

# Improved atom efficiency via an appreciation of the surface activity of alumina catalysts: Methyl chloride synthesis

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## Abstract

The hydrochlorination of methanol over a commercial grade  $\eta$ -alumina catalyst has been investigated via temperature-programmed reaction (TPR). Experiments were conducted over a temperature range of 295–1000 K using: (i) a methanol-only feed stream and (ii) a methanol/HCl mixed feed stream in a 1:1 mole ratio. Methanol-only studies showed activity for the formation of dimethyl ether (DME) above 450 K, consistent with temperature-programmed desorption studies. A rapid decline in DME activity and consumption of methanol at higher temperatures were observed and are attributed to a deactivation pathway, involving the conversion of methoxy species to surface formate species. At elevated temperatures these processes lead to the deposition of carbon on the substrate. The introduction of HCl to the reaction stream resulted in the formation of methyl chloride (MC) over a temperature range of 400–750 K. Relatively small quantities of DME by-product were also observed over a similar temperature range. The coincidence of the reaction profiles of both MC and DME imply that the same reactive methoxy species are involved in both processes. The rate of reaction for the formation of both products declines rapidly above 700 K. This is attributed to the methoxy decomposition pathway to formate and, ultimately, to carbon retention by the catalyst.

The effect of carbon deposition was also investigated via a subsequent cooling process carried out immediately after TPR experiments. Reaction profiles showed comparable activity for the formation of both products with respect to initial TPR experiments. Taken together, these results indicate an optimum reaction temperature for the formation of methyl chloride from the hydrochlorination of methanol. At such temperatures, carbon deposition is minimized and high conversion is maintained.

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## 1. Introduction

Methyl chloride is an important industrial product with a global production capacity of *ca.* 900 kt. It is a valuable starting material in the production of higher chlorinated products, silicones, and methyl cellulose. It also has applications as a methylating agent [1–3]. The manufacture of methyl chloride can be achieved via two established routes [1]. The first involves the thermal chlorination or catalytic oxychlorination of methane. The second proceeds via the hydrochlorination of methanol. It is the latter route that is commercially most important today, due mainly to the low cost of methanol and the

growing surplus of HCl from various chlorination processes [1]. The process can be carried out in the liquid phase without a catalyst, with a slight excess pressure of HCl, or catalytically in the presence of zinc chloride or iron chloride. It can also be carried out in the gas phase, at temperatures typically of *ca.* 350 °C, over alumina and silica supported metal chloride catalysts [4–6]. Chlorinations using a  $\text{ZnCl}_2/\text{Al}_2\text{O}_3$  catalyst showed selectivity to methyl chloride (MC) of around 98% with respect to methanol (1), with a small amount of by-product produced in the form of dimethyl ether (DME) (2) [5]:



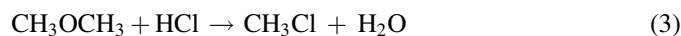
It has also been reported that  $\gamma$ -alumina is sufficiently active [7] and has a comparable selectivity to  $\text{ZnCl}_2/\text{Al}_2\text{O}_3$ , but is

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deactivated more rapidly due to coke formation. The high activity of  $\gamma$ -alumina and relatively low cost make it the industrially favored catalyst for this reaction at present.

Despite the significance of the industrial scale manufacture of methyl chloride, it is a topic that has been given relatively little attention in the literature. The majority of the work reported in this area has concentrated on the kinetics of the process [4–10] with little consideration of the reagent–catalyst–product interactions, which will, ultimately, dictate favorable operating conditions. Ivanov and Makhlin [7] have additionally considered the role of a third reaction of dimethyl ether and HCl over a  $\gamma$ -alumina catalyst (3):



In addition to these kinetic studies, Yates and co-workers [11,12] have conducted spectroscopic investigations on the interaction of methyl chloride with alumina surfaces. They concluded that methoxy groups coordinated to Al centers were the dominant surface moiety, when methyl chloride was adsorbed on the surface. The consumption of surface hydroxyl groups and liberation of HCl to the gas phase indicated that hydroxyl groups were involved in the methoxy species formation reaction [11].

