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Organically Doped Metals—A New Approach to Metal Catalysis: Enhanced Ag-Catalyzed Oxidation of Methanol**

By Gennady E. Shter, Hanna Behar-Levy, Vladimir Gelman, Gideon S. Grader,* and David Avnir*

We report here a new approach for the modification of the performance of metal catalysts: organic doping of the metal. Specifically, we report that the doping of Ag with Congo Red (CR@Ag) significantly improves the performance of Ag as a catalyst for methanol oxidation to formaldehyde, outperforming both pure Ag and CR-coated Ag (CR/Ag) in terms of lowering the temperature needed for maximal conversion by $100 \,^{\circ}$ C, lowering the temperature by $200 \,^{\circ}$ C to reach the maximal selectivity (aldehyde formation), and increasing the maximal space velocity by a factor of two. We were led to this discovery by a detailed investigation of the thermal behavior (thermogravimetric and differential thermal analysis and mass spectroscopy) of CR@Ag under an oxidative atmosphere, which has indicated that the metal is strongly catalyzing the CR oxidation, and which pointed to the relevant temperature for activation of the catalyst.

1. Introduction

We report here a new approach for activation of metal catalysts: organic doping of the metal. We also report that this doping can be used to alter the catalytic properties of the metal. The study of catalysis by using metals has always been based on the study of the chemistry and physics of these materials, since the latter has led to the control and design of catalytic performance. Some of the main metal variables that have been used in these studies include the type of the metal, the use of alloys of various compositions, controlling the level of dispersion, and the surface morphology.^[1–7] The new methodology of metal doping with organics^[8–10] has opened a new, powerful possibility of control of performance, which—as will be detailed below—can lead to significant improvement of the performance of the catalytic metal. To the best of our knowledge, catalytic applications of this novel family of composite materials have not been reported.

Specifically, we report that the doping of Ag with Congo Red (CR) significantly improves the performance of Ag as a catalyst for methanol oxidation to formaldehyde:

$$CH_{3}OH \xrightarrow{O_{2}/CR@Ag} CH_{2}=O+H_{2}O$$
(1)

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The doping approach is based on reducing Ag^+ in the presence of a solution of the molecule to be entrapped.^[9] This requires the selection of a suitable reducing agent, which, as detailed in the literature^[9] was found to be sodium hypophosphite, as shown in Equation 2.

$$2 \operatorname{AgNO}_3 + \operatorname{NaH}_2 \operatorname{PO}_2 + \operatorname{H}_2 \operatorname{O} \rightarrow 2 \operatorname{Ag} + \operatorname{NaH}_2 \operatorname{PO}_3 + 2 \operatorname{HNO}_3 \quad (2)$$

The doping methodology was found to be quite general: Hydrophilic molecules,^[9] hydrophobic molecules,^[9] and various polymers^[8,10] have been successfully entrapped, leading to the new composites. As mentioned above the specific composite that showed the interesting catalytic performance reported here was CR entrapped in Ag (CR@Ag), which was found to outperform both pure Ag and CR-coated Ag (CR/Ag) in terms of lowering the temperature by 100 °C needed for maximal conversion, lowering the temperature by 200 °C to reach the maximal selectivity (aldehyde formation), and increasing the maximal space velocity by a factor of approximately two. Thus, a high level of methanol conversion of about 90 % was reached already at 320 °C, whereas for Ag and CR/Ag the conversion was under 50% at that temperature; and, at that temperature the selectivity on CR@Ag was nearly 70%, but only about 30% and 20% for Ag and CR/Ag, respectively.

We were led to this discovery by a detailed investigation of the thermal behavior of CR@Ag under an oxidative atmosphere, which has indicated that the porous metal is strongly catalyzing the CR oxidation, again, compared with pure CR and CR/Ag. We therefore provide also a detailed analysis of



^[*] Prof. D. Avnir, Dr. H. Behar-Levy Institute of Chemistry, The Hebrew University of Jerusalem Jerusalem 91904 (Israel)
E-mail: david@chem.ch.huji.ac.il
Prof. G. S. Grader, Dr. G. E. Shter, V. Gelman Chemical Engineering Department, Technion Haifa 32000 (Israel)
E-mail: grader@tx.technion.ac.il