

Letter

A novel ESR method based on dilute solid solutions of $\text{Mn}^{3+}/\text{Mn}^{2+}$ ions in MgO for detecting spillover of hydrogen from noble metals

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Abstract

Dilute solutions of Mn^{3+} ions in pure MgO are ESR silent, but on reduction by spillover hydrogen from noble metals show strong ESR signals characteristic of Mn^{2+} ions in this matrix. The same solids are also active for the dehydrodimerization of triphenylamine at room temperature as shown by the presence of both radical cations and Mn^{2+} ions. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Using FTIR Baumgarten et al. [1] found evidence for hydrogen spillover through the gas phase transport of hydrogen atoms from a Pd/SiO₂ catalyst to several reducible compounds, diphenylpicrylhydrazyl, anthracene, or anthraquinone adsorbed on silica. Even though the organic detector and the Pt/SiO₂ sample were separated physically in a flow line a positive response was found even at temperatures as low as 333–373 K, and the authors also confirmed that both gaseous H₂ and the metal catalyst were required. Their conclusion was queried by Spencer et al. [2] who cited an earlier analysis [3] that temperatures greater than 800 K would be required to generate a sufficient

flux of free hydrogen atoms using typical noble metal catalyst systems.

We report here a very convenient reversible novel detector for hydrogen atoms which could be used to investigate further this problem, and perhaps that of oxygen spillover as well. When a dilute solid solution of Mg^{2+} ions in MgO is examined by ESR spectroscopy a very well resolved intense symmetrical signal is observed ($g = 2.0014$) consisting of a sextet of lines each of which is further split into a quintet [4]. The six major lines are due to nuclear hyperfine coupling (Mn^{2+} ions, $I = 5/2$), and the five-line patterns arise from octahedral zero-field splitting for a d^5 ion. When the Mn^{2+} ions in MgO are oxidised to the (III) state the ESR signal disappears. Thus the $\text{Mn}^{2+}/\text{Mn}^{3+}/\text{MgO}$ redox system should constitute an excellent convenient means of detecting spillover of hydrogen.

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The detector can easily be restored to its original state by oxidizing the Mn^{2+} ions simply by calcining in air.

2. Experimental, results and discussion

In the initial experiments “Analar” BDH MgO, 97% pure, containing manganese and other metal ions was used. A sample was impregnated by an alcoholic solution of the platinum salt obtained by prior treatment of $\text{H}_2\text{Pt}(\text{OH})_6$ with concentrated nitric acid in the manner previously described [5a,5b], using sufficient Pt to give a loading of 2 wt.% on the MgO. The resulting material was then dried out at 393 K for several hours and then calcined in air overnight at 773 K. When this was cooled to room temperature and then examined under argon it was found to be ESR silent. However, when the calcined material was reduced in a hydrogen flow, first for 2 h at 393 K and then overnight at 773 K, cooled to room temperature in hydrogen and then transferred under argon to a sample tube it showed strong ESR activity (Fig. 1a). The characteristic signal for $\text{Mn}^{2+}/\text{MgO}$ [4] is evident, accompanied by an intense singlet at $g = 1.979$. The MgO alone was then examined in the same way after treatment in hydrogen overnight at 653 K. A weak signal at $g = 1.979$ was still present without significant increase, but the Mn^{2+} ion sextet was now just

barely visible (Fig. 1b). On calcining again in air at 723 K the latter signal disappeared leaving the weak singlet. In all experiments the hydrogen gas stream was first passed over a Pt/SiO₂ catalyst at 473 K and then through activated 4A sieve at 77 K in order to remove O₂, H₂O, and other impurities. ESR spectra were recorded at X-band frequencies.

Quite clearly the ESR signals shown in Fig. 1a are intense for the Pt/MgO sample because of reduction by spillover hydrogen. When a 2 wt.% Rh/MgO sample was prepared by impregnation with $\text{Rh}(\text{NO}_3)_3$ from aqueous solution and finally treated overnight with hydrogen gas at 753 K, ESR analysis in the usual fashion showed a strong signal almost identical to that in Fig. 1a. The singlet at $g = 1.979$ is therefore inherently due to a reduction process within the support, and is that expected from a dilute solid solution of Cr^{3+} ions in MgO [4], although chromium is not mentioned as one of the impurities in the BDH material.

A very pure MgO, Premier-Periclase Type PC-210G, [5a,5b] was then used. A sample was impregnated with “Analar” $\text{Mn}(\text{NO}_3)_3$ from solution in conductance water to give a loading of 0.02 wt.% Mn. This material was dried overnight at 393 K and finally calcined in air for 19 h at 973 K. It was found to be ESR inactive even when treated overnight in hydrogen at 523 K, and the singlet attributed to Cr^{3+} ions in the BDH MgO was completely absent.

At this stage we decided to examine the oxidising properties of this Mn^{3+} ion doped MgO using the following organic test. When triphenylamine is absorbed from solution onto surfaces of oxides, e.g. $\text{SiO}_2\text{-Al}_2\text{O}_3$, containing electron acceptor sites the $\Phi_3\text{N}$ radical-cation ($\Phi = \text{phenyl}$) is formed and rapidly participates in a dimerization process as shown in Scheme 1. Even PtO_2 is active in this respect.

