts are tabulated in table 1 along with those of the reference manganese oxides. Chemical shifts of the reference manganese oxides increase progressively with the increase in the oxidation state of manganese or the decrease in the number of  $d$ -electrons. From figure 2 we see that the curve correlating

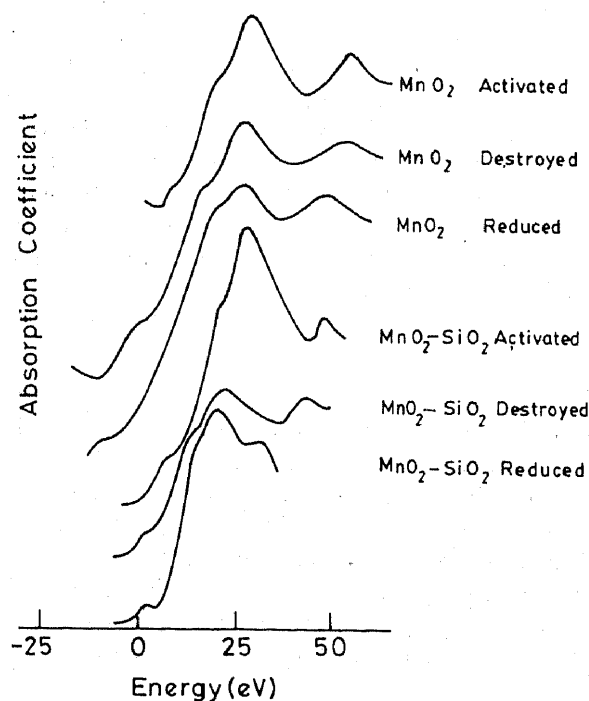


Figure 1. X-ray absorption  $K$ -edge spectra of  $MnO_2$  and  $MnO_2-SiO_2$  catalysts.

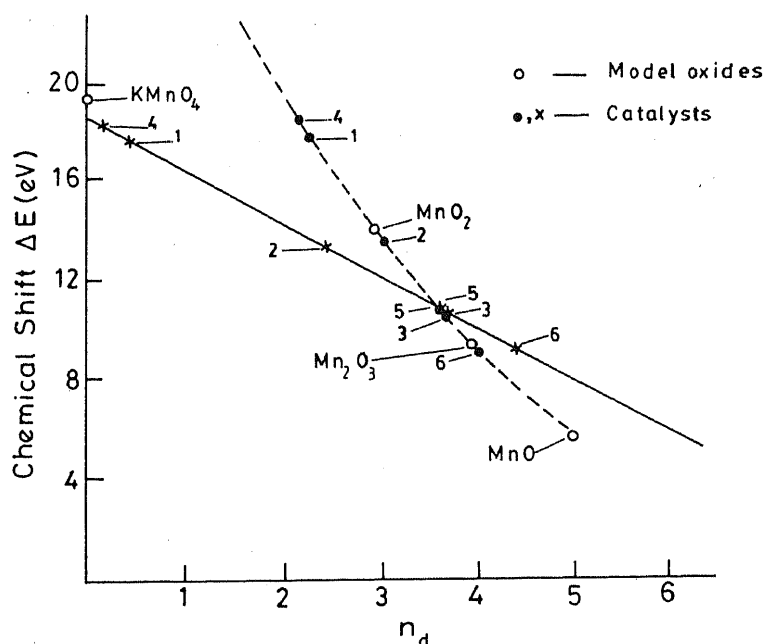


Figure 2. Plot of the chemical shift against the number of *d* electrons,  $n_d$ . 1. MnO<sub>2</sub> activated; 2. MnO<sub>2</sub> deactivated; 3. MnO<sub>2</sub> reduced; 4. MnO<sub>2</sub>-SiO<sub>2</sub> activated; 5. MnO<sub>2</sub>-SiO<sub>2</sub> deactivated; 6. MnO<sub>2</sub>-SiO<sub>2</sub> reduced.

