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Comments on "The use of MoO_3 and NiO (pure or mixed) oxide catalysts in the decomposition of $KMnO_4$" by S.A. Halawy and M.A. Mohamed

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Abstract

The recent paper by Halawy and Mohamed [S.A. Halawy, M.A. Mohamed, Thermochim. Acta 345 (2000) 157] has raised several problems which need to be resolved. Our comments are given under the headings of the sections of the original paper.

Keywords: Kinetics; Decomposition; $KMnO_4$

1. Thermal analysis

Throughout the text the terms "TG" and "DTG" are used to describe data (represented for example in Figs. 3 and 4 of [1]) not cast as a change in mass against temperature, but in the form "% oxygen evolution" and "($\Delta V/\Delta T$) (au)" against temperature. Elsewhere Halawy and Mohamed call their technique "gasometric" [1] and refer to detailed description in an earlier paper by Halawy [2], from which it becomes clear that the technique actually used is the exchanged gas detection (EGD) method. The "TG" and "DTG" references throughout the text are thus misleading.

The results presented in Fig. 3 of [1] are inconsistent with most of the literature data as well as with the authors' hypothesis about the stoichiometry of the investigated reaction. Assuming that the values on the *Y*-axis labeled as "% oxygen evolution" actually represent the amount of evolved oxygen (in mol%) related to the total oxygen content in $KMnO_4$, Fig. 3 of [1] can be converted into Table 1. The resulting data indicate that there is no correlation between the amount of the evolved oxygen and the composition of the sample. The amount of evolved oxygen from the sample (PP + Cat-70) in the temperature range 0–300°C is almost one-third (28.4%) greater than for pure $KMnO_4$. On the other hand, if only the range of the fast oxygen evolution is taken into account (column 1 in Table 1) than sample (PP + Cat-50) evolves 54.1% oxygen when pure $KMnO_4$ only 51.0% oxygen.

There are two possible reasons for these discrepancies:

1. the data presented contain artifacts, or
2. the amount of evolved oxygen depends on the sample composition.

In either case the stoichiometric conclusions about $KMnO_4$ decomposition based on the results presented

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Table 1
The amount of oxygen (mol%) evolved in different temperature regions and the total amount of oxygen in pure $KMnO_4$ and in its mixtures with catalysts

Sample	0–300°C	T_{onset}–300°C[a]	O_2 in $KMnO_4$	Total O_2[b]
$KMnO_4$ (PP)	63.4	51.0	100	100
PP + MoO_3	57.9	49.7	90	98.22
PP + NiO	56.7	49.0	90	95.28
PP + Cat-50	58.2	54.1	90	97.23
PP + Cat-70	81.4	44.9	90	96.61

[a] Oxygen evolution between the temperature at which the presented curves decline from the straight-line (e.g. 248°C for PP) and 300°C.

[b] Total amount of oxygen in the sample, i.e. together in $KMnO_4$ (90 mass%) and respective catalysts (10 mass%).

are meaningless. Even if the reported data are correct, they do not confirm the proposed Eq. (5) of [1]. According to this equation, 5 of 12 oxygen molecules are evolved during the decomposition, which amounts to 41.66% of oxygen evolution. A closer look at the data in Table 1 suggests that the proposed Eq. (5) does not adequately represent the decomposition of $KMnO_4$ and is far off from the values commonly reported in the literature. Reported amounts of evolved oxygen lay generally between 25 and 30% according to reactions proposed by Prout and Tompkins [3] and Herbstein et al. [4], respectively

$$2\,KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2, \qquad \Delta m = 10.12\%$$

$$10\,KMnO_4 \rightarrow 2.65\,K_2MnO_4 + (2.35\,K_2O \cdot 7.35\,MnO_{2.05}) + 6O_2, \quad \Delta m = 12.14\%$$

Halawy and Mohamed have left another fact unexplained. According to Fig. 3 of [1], all analyzed samples start to release oxygen at room temperature, an effect never previously reported for thermal decomposition of $KMnO_4$. The effect is especially profound in the "PP + Cat-70" system. If the reported results are correct, the sample would have been significantly decomposed after a few hours at room temperature.

