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# ON THE NATURE OF THE BONDING IN AND REACTIVITY OF SILICA GEL SUPPORTED PERMANGANATE

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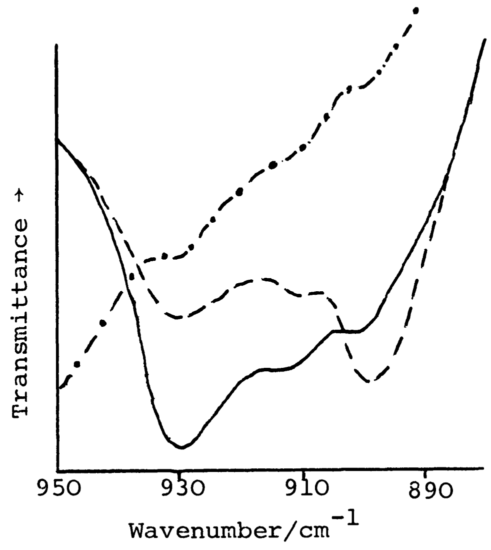
Infrared spectroscopic studies of silica gel supported permanganate reveal the presence of a discrete physisorbed salt monolayer which is thought to be responsible for the observed enhancement in permanganate reactivity.

Impregnation of synthetically useful reagents onto inorganic support materials resulting in improved reagent activity or selectivity is a subject of considerable current interest as the technique is seen as an attractive alternative to related methods such as phase transfer catalysis.[1] Despite the large volume of literature devoted to the synthetic applications of reagent-support adducts of this type, remarkably little is known about the nature of these adducts or about the factors responsible for observed changes in reagent reactivity. One of the more spectacular examples of improved reactivity through impregnation is supported $KMnO_4$ which is capable of rapidly oxidising alcohols under conditions where reagent grade $KMnO_4$ or aqueous $KMnO_4$ has no observable effect.[2] We wish to report our preliminary results from a variable temperature infrared spectroscopic study of silica gel supported permanganate.

Solid $KMnO_4$ shows a broad infrared absorption band at 900 $cm^{-1}$ due to the degenerate $\nu_3$ $(F_2)$ vibration of the tetrahedral $MnO_4^-$. $KMnO_4$-silica gel prepared by the reported method[2] shows, in addition to the 900 $cm^{-1}$ band, two weaker bands at 910 $cm^{-1}$ and 930 $cm^{-1}$ in this region of the spectrum. Pumping the adduct at temperatures around 100 °C results in an increase in relative intensities of the higher energy bands at the expense of the 900 $cm^{-1}$ band. Adducts prepared by identical methods but at lower $KMnO_4$ loadings show progressively weaker 900 $cm^{-1}$ bands and at a loading ca. 0.51 mmol $KMnO_4$/g silica gel, drying the sample in the above way leaves what appears to be a highly unsymmetrical triplet centred at ca. 920 $cm^{-1}$. Further reduction in the $KMnO_4$ loading does not appear to result in any further changes in this region of the spectrum other than a reduction in the intensity of the "triplet". Similar results were obtained when $KMnO_4$ was replaced by $NaMnO_4$. Representative infrared spectra are shown in the Figure.

Figure. Infrared spectra (950-880 $cm^{-1}$) of silica gel supported $KMnO_4$ at approximately optimum monolayer coverage (see text), after initial adduct formation at ca. 50°C (----); after pumping at ca. 100°C to remove physisorbed water (——); and after pumping at ca. 200°C (partial decomposition) (-•-•).



The observed splitting of the $\nu_3$ band indicates a symmetry lower than $T_d$ and the apparent triplet nature of this band suggests a symmetry lowering towards $C_{2v}$ (i.e. two Mn-O bonds directed towards the surface). Distortion of $T_d$ symmetries producing closely packed $\nu_3$ vibrations are known to occur in metal perchlorates, for example.[3]

There is no spectroscopic evidence to suggest that chemisorption between permanganate and the surface occurs to any significant extent and aqueous washing of the adducts results in almost complete recovery of the permanganate. Heating the adducts to high temperatures does result in decomposition of the permanganate and infrared monitoring suggests that this occurs more readily for the physisorbed monolayer but we have found no evidence to suggest that this decomposition occurs via a chemisorbed intermediate.

At optimum monolayer coverage (after removal of physisorbed water) the loading of ca. 0.51 mmole $KMnO_4$/g silica corresponds to a $MnO_4$:surface OH ratio of ca. 1:5 and the surface area effectively covered by a permanganate moiety is ca. 1 $nm^2$.[4]

The calculated loading for optimum monolayer coverage is appreciably less than the loading used previously[2] and may therefore explain the observation that much of the "adsorbed" permanganate in the latter adducts is unreactive. In order to test this hypothesis we have carried out preliminary tests on $KMnO_4$-silica gel adducts at different loadings and have found that at optimum monolayer coverage there is a marked improvement in reaction efficiency. Representative results are given in the Table.

TABLE Comparison of Reaction Efficiencies of Silica Gel Supported $KMnO_4$ in the Oxidation of Benzyl Alcohol[a]

| $KMnO_4$ loading (mmol/g silica) | Mol ratio $KMnO_4$:alcohol | Conversion to benzaldehyde (%)[d] | Total oxidation yield (%)[d] |
|---|---|---|---|
| 2.53[b] | 2.8 | 45 | 90 |
| 0.51[c] | 2.8 | 100 | 100 |
| 0.51[c] | 0.57 | 80 | 80 |

[a] All reactions were carried out in benzene at ca. 70°C for 2 h.
[b] Prepared as in ref. 2. [c] Prepared as described in text.
[d] Yields based on nmr and are to ± 5%.

These results not only seem to confirm our initial hypothesis that more advantageous reactivity manifestations of supporting reagents can be achieved through a better understanding of the reagent-support interaction but also show that synthetically useful adducts are not limited to those involving chemisorbed or strongly associated species. The observed enhancement in permanganate reactivity and selectivity is probably due to increased dispersion of the reagent on the support surface and possibly to a reduced entropy of activation for oxidations brought about by direct surface contact of the reactant molecules rather than any major changes in the nature of the anion resulting from a process such as chemisorption.

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References

1. See for example, A. McKillop and D.W. Young, Synthesis, 401 and 481 (1979).

2. S.L. Regen and C. Koteel, J. Am. Chem. Soc., 99, 3837 (1977).

3. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd edn., Wiley, London, 1970.

4. The surface area of the micron-size silica gel (150 Å average pore diameter) used was found by experiment to be *ca*. 320 $m^2/g$ which for a normal silica gel with 4-5 surface hydroxyls/$nm^2$ corresponds to *ca*. $1.4 \times 10^{21}$ hydroxyl groups/g.

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