$\Delta E$  and the number of *d* electrons of MnO, Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> is essentially parabolic. The point due to KMnO<sub>4</sub> deviates markedly from this parabolic plot possibly due to the different coordination and bonding in KMnO<sub>4</sub>. We can draw a mean line taking all the points (MnO, Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub> and KMnO<sub>4</sub>) into account. We have estimated the number of *d*-electrons,  $n_d$  in the catalyst samples from both the working plots in figure 2. The range of  $n_d$  in the catalysts obtained from the two plots are given in table 1. The values of  $n_d$  in deactivated and reduced MnO<sub>2</sub> and MnO<sub>2</sub>-SiO<sub>2</sub> catalysts are around the same from the two plots, but differ considerably in the case of the activated catalysts. The  $n_d$  values of the activated samples turn out to be 2.5 for MnO<sub>2</sub> and 2.4 for MnO<sub>2</sub>-SiO<sub>2</sub> from the parabolic working plot based on MnO, Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>; from the working curve which includes KMnO<sub>4</sub>,  $n_d$  is too low (0.5 and 0.2 for activated MnO<sub>2</sub> and MnO<sub>2</sub>-SiO<sub>2</sub> catalysts respectively). The correct value is likely to be in between these two extremes. It appears that x-ray absorption edge measurements cannot provide good estimates of the number of *d*-electron states (or the oxidation state of the metal in these catalysts). This limitation may be because the chemical shift is really related to the effective atomic charge of the metal rather than the oxidation state or the number of *d*-electrons (Sankar *et al* 1983).

A feature of the x-ray absorption spectra which is sensitive to the number of *d*-electrons of the metal is the intensity of  $1s \rightarrow 3d$  transition. The  $1s \rightarrow 3d$  peak intensity can be normalised with respect to the intensity of the  $1s \rightarrow 4p$  transition, which does not vary (Knapp *et al* 1982) since the  $4p$  occupancy remains the same through the series of substances studied. The  $1s \rightarrow 3d/1s \rightarrow 4p$  intensity ratio of MnO<sub>2</sub> and MnO<sub>2</sub>-SiO<sub>2</sub>

**Table 1.** K-absorption edge and Auger results on MnO<sub>2</sub> catalysts and model compounds.

	K-absorption edge			Auger	
	$\Delta E(\text{eV})^a$	$n_d^b$	$I(1s \rightarrow 3d)/I(1s \rightarrow 4p)$	$I(\text{LVV})/I(\text{LMV})$	$n_d$
Mn	—	—	—	0.347 <sup>c</sup>	5
MnO	5.4	5	—	0.297	5
Mn <sub>2</sub> O <sub>3</sub>	9.0	4	—	0.251	4
MnO <sub>2</sub>	13.9	3	—	0.220	3
KMnO <sub>4</sub>	19.1	0	—	—	—
1. MnO <sub>2</sub>	17.3	0.5-2.5	0.11	0.185	1.6
2. MnO <sub>2</sub> deactivated	13.4	2.6-3.1	0.10	0.230	3.2
3. MnO <sub>2</sub> reduced	10.4	3.7-3.8	0.09	0.237	3.4
4. MnO <sub>2</sub> -SiO <sub>2</sub> activated	18.1	0.2-2.4	0.24	0.162	1.0
5. MnO <sub>2</sub> -SiO <sub>2</sub> deactivated	10.6	3.6-3.7	0.11	0.240	3.5
6. MnO <sub>2</sub> -SiO <sub>2</sub> reduced	8.9	4.0-4.4	0.07	0.245	3.7

<sup>a</sup> With reference to Mn metal; <sup>b</sup> range in the number of *d*-electrons given by the two plots in figure 2; <sup>c</sup> in Mn metal, we have to take the two 4*s* electrons into account since it is the total number of valence electrons that determines the metal Auger intensity ratio.

catalysts are listed in table 1 to illustrate the progressive increase in the intensity ratio as we go from the reduced form to the activated form of MnO<sub>2</sub>; the deactivated form shows an intermediate value. This reflects that the *d* orbital occupancy of the metal in activated MnO<sub>2</sub> is lower than that in deactivated MnO<sub>2</sub> which in turn is lower than that in reduced MnO<sub>2</sub>. We find similar behaviour in MnO<sub>2</sub>-SiO<sub>2</sub> catalysts where the activated MnO<sub>2</sub>-SiO<sub>2</sub> sample shows the highest intensity ratio corresponding to the lowest occupancy of the *d*-orbital.

### 3.2 Auger studies

X-ray induced Mn(LVV) and Mn(LMV) Auger spectra of manganese metal, MnO<sub>2</sub> and activated MnO<sub>2</sub> are shown in figure 3. Unlike the LMV transition, the LVV transition shows significant changes in intensity as well as width. This is expected since the two-hole final state in the LVV transition would be more sensitive to changes in the number of valence electrons (3*d* + 4*s*) as compared to the one-hole final state in the LMV transition.

