

## Catalytic Oxidation of Organic Substrates using Alumina Supported Chromium and Manganese<sup>1,2</sup>

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Supported reagents prepared by adsorption of chromium(vi) and manganese(vii) on alumina are capable of catalysing the aerial oxidation of organic substrates.

The use of high oxidation state transition metals for organic oxidation reactions is well established, but suffers from serious drawbacks. In the case of chromium(vi) oxidations, for example, the oxidant is not actually catalytic, nor readily regenerated. The associated high cost and toxic effluent are increasingly serious problems especially on an industrial scale. Furthermore, forcing conditions of high temperatures and pressures may often be required. For these reasons we have become interested in the use of supported reagents for oxidation reactions. Supported reagents frequently enable reactions to take place under significantly milder conditions, and with simpler work-up procedures and reduced environmental problems compared with the unsupported reagents.<sup>3</sup> Enhanced activity has been reported using alumina supported Cr<sup>VI</sup> or Mn<sup>VII</sup> reagents for the oxidation of alcohols and sulphides,<sup>4</sup> although these reactions are stoichiometric.

We now report what we believe to be the first truly catalytic oxidations using alumina supported chromium or manganese. The oxidation of diphenylmethane to benzophenone was chosen as our model reaction, this substrate being less active than the alcohols and sulphides previously reported in stoichiometric oxidations. Thus, the efficient mixing of diphenylmethane (0.5 mol) with 5 g of a supported reagent (2 mmol g<sup>-1</sup> potassium permanganate supported on alumina by slow rotary evaporation of water) at 150 °C, in a stream of air, results in a conversion of 8% in the first hour. However, this reaction rate then decreases to a constant 0.2% h<sup>-1</sup> conversion for the next 17 h, when the reaction was stopped. Although slow, this is clearly catalytic with only 10 mmol of Mn<sup>VII</sup> converting 57 mmol of diphenylmethane to benzo-

phenone. Using identical conditions with a 2 mmol g<sup>-1</sup> dichromate on alumina catalyst the initial reaction proceeds at 1% h<sup>-1</sup> conversion for *ca.* 24 h but decreases relatively little compared to the permanganate case; after 116 h 82% conversion is achieved. At this stage the reaction slows due to the low concentration of substrate. Thus 10 mmol of dichromate oxidises 410 mmol of diphenylmethane. The rate of reaction may be enhanced by co-supporting cobalt(II) chloride with dichromate (1% CoCl<sub>2</sub> by weight with respect to K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) onto the alumina giving 1.6% h<sup>-1</sup> initially compared to 1% h<sup>-1</sup> without CoCl<sub>2</sub>.

The use of other support materials (silica, charcoal, or montmorillonite) for dichromate results in very much slower reaction than for alumina (Table 1). Furthermore, the choice of alumina is also important; neutral alumina results in a more effective catalyst than acidic or basic alumina.

The two stages of the reaction, described above, have been investigated. We now believe that the initial relatively rapid reaction is due in part to a noncatalytic reaction promoted by physisorbed 'excess' dichromate or permanganate. However, the true catalyst is a strongly adsorbed or possibly chemisorbed species. For example, when a catalyst is prepared by stirring alumina (15 g) in a solution (250 ml; 0.2 M) of potassium dichromate, followed by filtering and cold water washing until no further Cr<sup>VI</sup> is removed, a loading of approximately 0.075 mmol g<sup>-1</sup> is achieved. Using this 'alodic' catalyst (18 g), diphenylmethane (1.8 mol) may be oxidised at 1.3% h<sup>-1</sup> with no decrease in rate until 70% conversion has been achieved. Using a similarly prepared permanganate reagent the reaction was only slightly slower at 1.1% h<sup>-1</sup> (in

Table 1. Formation of benzophenone using supported chromium or manganese.<sup>a</sup>

Support	Reagent	Loading/mmol g <sup>-1</sup>	Conversion rate of Ph <sub>2</sub> CH <sub>2</sub> to Ph <sub>2</sub> CO/% h <sup>-1</sup>	Notes
Alumina neutral	None	—	0	
neutral	Dichromate	2	1.0	Linear to >70%
neutral	Dichromate	10	0.1	Overloaded reagent
neutral	Permanganate	2	8.0	Rate decreases rapidly to 0.2% h <sup>-1</sup>
Alumina acidic	Dichromate	2	0.8	
Alumina basic	Dichromate	2	0.3	
Alumina neutral	Dichromate	0.075	1.3	'Chemisorbed' reagent <sup>b</sup> Linear rate to >70%
neutral	Permanganate	0.02	1.1	'Chemisorbed' reagent <sup>b</sup> Linear rate to >70%
Silica	Dichromate	2	1.0	Not catalytic <sup>c</sup>
Charcoal	Dichromate	2	0.1	Not catalytic
Montmorillonite-K10	Dichromate	2	0.1	Not catalytic
Alumina neutral	[ Dichromate Cobalt(II) ]	[ 2 0.04 ]	[ 1.75 ]	Co-supported reagents

<sup>a</sup> Reaction of 0.5 mol Ph<sub>2</sub>CH<sub>2</sub> with 5 g supported reagent and a flow of *ca.* 800 ml min<sup>-1</sup> of air into the stirred mixture at 150 °C.

<sup>b</sup> Reaction of 1.8 mol Ph<sub>2</sub>CH<sub>2</sub> with 18 g supported reagent. <sup>c</sup> 50 g supported reagent.

this case the loading of reagent is lower at 0.02 mmol g<sup>-1</sup>). These catalysts are thus highly efficient, in the order of several thousand turnovers with respect to metal, and may also be reused. Results indicate that efficient mixing of the three phase system is important in order to maximise the reaction rate. Alumina itself is inactive in the reaction.

Initial investigations show that the alodic reagent (and corresponding permanganate reagent 'aloman') also catalytically oxidises benzyl alcohol (1% h<sup>-1</sup>) to benzaldehyde and chlorodiphenylmethane to benzophenone (4.8% h<sup>-1</sup>). Further details of these catalysts and their reactions will be published elsewhere. The catalytic character of our catalysts, their ease of use, and the low environmental problems associated with their use, make them extremely attractive alternatives to more conventional oxidants.

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## References

- 1 A. P. Kybett, 'Friedel-Crafts and Oxidation Catalysis Using Supported Reagents,' D. Phil., York, 1988.
- 2 Eur. Pat. Appl. 89303434.8
- 3 (a) A. McKillop and D. W. Young, *Synthesis*, 1979, 401, 481; (b) P. Laszlo, ed., 'Preparative Chemistry Using Supported Reagents', 1987, Academic Press, London.
- 4 (a) R. P. Singh, H. N. Subbarao, and S. Dev, *Tetrahedron*, 1979, **35**, 1789; (b) G. Cainelli, G. Cardillo, M. Orena, and S. Sandri, *J. Am. Chem. Soc.*, 1976, **98**, 6737; (c) N. A. Noureldin and D. G. Lee, *Tetrahedron Lett.*, 1981, **22**, 4889; (d) E. Santaniello and P. Ferraboschi, *Nouv. J. Chim.*, 1980, **4**, 279.