# Chemical and physical properties of the solid products of thermal decomposition of copper(II) and nickel(II) permanganates

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The thermal decomposition of copper and nickel permanganates has been studied up to 1100 K with a view to the formation of catalytically active mixed oxides. XRD, TG and magnetic moment determinations have been used to characterize the reaction products. Both compounds produce an amorphous, high surface area intermediate at low temperatures. The copper series crystallizes to the inverse spinel $CuMn_2O_4$ below 725 K, while the nickel series produces $NiMnO_3$ at 725 K and the inverse spinel at 1100 K.

Thermal decompositions of metal permanganates have been the subject of many kinetic and mechanistic studies, with the breakdown of the potassium salt[1] ranking as one of the most intensively investigated of all solid-state reactants. More recent work has extended the range of reactants to include the pyrolysis of copper[2] and nickel[3] permanganates in vacuum. As with other salts containing the $MnO_4^-$ anion, kinetic behaviour was described by the Avrami–Erofeyev equation, with $n=2$, and activation energies were $115\pm15$ kJ mol$^{-1}$ (335–370 K) for the copper and $100\pm5$ kJ mol$^{-1}$ (355–400 K) for the nickel compound. In addition to a comparison with the extensively studied alkali-metal permanganates, this work was undertaken to investigate the possibility that such compounds, containing two transition-metal cations, could be used for the preparation of active mixed oxides, potentially of interest as catalysts. The kinetic studies referred to above[2,3] did not characterize the residual solid products unequivocally, but the following equations represented the reaction stoichiometry $Cu(MnO_4)_2=[CuMn_2O_{5.45}]+1.27O_2$, where it is inferred that manganese is in more than one oxidation state.[2]

$$[CuMn_2O_{5.45}]=CuMnO_4+0.5Mn_2O_3$$

$$Ni(MnO_4)_2=[NiMn_2O_5]+1.54O_2$$

Possible representations for $[NiMn_2O_5]$ are:[3]

$$[NiMn_2O_5]=NiO+2MnO_2 \text{ or } NiMnO_3+MnO_2$$

The present work was undertaken to characterize further the low-temperature decomposition products, and the changes that occur upon heating at higher temperatures.

## Experimental

### Starting materials

The starting materials were prepared by mixing saturated aqueous solutions of barium permanganate and copper or nickel sulfate in the required ratio. The precipitated barium sulfate was removed by filtration, and the remaining solution concentrated by evaporation at room temperature until crystals were formed. These separated products retained slightly less than the expected six molecules of water of crystallization,[4] but this was considered to be unimportant because the present work was concerned with the anhydrous compounds. The prepared anhydrous compounds were dried to constant mass at 373 K and were coded Cu373 and Ni373; these were used in all subsequent investigations described below.

### Experimental methods

Temperature programmed heating (5 K min$^{-1}$) of both reactants (Cu373 and Ni373) was carried out under nitrogen and oxygen atmospheres. Typical traces are shown in Fig. 1.

Samples of both reactants were heated isothermally at higher temperatures to constant mass, to produce samples Cu473, Cu573, Cu723, Cu773, Cu873 and Cu1073, and a similar group of nickel samples.

XRD (Cu-Kα radiation) was used for identification of phases, and the magnetic moments of all of these samples were measured.

Water sorption on each of the heated materials was studied by storing weighed samples in desiccators containing saturated aqueous potassium carbonate solution ($p/p_0=0.42$).[5] These were monitored until constant mass was reached.

## Results

### TG mass losses

The mass loss–temperature profiles for both reactants (Cu373 and Ni373) were very similar and were not influenced appreciably by the change in atmosphere between oxygen and nitrogen. A single intermediate was produced at low temperatures (*ca.* 635 K) representing a 16% mass loss for the copper salt and 18% for the nickel salt. Both of these correspond approximately to a stoichiometry of $MMn_2O_5$,[2,3] and both lose further