Work carried out on this reaction system thus far has almost exclusively focused on  $\gamma$ -alumina [7,11,12]. However, recent industrially based studies have shown that  $\eta$ -alumina offers considerable potential as a methyl chloride synthesis catalyst [13], although little information is available as to the nature of the adsorbate–substrate interactions and the reaction pathways accessible with this particular catalyst. To the best of our knowledge, no studies have examined the same reaction system using an  $\eta$ -alumina catalyst, an inherently more acidic form of alumina [14,15], that additionally has applications in catalytic reforming reactions [16]. This latter substrate is worthy of further investigation, as its enhanced surface acidity offers the possibility of affecting selectivity profiles by moderating a broader distribution of acid sites by selective poisoning strategies.

Previously, we have reported a spectroscopic analysis of methanol adsorbed on  $\eta$ -alumina and subsequent transformations observed during thermal treatment [17,18]. These studies confirm methoxy species to be the dominant surface moiety. Thermal transformations initially yielded dimethyl ether, formed from the combination of two methoxy groups on the surface [18], at temperatures between 400 and 650 K. At temperatures above 650 K, the decomposition of methoxy groups to form a non-bridging bidentate formate species was observed. This species decomposed on further warming and is described as an intermediate in the decomposition of methanol on  $\eta$ -alumina [18]. These processes have been described within the context of a four-site model for  $\eta$ -alumina [19]. Importantly, that work indicates dimethyl ether and formate formation to be associated specifically with stronger Lewis acid sites. It is acknowledged that under homogeneous conditions, ethers can be prepared from simple alcohols by heating them with acids, with the alcohol acting as a nucleophile [20]. However, the solution phase reactions feature Brønsted acidity

and, as no Brønsted acidity could be detected with the  $\eta$ -alumina used in the current studies [19], this chemistry is thought not to play a role on this catalyst, as it presents only Lewis acid sites.

The present study examines the hydrochlorination of methanol over an  $\eta$ -alumina catalyst via temperature-programmed reaction (TPR) [21]. In the presence of methanol and methanol/HCl feed streams, the formation of dimethyl ether and methyl chloride is observed. The role of the methoxy decomposition pathway leading to: (i) the loss of conversion to MC and DME at high temperatures and (ii) the deposition of carbon on the substrate is considered. The investigation defines a reaction temperature operational window, within which there is minimal carbon laydown on the catalyst. Avoidance of deactivation pathways leads to an improved atom efficiency, a prerequisite for a sustainable process.

## 2. Experimental

### 2.1. Catalyst characterization

The  $\eta$ -alumina catalyst is a commercial grade catalyst [22], the characterization of which has been described elsewhere [19]. The  $\eta$ -alumina sample was activated by heating to 623 K under flowing helium (BOC, 99.999%) for 150 min, and then allowed to cool to reaction temperature. Throughout all of the experimental procedures the sample was continuously flushed with helium gas passed through an in-line purifier (Oxysorb, Messer Griesheim).

### 2.2. Temperature-programmed reaction

Temperature-programmed reaction (TPR) experiments were carried out with the catalyst sample contained within a packed-bed tubular reactor (1/4 in. o.d. stainless steel) located within a temperature programmable oven (Neytech 25 PAF). A mass spectrometer (Leda Mass Gas Analyser, LM22, closed ion source) sampled the eluting gases via a differentially pumped capillary line and a sintered-metal precision leak. The sample was activated as above before dosing with methanol vapor, obtained by passing helium gas through liquid methanol maintained at 293 K. The eluent stream was monitored on the mass spectrometer. Once constant flow had been achieved, indicating steady state operation, TPR runs were performed at a linear heating rate of 8 K min<sup>-1</sup>. The eluent stream from the reactor was continually monitored by the mass spectrometer. TPR experiments were also carried out using a methanol/HCl mixed feed stream. During these experiments, HCl was added to the methanol vapor via a mass flow controller (Brooks, 5850 TR), such that the HCl molar flow rate equaled that of the methanol. Once steady state operation was attained, TPR experiments were carried out as described above. All experiments were performed at least in duplicate, with the results presented here being representative of the observed performance of the reaction system.

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