2. X-ray diffraction analysis

The interpretation of the reported XRD data [1] is incorrect for the following reasons:

1. Reported values of *d* are inconsistent with the values presented in ICDD cards. Fig. 1 demonstrates the difference between the values that Halawy and Mohamed report for MoO_3 and NiO and the correct *d* values from ICDD files.
2. The file 16-205 cannot confirm the existence of $K_2Mn_4O_3$ because it reports the data for $K_2Mn_4O_8$. Assuming a misprint in Table 1 of [1], one still cannot confirm the existence of the latter phase in the mixture of the products reported in Table 1 of [1]. This is illustrated in our Fig. 2 by comparing the XRD patterns for the proposed phases. Even for very well crystallized phases, which is certainly not the case of intermediates or products of $KMnO_4$ decomposition, the identification of this phase would be practically impossible.

The existence of the phase Ni_2O_3 in the catalyst Cat-30 is very doubtful. It cannot be confirmed by "three diffraction lines at $d = 2.29$, 2.15 and 1.36 Å (ICDD card no. 14-0481)" [1] because ICDD file 14-0481 does not contain these interplanar *d* spacing values. It should also be stressed that the quality of this file is described as "questionable". Besides, we could not detect the presence of the Ni_2O_3 phase in our experiment, in which the mixture of 1 mol MoO_3 (prepared from ammonium molybdate by Fluka) and 0.3 mol of NiO (Merck) was calcined at 500 and 600°C for 22 h. The XRD data (D5000 Siemens diffractometer, Cu Kα) suggest that only one solid product was formed during the reaction, namely $NiMoO_4$ (ICDD file 33-948). The results presented in Fig. 3 clearly demonstrate the absence of Ni_2O_3, which, according to Halawy and Mohamed, is responsible for retarding the decomposition process [1].

One cannot use the ICDD file 14-0644 to confirm the presence of MnO_2 phase because this file, which

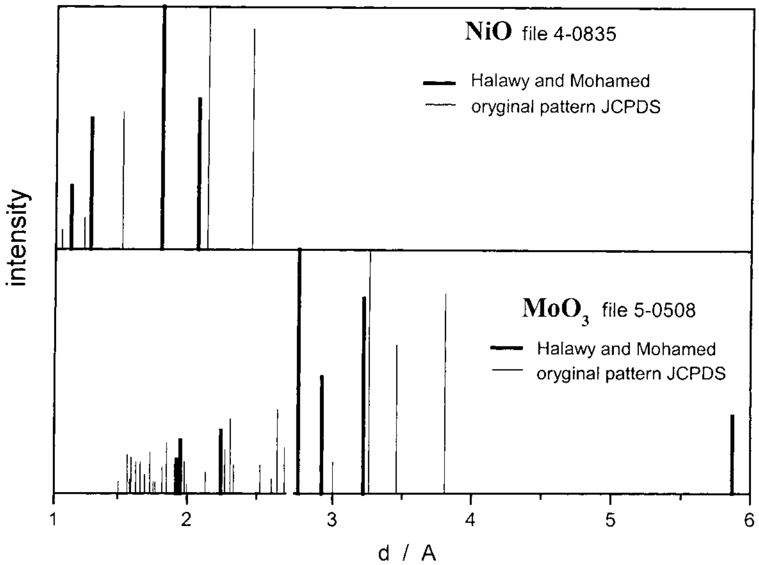

Fig. 1. Comparison of interplanar *d* spacing values and relative intensities for NiO and MoO_3 reported in [1] and JCPDS files.

contains the data for gamma (not delta!) MnO_2, has been removed from the acceptable set of files. The phase of delta-MnO_2 reported by Herbstein et al. [4] contained appreciable amounts of potassium, therefore one cannot use this information to reliably detect the existence of a pure MnO_2 phase, as is stated in Eq. (5) of [1].

Brown et al. [5] have recently reported that only the K_2MnO_4 product and $K_3(MnO_4)_2$ intermediate have been identified among the products of $KMnO_4$ decom-

