

Effect of Brucite–Periclase Transformation and KCl Promotion in retrieving the Reactivity of Magnesia supported CuCl_2 Catalysts†

V. Nageshwar Rao, P. S. Sai Prasad, K. B. S. Prasad, and P. Kanta Rao

Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India

KCl promotion in MgO supported CuCl_2 catalysis has been shown to reverse the reducibility by ethylene during brucite–periclase transformation.

Magnesia exhibits interesting support effects and, although it has a low surface area and a tendency to depress reactivity,^{1,2} MgO has been shown to stabilize the supported metal,³ retarding sintering and volatilization,⁴ and enhancing reactivity.⁵ During their preparation and pretreatment, MgO supports undergo phase transformations. The MgO (periclase)– $\text{Mg}(\text{OH})_2$ (brucite) transformation, and *vice versa*, in the presence and removal by specific reduction, of chloride containing species during impregnation and thermal treatment have been extensively studied in the case of Ru catalysts.^{6,7}

Although some interacting (Al_2O_3 , *etc.*)^{8–10} and non-interacting (silica, *etc.*)¹¹ supports have been extensively used in the preparation of KCl promoted CuCl_2 catalysts for the oxychlorination of ethylene and methane, MgO as a support seems to have been neglected. Here we report the first characterisation of unpromoted and KCl promoted CuCl_2 catalysts, with $\text{Mg}(\text{OH})_2$ and with MgO supports. The solid phase reducibility of CuCl_2 was used to express the catalyst activity. An interesting phenomenon of activity reversal was observed, and it was found that when promoted and activated to the required phase, MgO also forms a useful support.

Magnesium oxide powder was prepared by calcination of magnesium carbonate (Fluka, A.G., Switzerland) at 923 K, for 6 h. Aqueous cupric and potassium chloride (Analar, BDH, U.K.) solutions were used to prepare, by an incipient wetness method, unpromoted (CuCl_2 0.18 g/g MgO) and

promoted [Cu : K 8 (w/w)] catalysts. Initial drying at 393 K gave crystalline copper chloride with $\text{Mg}(\text{OH})_2$ as the support. The solid masses were then sieved with an 18/25 (BSS) mesh and were activated at 723 K for 4 h in flowing nitrogen. This temperature was chosen since the dehydration temperature increases with hydration time.¹² These four (unpromoted/promoted and unactivated/activated) catalysts were subjected to solid state reduction of CuCl_2 by ethylene (Matheson, U.S.A.) at various temperatures and times.

The catalyst could be quickly discharged from the tubular reactor (8 mm i.d.) when required. The catalyst bed (~1 g)

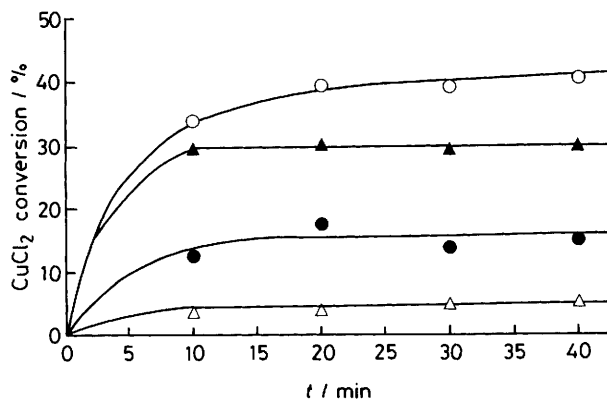


Figure 1. Extent of copper(II) chloride conversion with time at 503 K. ○ $\text{CuCl}_2/\text{Mg}(\text{OH})_2$; ● CuCl_2/MgO ; △ $\text{CuCl}_2\text{-KCl}/\text{Mg}(\text{OH})_2$; ▲ $\text{CuCl}_2\text{-KCl}/\text{MgO}$.

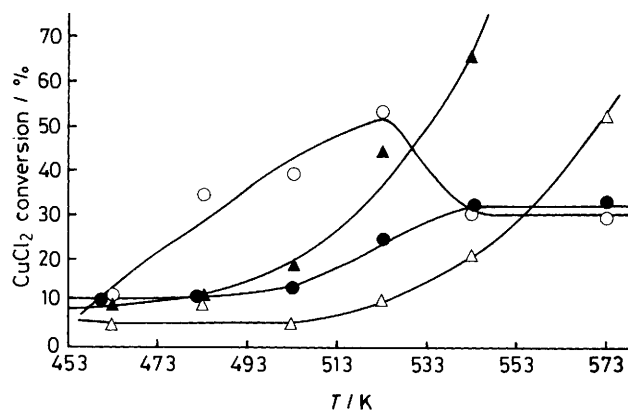


Figure 2. Effect of reaction temperature on CuCl_2 reactivity after 30 min. \circ $\text{CuCl}_2/\text{Mg}(\text{OH})_2$; \bullet CuCl_2/MgO ; \triangle $\text{CuCl}_2\text{-KCl}/\text{Mg}(\text{OH})_2$; \blacktriangle $\text{CuCl}_2\text{-KCl}/\text{MgO}$.