The radical cations, $g = 2.0025$, are readily detected by ESR analysis [7], but the main interest here is to see if the hydrogen atoms released after dimerization are capable of reducing some Mn^{3+} to Mn^{2+} ions. When the cal-

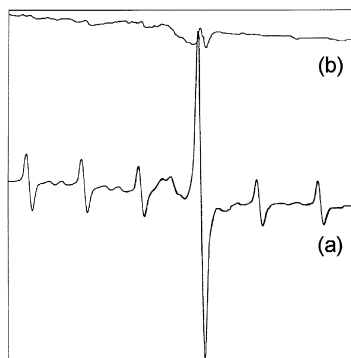
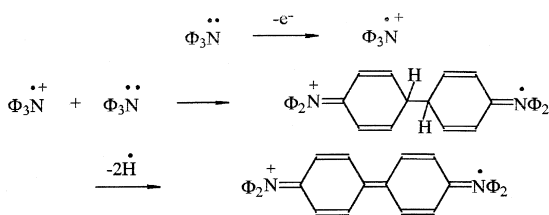


Fig. 1. ESR spectra of samples reduced in H₂ at 773 K: (a) Pt/MgO (BDH), (b) MgO (BDH).



Scheme 1.

calcined $\text{Mn}^{3+}/\text{MgO}$ material was treated with a solution of $\Phi_3\text{N}$ in dry benzene at room temperature a strong singlet, $g = 2.0025$, attributable to the radical-cations developed (Fig. 2) but some reduction of Mn^{3+} to Mn^{2+} ions was also evident from the simultaneous appearance of the Mn^{2+} sextet. After the ESR tests the sample was treated with ether and the organic product extracted and analysed using mass spectroscopy; a strong parent peak, $m/e = 488$, was observed thereby confirming that dimerization had occurred.

We then decided to try the Baumgarten experiment [1] by placing a sample of the calcined $\text{Mn}^{3+}/\text{MgO}$ downstream from a 1-wt.% Pt/ SiO_2 catalyst in the flow of purified H_2 . The separation of the two solids was 3 cm and both were maintained at 653 K, but occasionally the Mn/MgO sample was cooled to room temperature, a portion extracted and analysed under argon for ESR activity. A very intense Mn^{2+} sextet was observed which grew over a period

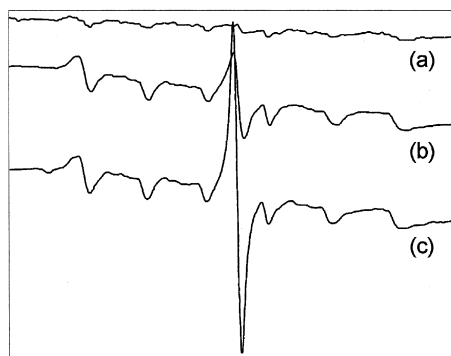


Fig. 2. ESR spectra; (a) calcined $\text{Mn}^{3+}/\text{MgO}$ (pure); (b) calcined $\text{Mn}^{3+}/\text{MgO}$ (pure) treated with triphenylamine; (c) same as in (b) after further 168 h.

of 48 h (Fig. 3) so there does seem to be spillover of hydrogen through the gas phase as claimed [1], although the temperature here is much higher. For the purposes of comparison the amplification in Figs. 1 and 2 is 5 and 20 times respectively that in Fig. 3.

At this stage these preliminary results may be useful in drawing attention to the advantages of MgO doped with manganese ions, and perhaps chromium ions as well, as convenient reversible detectors for hydrogen spillover. The same detectors could also be investigated for oxygen spillover.

Transport through the gas phase is an entirely reasonable explanation especially if some H atoms formed on the Pt move downstream and react with the MgO and the surface of the glass in contact with the detector, thereby creating new sites for dissociative adsorption of H_2 . In this way the density of H atoms available to reduce the Mn^{3+} ions in the detector is greatly increased. This aspect of spillover of both hydrogen and oxygen has been reviewed by Teichner [8]. There is no doubt that bombarding an insulator such as silica by atomic free radicals will cause the formation of catalytically active paramagnetic centers. Spillover via the gas phase and spillover via physical contact between surfaces may always be intimately mingled in this fashion even when the support for the noble metals is itself the detector.



Fig. 3. ESR spectra of $\text{Mn}^{3+}/\text{MgO}$ (pure) after hydrogen spillover at 653 K from Pt/ SiO_2 for: (a) 4 h; (b) 24 h; (c) 48 h.

3. Uncited reference

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References

- [1] E. Baumgarten, C. Lentz-Wagner, R. Wagner, *J. Catal.* 117 (1989) 533.
- [2] M.S. Spencer, R. Burch, S.E. Golunski, *J. Catal.* 126 (1990) 311.
- [3] R.B. Levy, M. Boudart, *J. Catal.* 32 (1974) 304.
- [4] J.E. Wertz, J.R. Bolton, *Electron Spin Resonance: Elementary Theory and Practical Applications*, McGraw-Hill, 1972.
- [5a] J.K.A. Clarke, M.J. Bradley, L.A.J. Garvie, A.J. Craven, T. Baird, *J. Catal.* 143 (1993) 122.
- [5b] T. Baird, E.J. Kelly, W.R. Patterson, J.J. Rooney, *J. Chem. Soc., Chem. Commun.* (1992) 1431.
- [6] B.R.T. Garrett, J.J. Rooney, *Catal. Lett.* 57 (1999) 205.
- [7] D.N. Stanmires, J. Turckevich, *J. Am. Chem. Soc.* 85 (1963) 2557.
- [8] S.J. Teichner, *Appl. Catal.* 62 (1990) 1.