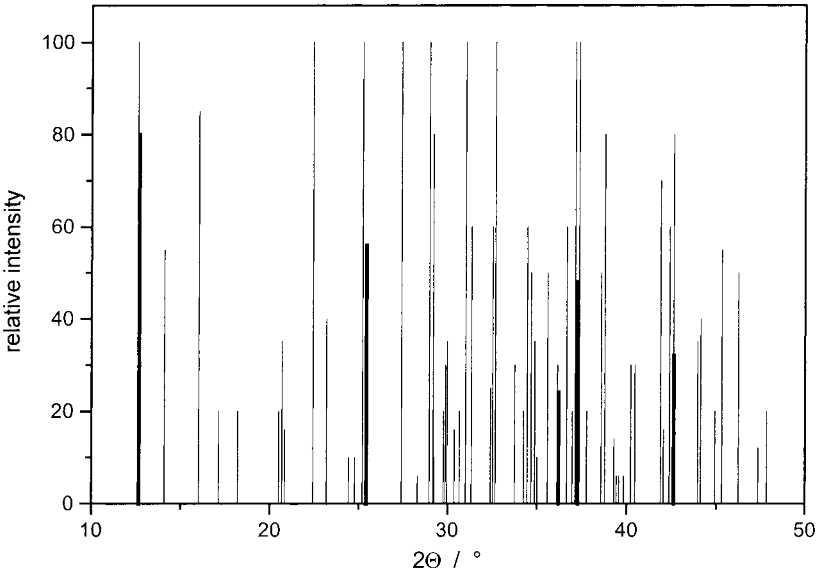

Fig. 2. The XRD patterns of the phases listed in Table 1 of [1] as compared with the pattern of JCPDS 16-0205 file (bold).

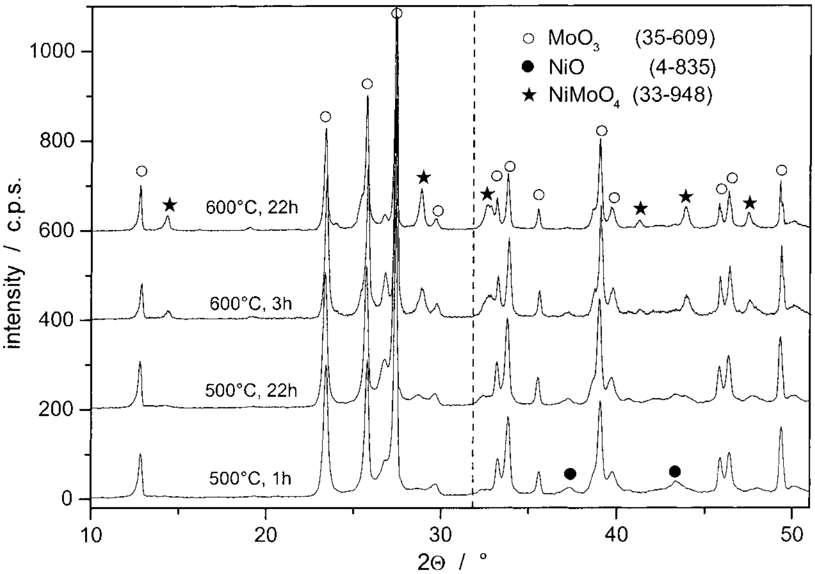

Fig. 3. The results of XRD analysis of a sample containing 1 mol MoO_3 and 0.3 mol NiO calcined at 500 and 600°C. The position of the strongest line of the questionable Ni_2O_3 suggested by Halawy and Mohamed (file 14-0481) is indicated as a dashed line.

position. Brown et al. also claim that a great part of the solid residue remains uncharacterized and does not appear to be crystalline or composed of any well-defined stoichiometric products. Nevertheless Halawy and Mohamed suggest that free K_2O and MnO_2 can be the products of $KMnO_4$ decomposition. Almost 35 years ago, Leyko and Maciejewski [6] suggested the formation of the poorly crystalline cryptomelane structure with composition $2K_2O{\cdot}7MnO_2$. The formation of this product was later confirmed by Herbstein et al. [4,7], who after extensive examination of the residual solids proposed the formula $2.35K_2O{\cdot}7.35\ MnO_{2.05}$. Additionally, the most recent paper by Kim at al. [8] reports the formation of layered compounds possessing formulas $K_{0.27}MnO_{2.12}{\cdot}0.89H_2O$ and $K_{0.31}MnO_{2.13}{\cdot}0.76H_2O$ during the thermal decomposition of $KMnO_4$ at 200 and 400°C, respectively.

3. Kinetic analysis

A few years ago Galwey [9] proposed that authors should give some positive justification for the method employed for kinetic analyses. Without any justification, Halawy and Mohamed use the Coats–Redfern method that is based on fitting of single heating rate data to the reaction models. It has been shown in a number of publications (cf. Flynn [10,11], Malek [12], Vyazovkin and Wight [13,14], and others) that such methods tend to produce highly uncertain Arrhenius parameters. This happens because in a single non-isothermal experiment both the temperature, T and extent of conversion, α vary simultaneously, and the approach generally fails to achieve a separation of the reaction rate into the temperature dependence, $k(T)$, and the reaction model, $f(\alpha)$. As a result, almost any $f(\alpha)$ can satisfactorily fit data at the cost of drastic variations in the Arrhenius parameters, which compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown reaction model. Most recently this effect and its implications have been exhaustively addressed by Vyazovkin and Wight [14]. All the above mentioned works [10–14] suggest that multi-heating rate methods (Friedman, Ozawa, Flynn and Wall, etc.) should be used as a reasonable alternative. The same conclusion has been arrived at as a result of the ICTAC Kinetics Project [15].