was heated under flowing nitrogen to the required temperature by an electric heater and left at that temperature for 1 h, during which time ethylene at a flow rate sufficient to eliminate mass transfer effects, was admitted by means of a four-way stop-cock. After the specified time the catalyst was quickly discharged into a standard iron(III) ammonium sulphate solution under flowing nitrogen. The resultant iron(II) species was then titrated with standard cerium(IV) sulphate using ferroin as an indicator,¹³ and the extent of conversion of CuCl_2 to Cu_2Cl_2 was determined. The blank analyses for Cu_2Cl_2 , after heating the catalyst at the various temperatures in nitrogen, did not give any observable conversions of CuCl_2 .

Reducibility of solids has been used earlier as a means of characterising their surfaces¹⁴ and is related to the activity in the case of hydrodesulphurisation¹⁵ and polymerisation catalysts.¹⁶ In the present study we followed the ability of ethylene to reduce CuCl_2 at various temperatures, thereby gaining an insight into the catalyst surface and the metal support interaction.

The typical reaction curves at 503 K for promoted and unpromoted catalysts, with $\text{Mg}(\text{OH})_2$ and MgO as supports, are shown in Figure 1. From the similar curves obtained at various temperatures, a uniform reaction time of 30 min was chosen to express the extent of conversion with respect to reaction temperature (Figure 2). The surface areas of all the catalysts are found to be $15 \pm 1 \text{ m}^2 \text{ g}^{-1}$.

Sigmoidal shape curves, as shown in Figure 1, are observed in solid state reactions involving nucleation.¹⁴ Figure 2 shows that the reactivity of unpromoted CuCl_2 with $\text{Mg}(\text{OH})_2$ as support is greater than that of the MgO supported CuCl_2 up to 543 K; at $>543 \text{ K}$ they exhibited equal activities. The reverse is true of promoted catalysts, the MgO supported catalyst showing a higher activity than the $\text{Mg}(\text{OH})_2$ supported catalyst. The dried and activated catalysts were analysed by XRD studies. The catalysts dried at 393 K exhibited $\text{Cu}_2(\text{OH})_3\text{Cl}$ and $\text{Mg}(\text{OH})_2$ phases, whereas these samples when activated at 723 K revealed the presence of an MgO phase and no crystalline copper(II) chloride. The role of chloride in the periclase-brucite transformation, as is clear from the literature,⁷ is *via* early release of water and a decrease in the surface area. Loss of copper and/or chloride during heating to 723 K was ruled out by atomic absorption and argentometric analyses. A weight loss corresponding to the stoichiometric reduction of $\text{Mg}(\text{OH})_2$ to MgO was observed due to the loss of water, as also reported by Mirodatos *et al.*¹⁷

In the case of unpromoted CuCl_2 catalysts the reactivity increased up to 523 K as long as the support was $\text{Mg}(\text{OH})_2$.

However, once the periclase formed, as confirmed by differential thermal analysis (DTA), the reactivity decreased, and at 543 K the solubility of MgO in CuCl_2 reached a maximum.

The reduced activity in CuCl_2/MgO can be explained in terms of the decoration model proposed by Logan *et al.*¹⁸ for RuCl_3 supported on MgO . Some of the MgO will have dissolved in acidic CuCl_2 during aqueous impregnation and drying, and decoration of the CuCl_2 surface by MgO derived species might have reduced the solid state reactivity. We extend the same argument to the promoted catalysts. Addition of KCl reduced the acidity (presumably by the formation of double salts, *e.g.*, KCu_xCl_y) and hence the solubility of MgO in CuCl_2 , thus preventing 'decoration' of the surface. Further, there is no possibility of binding an electron donor element such as potassium with MgO ; the KCl must have been driven to the surface.¹⁹ Thus the surface availability of CuCl_2 for ethylene is reduced when the support is $\text{Mg}(\text{OH})_2$, leading to lower reactivities. The decrease in particle size which increases the solid phase reactivity,²⁰ and the absence of 'decoration' must have created more nuclei in the case of promoted CuCl_2/MgO , giving a high, steady increase in conversion. Thus KCl promotion and activation at a carefully chosen temperature could lead to MgO as a useful support for oxychlorination catalysts.

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