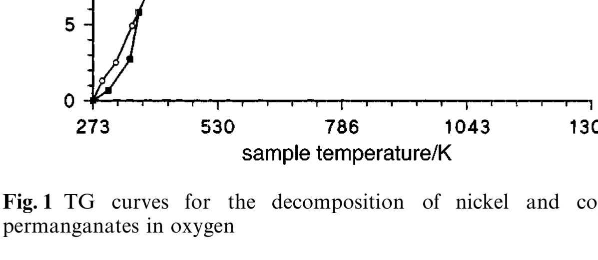

**Fig. 1** TG curves for the decomposition of nickel and copper permanganates in oxygen

**Table 1** Mass losses in nitrogen

| sample | temperature range/K | total mass loss (%) | number of oxygen atoms lost | phases detected |
|---|---|---|---|---|
| Cu373 | 295–625 | 16.2 | 3.05 | $CuMn_2O_5$[a] |
| | 625–1175 | 21.5 | 4.05 | $CuMn_2O_4+Mn_2O_3$ |
| Ni373 | 295–605 | 17.7 | 3.30 | $NiMn_2O_5$[a] |
| | 605–1175 | 22.6 | 4.20 | $NiMnO_3+Mn_2O_3$ |
| | 1175–1240 | 25.1 | 4.60 | $NiMn_2O_4$ |

[a] Largely amorphous.

**Table 2** Mass losses in oxygen

| sample | temperature range/K | total mass loss (%) | number of oxygen atoms lost | phases detected |
|---|---|---|---|---|
| Cu373 | 295–655 | 16.3 | 3.07 | $CuMn_2O_5$[a] |
| | 655–1175 | 21.5 | 4.05 | $CuMn_2O_4$ |
| Ni373 | 295–595 | 18.1 | 3.36 | $NiMn_2O_5$[a] |
| | 595–1075 | 22.9 | 4.24 | $NiMnO_3$ |
| | 1075–1175 | 24.9 | 4.62 | $NiMn_2O_4$ |

[a] Largely amorphous.

oxygen upon heating to higher temperatures. Mass loss data for reactions in oxygen and nitrogen are summarized in Tables 1 and 2, respectively.

## XRD results

The XRD patterns of Cu373, Cu573, Ni373 and Ni573 were extremely simple, consisting of two broad peaks for each compound, centred at 0.245 and 0.140 nm. These materials are largely amorphous and are considered to be similar.

During isothermal heating at higher temperatures, both reactants crystallized to give phases showing reasonably sharp peaks, as shown in Fig. 2 and 3. Also included, for comparison, are the XRD patterns for $Mn_2O_3$, $CuMn_2O_4$, $NiMn_2O_4$ and $NiMnO_3$ from the JCPDS files.[6] Qualitatively, the copper compounds show the low-temperature (725 K) formation of the spinel phase, $CuMn_2O_4$, and $Mn_2O_3$ appears above 773 K. The nickel series first produced the perovskite phase $NiMnO_3$ and $Mn_2O_3$ before the appearance of the spinel phase at *ca.* 1100 K.