In order to determine the number of *d* electron states in MnO<sub>2</sub> catalysts, we have made use of the LVV/LMV intensity ratios. These ratios in the Mn metal, reference oxides and catalyst samples are listed in table 1. A plot of the ratios in Mn metal and the reference oxides against the total number of valence electrons, *n*, is essentially linear (figure 4); the number of *d* electron states,  $n_d$  is given by  $n-2$ . In figure 4, we have also shown the LVV/LMV ratios corresponding to the variously treated MnO<sub>2</sub> and MnO<sub>2</sub>-SiO<sub>2</sub> catalysts. We readily see that the value of  $n_d$  is significantly lower (oxidation state of Mn is higher) in activated MnO<sub>2</sub> and MnO<sub>2</sub>-SiO<sub>2</sub> compared to ordinary MnO<sub>2</sub> prepared by the decomposition of the nitrate. The reduced catalysts, on the other hand, have oxidation states lower than 4+ with a considerably greater number of *d* electrons than 3. The Auger intensity method appears to be reliable for determining the number of *d*-electron states in these catalysts. We believe that the technique would be of considerable value in studying electron states of various metal catalysts. In this context,

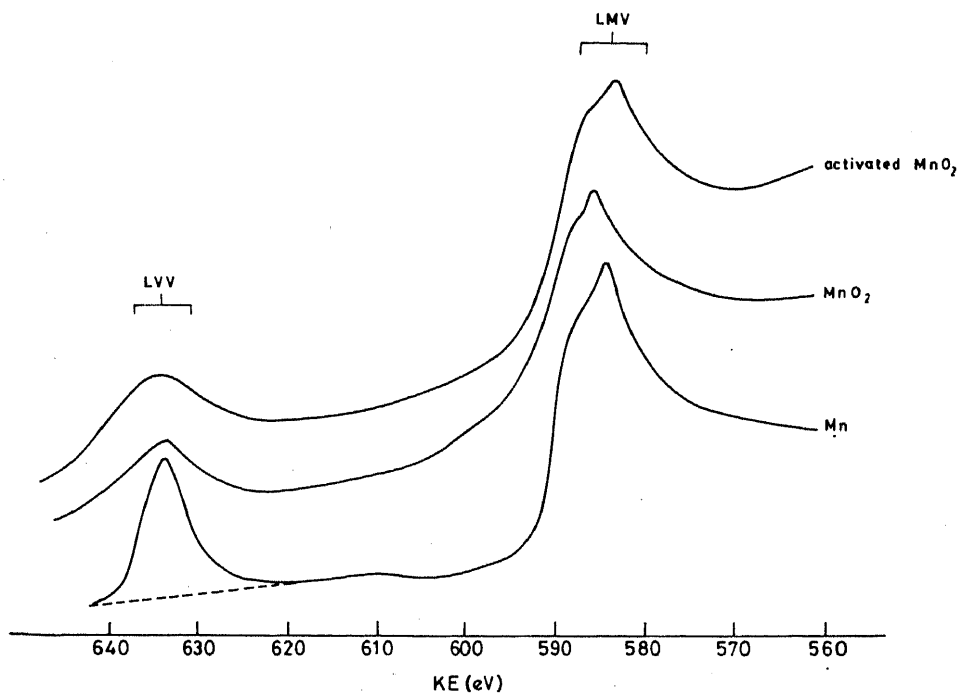


Figure 3. X-ray induced Auger transitions in the LVV and LMV regions of Mn.

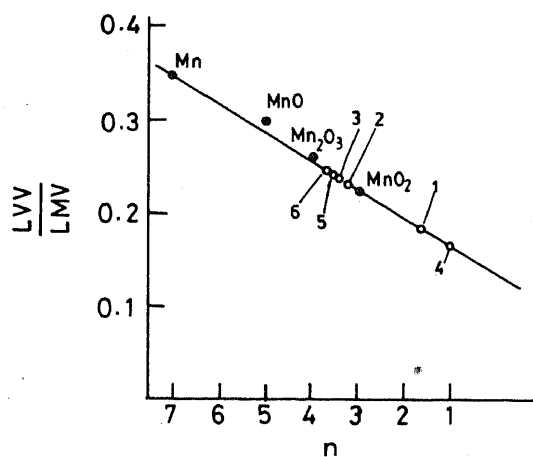


Figure 4. Plot of L<sub>2,3</sub>VV/L<sub>2,3</sub>MV Auger intensity ratio against the number of valence electrons, n; the numbers designating points stand for the samples described in figure 2.

it should be pointed out that electron energy loss spectroscopy may also provide useful information on the number of *d* electron states of catalysts, but the study has hitherto been limited to model oxides only (Rao *et al* 1984a, b).

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