Even if we assume, for the sake of argument, that the Coats–Redfern method managed somehow to cleanly separate the temperature and conversion dependence, the reported values [1] of the activation energy still would have been questionable! Halawy and Mohamed, respectively, report single values of the activation energy for the thermal decomposition of $KMnO_4$ as well as for its mixtures. This means that they implicitly assume that, in each case, the whole decomposition process is described by single-step kinetics. This assumption contradicts the multi-step nature of solid-state reactions (see the classical text by Jacobs and Tompkins [16], or the recent book by Galwey and Brown [17], or a review paper by Vyazovkin [18]). This assumption also contradicts to multi-step mechanism that Halawy and Mohamed suggest on p. 161 (Eqs. (1)–(5)) [1]. The kinetic complexity of the thermal decomposition of $KMnO_4$ has been repeatedly documented since the classic work of Prout and Tompkins [3], who proposed a kinetic model of this process and found that the acceleratory and deceleratory parts of it were described by different rate constants. Galwey [19] also illustrated this fact. Hill et al. [20] demonstrated that the acceleratory part of the decomposition (actually $0.1 < \alpha < 0.25$) is characterized by an activation energy of 155 kJ mol^{-1}, whereas the later stages of decomposition (i.e. mostly deceleration) have an activation energy of $\sim$130 kJ mol^{-1}. Urbanovici and Segal [21] reported that the activation energy of $KMnO_4$ decomposition increases significantly ($\sim$80–150 kJ mol^{-1}) with the extent of reaction. Herbstein et al. [7] have proved that the decomposition proceeds in two successive steps. The first step is decomposition of $KMnO_4$ to $K_3(MnO_4)_2$ and δ-MnO_2 with release of about half the total amount of oxygen. This step is followed by decomposition of $K_3(MnO_4)_2$ to K_2MnO_4, with formation of more δ-MnO_2, and release of the remaining oxygen. In the light of these reports, it is rather unreasonable to try to describe the whole decomposition process with a single activation energy.

Halawy and Mohamed also assume that the decomposition of $KMnO_4$ can be described in terms of a reaction-order model. The limited applicability of this model to solid-state reactions has been extensively discussed in the literature (cf. Sestak [22]). Only a few values of n may have a physical meaning for solid-state reactions, e.g. the contracting geometry models, $n = 1/2$ and 2/3, and Mampel's model, $n = 1$. Halawy and Mohamed found $n = 0.25$ (Table 2) [1] and no discussion as to the meaning of this value was given. The reaction-order model describes decelerating kinetics, whereas the thermal decomposition of $KMnO_4$ is known to demonstrate a significant acceleratory period followed by a deceleration. Only the latter could thus, in principle, be described by a reaction-order model.

Halawy and Mohamed also claim that their value of the activation energy, 151 kJ mol^{-1}, is in good agreement with the value reported by Hill et al. [20]. However, the value of 155 kJ mol^{-1} was reported by Hill et al. [20] for only a small part of the acceleratory decomposition, and the same authors reported a significantly smaller activation energy for the rest of the process (see above). Methods such as the Coats–Redfern method that use fitting of a single heating rate experiments to the reaction models are known (cf. [13,14]) to produce values of Arrhenius parameters that are strongly dependent on the choice of reaction model. For this reason, by varying reaction models (or the value of reaction order) one always has a good chance of finding a value which agrees with a value reported by another worker.

Kinetic evaluations also require one to choose the initial and final temperatures of decomposition that are, respectively, related to α of 0 and 1. For instance, the initial temperature is chosen as the point at which the measured signal starts to depart from the baseline, which should be zero in the case of measuring the volume of a released gas (EGD measurements). According to Fig. 3 of [1], the decompositions start from $\sim$0°C and are not finished by 500°C, so it is not clear how one can choose the initial and final temperatures and the proper choice of the temperature region is critical to correct estimation of Arrhenius parameters.

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