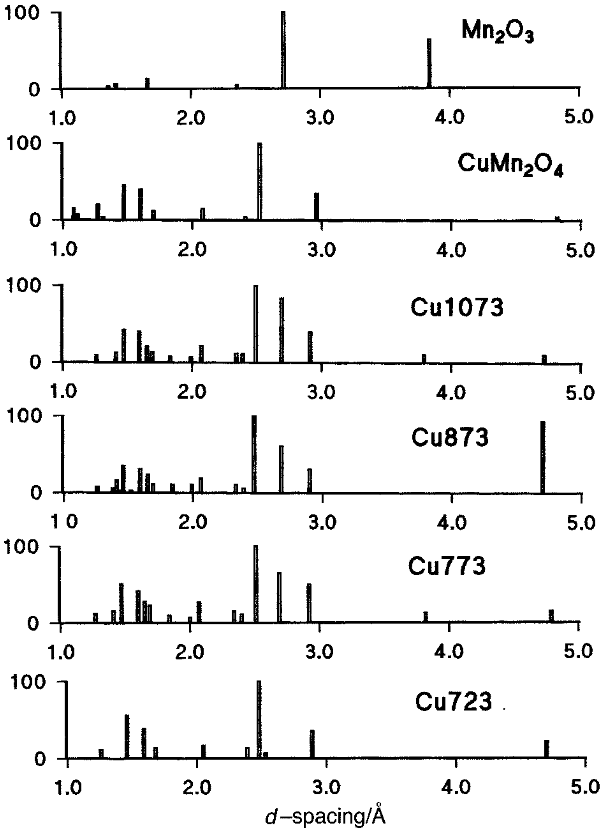

**Fig. 2** XRD patterns for copper compounds

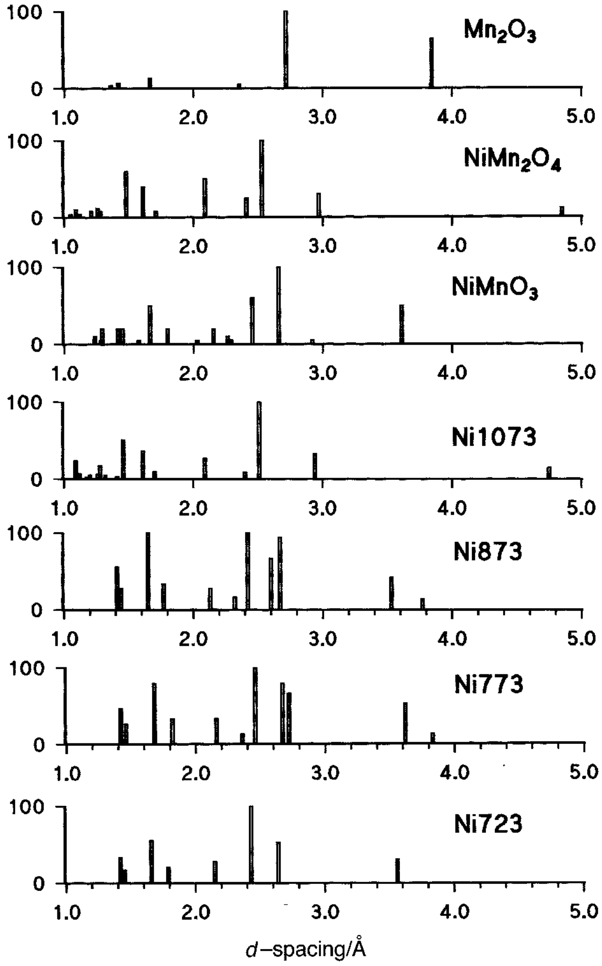

**Fig. 3** XRD patterns for nickel compounds

## Magnetic moments

Measured magnetic moments for the reactants and the isothermally heated products are shown in Table 3, which also includes estimates of the number of unpaired electrons, based on the spin-only formula.[7] Moments for some of the nickel compounds were too high (*i.e.* $>10\,\mu_B$) to be measured with the equipment available.

## XPS results

Limited XPS measurements were made for the copper salts and the results are summarized in Table 4. These indicate that

**Table 3** Magnetic moments

| compound | $\mu_{Cu}/\mu_B$ | $n^a$ | $\mu_{Ni}/\mu_B$ | $n^a$ |
|---|---|---|---|---|
| M373 | 5.71 | 5 | 5.65 | 5 |
| M673 | 5.38 | 4/5 | 5.53 | 4/5 |
| M723 | 6.74 | 6 | >10 | >9 |
| M773 | 6.68 | 6 | >10 | >9 |
| M873 | 7.24 | 6/7 | >10 | >9 |
| M1073 | 7.28 | 6/7 | 6.74 | 6 |

[a] $n$ = unpaired electrons from spin-only formula.

**Table 4** XPS results

| temperature/K | $E_{\beta}{}^{a}$/eV | Cu/Mn ratio |
|---|---|---|
| 473 | 934.3 | 2.0 |
| 673 | 936.0 | 1.4 |
| 723 | 931.1 | 2.1 |
| CuO | 934.4 | |
| $Cu_2O$ | 932.7 | |

[a] Cu 2p binding energy.

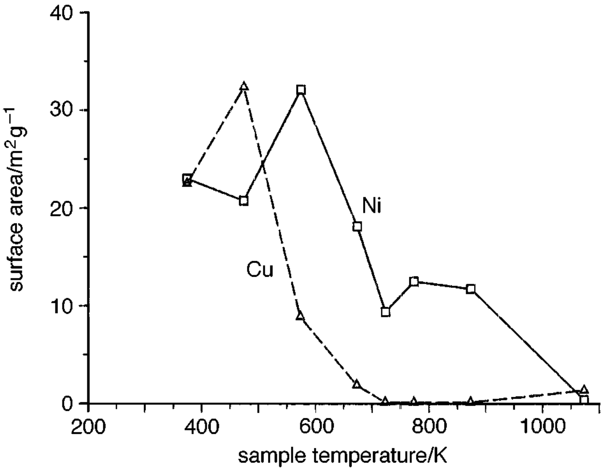

**Fig. 4** Water sorption on decomposition products

copper(II) is present at low temperatures, converting to copper(I) by 725 K.

### Water sorption

The mass gains measured for sorption of water were converted into surface areas on the assumption[8] that a water molecule occupies 0.125 nm$^2$, and the results are shown in Fig. 4. The relatively large areas characteristic of reactants heated at low temperatures correspond only to the amorphous materials. As crystallization to recognizable product phases proceeds, the surface areas diminish. The changes in surface area with heating for the copper compounds are relatively simple, with the reduction in area (to 0.1 m$^2$ g$^{-1}$) associated with formation of spinel, followed by a slight increase with the formation of $Mn_2O_3$. The nickel compounds, with a minimum at *ca.* 700 K, reflect the formation of $NiMnO_3$ as an intermediate.

## Discussion

### Reactions below 600 K

The thermogravimetry data and results in Table 1 confirm that both reactant salts decompose to yield residual material with an overall composition close to $MMn_2O_5$. The amount of oxygen evolved from the nickel salt was slightly greater than that from the copper salt, consistent with previous observations.[2,3]

X-Ray diffraction evidence confirms the similarity of both materials, which are largely amorphous, except for broad maxima at *d*-spacings of 0.245 and 0.140 nm. These peaks are not characteristic of any identifiable crystalline product phase[9] but are attributed to a manganese oxide phase because they appear in both of the products and are also the only two broad reflections in the largely amorphous, *z*-disordered ($z_d$), hydrated phyllomanganate mentioned by Giovanoli.[10]

**$CuMn_2O_5$.** Measured magnetic moments are higher ($n=5$) than can be ascribed to simple mixtures of oxides ($CuO+2MnO_2$ or $CuO+Mn_2O_3$), providing evidence of more complicated interactions between the constituent cations of this poorly crystallized material. The presence of appreciable amounts of $Cu^{3+}$ under the conditions used appears improbable, and the XPS observations confirm that the copper in the low-temperature materials was in the divalent state. Adsorption evidence suggests very small particle sizes, with edges $<0.1$ μm.

**$NiMn_2O_5$.** The measured magnetic moment ($n=5$) is close to that expected for either $NiMnO_3+MnO_2$ ($n=4$) or $NiMnO_3+Mn_2O_3$ ($n=5$), though these phases were not present as well crystallized solids. Again adsorption is consistent with highly divided material.

### Reactions above 625 K

The changes that occur on heating the two intermediate materials, of nominal compositions $MMn_2O_5$, are sufficiently different for them to be discussed separately.

**$CuMn_2O_5$.** The spinel phase, the final high-temperature product, crystallizes at about 725 K. The mass loss (Tables 1 and 2) is close to that required for the reaction:

$$CuMn_2O_5 \rightarrow CuMn_2O_4 + 0.5O_2$$

This representation must, however, be regarded as a simplification of the changes occurring. The appearance of $Mn_2O_3$ shows that not all of the material is converted to spinel, although no evidence of CuO was found.

The oxygen evolution may result from the dissociation of either oxide present in the intermediate that contains $CuO:2MnO_2$. The breakdown of $MnO_2$ (to give $Mn_2O_3+0.5O_2$) is considered the more probable because CuO is by far the more thermally stable.[11,12] $MnO_2$ is regarded as the expected precursor to $Mn_2O_3$ from consideration of the phases present in this temperature range.[12] Spinel may, therefore, be formed by the reaction

$$CuO + Mn_2O_3 \rightarrow CuMn_2O_4$$

Retention of $Mn_2O_3$ in the products (Fig. 2) shows that this reaction does not proceed to completion either for kinetic reasons or owing to reactant compositional inhomogeneities. Such inhibition must be effective because it is known from the Cu–Mn–O phase diagram[11] that at a Cu/Mn ratio of 0.5, the spinel and $Mn_2O_3$ do not coexist at equilibrium. Inhomogeneity is also suggested by the Cu/Mn ratios given in Table 4. The low Cu content of Cu673 (Cu/Mn$=$1.4) is not caused by loss of copper, because the ratio rises at higher temperatures, but must be due to the non-detection of copper in an inhomogeneous mixture (because of the small sampling depth of ESCA).

Copper manganate, $Cu^{2+}Mn_2{}^{3+}O_4$, the normal spinel,[13] is expected to contain nine unpaired electrons, which is much higher than the value obtained here. The alternative formulation, $Cu^{+}(Mn^{3+}Mn^{4+})O_4$, suggested on the basis of the cubic unit cell,[14] contains seven unpaired electrons which is in closer agreement with the value measured for our product (Table 3). The presence of $Cu^{I}$ in the spinel is confirmed by the XPS results (Table 4), and agrees with the results of Di Castro *et al.*,[15] who studied the reactions of CuO dispersed on a manganese dioxide support and showed that the reduction of copper(II) took place below 540 K. Retexturing, with growth of well crystallized products, explains the marked drop in surface area shown in water sorption measurements (Fig. 4).

**$NiMn_2O_5$.** XRD observations (Fig. 3) show that this intermediate reacts above 773 K to form $NiMnO_3$ and $Mn_2O_3$. Again $MnO_2$ may be the precursor to $Mn_2O_3$ which was not detected after heating at 723 K, although $NiMnO_3$ was present.

The overall reaction may be represented as

$$NiMn_2O_5 \rightarrow [NiMnO_3 + MnO_2]$$
$$\rightarrow NiMnO_3 + 0.5Mn_2O_3 + \tfrac{1}{2}O_2$$

The expected magnetic moment for these phases would be close to six unpaired electrons. The inverse spinel, represented[14] as $Mn^{2+}(Ni^{2+}Mn^{4+})O_4$ would contain ten unpaired electrons, which is in better accord with the observed moment (Table 3). The higher temperatures required to complete these reactions, compared with the copper salt, are consistent with the pattern of area reduction shown in Fig. 4.

## Conclusions

The residual products of the low-temperature ($<600$ K) decompositions of $Cu(MnO_4)_2$ and of $Ni(MnO_4)_2$ are largely amorphous, high surface area materials of approximate compositions $CuMn_2O_{5.5}$ and $NiMn_2O_5$. A proportion of the manganese is present as $Mn^{IV}$. On heating above 600 K both of these materials evolve *ca.* 1.0 atom oxygen per mol of reactant and later react to form mixtures containing $Mn_2O_3$ and phases that the magnetic evidence identify as inverse spinels: $Cu^+(Mn^{3+}Mn^{4+})O_4$ (confirmed by the XPS evidence) and $Mn^{2+}(Ni^{2+}Mn^{4+})O_4$. The intermediate $NiMnO_3$ was found in reactions of the nickel salt but no comparable phase was found during reactions of the copper salt (Fig. 2 and 3). There is also the clear probability that non-stoichiometric compounds or solid solutions are formed during these reactions. This would explain the observed discrepancies between the amounts of oxygen evolved and the stoichiometric balanced equations. High temperatures are required to form well crystallized products and these reactions are accompanied by a diminution of surface area. Problems in determining the stoichiometry of decompositions of alkali-metal permanganates[1] have been associated with incomplete reactions and restrictions in the formation of crystalline, well characterized products below 573 K.

The above observations show that relatively stable, high area mixed oxide phases exhibiting interesting magnetic properties are formed by the low-temperature decomposition of $Cu(MnO_4)_2$ and $Ni(MnO_4)_2$. It is thought that these phases may possess activity as heterogeneous oxidation catalysts.

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