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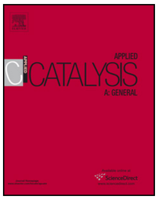

Preparation and characterization of neat and $ZnCl_2$ modified zeolites and alumina for methyl chloride synthesis

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ABSTRACT

A range of zeolite and alumina based catalysts, neat and impregnated with $ZnCl_2$, were screened for gas-phase methyl chloride synthesis from methanol and HCl. The catalysts were characterized with FTIR, TEM, XPS, N_2-physisorption, XRD and EDX to identify the relationship between the catalyst characteristics and their activity and selectivity in methyl chloride synthesis. The work was focused on catalyst performance and stability, acid properties of catalysts and the influence of zinc impregnation. Upon modification with $ZnCl_2$, the number of strong and medium Brønsted acid sites (BAS) decreased, while the number of Lewis acid sites (LAS) increased. The zinc species detected on the catalyst surface is possibly similar to ZnOCl. The presence of $ZnCl_2$ as surface species is not probable, as chlorine is partially removed from the catalyst during calcination at 400 °C. However, the binding energy determined by XPS suggests a Zn^{2+} surface species. Zn^{2+} containing particles were observed on zeolites by TEM, which show a dependence of the particle size on the support acidity. The activities of the catalysts increased with the number of medium and strong LAS, whereas the methyl chloride selectivity slightly decreased giving dimethyl ether as a by-product. As the increase of acid sites upon modification with the same amounts of $ZnCl_2$ was most pronounced for zeolite catalysts, they exhibited the highest activity. However, the zeolite catalysts showed deactivation with time on stream. Zn/H-ZSM 5 zeolite catalysts exhibited a higher stability in the synthesis of methyl chloride than $ZnCl_2$ modified H-Beta and could be regenerated by burning the coke in air at 400 °C. Neat alumina and $ZnCl_2$ modified alumina catalysts were active and selective at 300 °C and higher temperatures, but zeolite catalysts might be suitable for methyl chloride synthesis at lower temperatures, i.e. 200 °C.

1. Introduction

Methyl chloride (MeCl) is a large-scale chemical intermediate with an annual production of ca. 10^6 t [1]. It is used as a general methylation agent, for example in the industrial production of methyl cellulose, silicones and rubber. Methyl chloride is mainly produced by gas-phase hydrochlorination of methanol, for which the reaction scheme is shown below:

$$CH_3OH + HCl \leftrightarrow CH_3Cl + H_2O \qquad \text{(I)}$$

$$CH_3OH \leftrightarrow (CH_3)_2O + H_2O \qquad \text{(II)}$$

$$(CH_3)_2O + HCl \leftrightarrow CH_3Cl + CH_3OH \qquad \text{(III)}$$

Alongside with methyl chloride, dimethyl ether (DME) is formed as a side product (II). DME can react further with HCl to form methanol (MeOH) and MeCl, but reaction (III) is considerably slower than reactions (I) and (II) [2]. For catalyzing these reactions, Lewis acid sites (LAS) are needed. Alumina, either neat or modified with zinc chloride is used industrially [3]. The catalysts modified with zinc chloride are more active and selective toward methyl chloride than neat alumina [4].

Although methyl chloride is a large-scale product, the kinetics and plausible catalysts have not been extensively studied in literature. The majority of the studies deal with γ-alumina, both neat and modified with different metal chlorides. Zinc chloride and cadmium chloride have shown the highest activity and selectivity to methyl chloride while neat alumina is comparably active and selective at elevated temperatures [4]. Furthermore, it has been reported, that alumina, aluminum silicate and silica supported catalysts are more active than carbon supported catalysts [4].

A few publications deal with the kinetics of this reaction over alumina catalysts [2,5–7]. The studies mainly deal with neat

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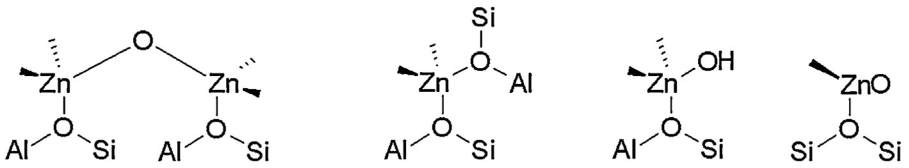

Fig. 1. Possible species of zinc on zeolites according to Lercher and co-workers [22] and Iglesia and co-workers [19].

alumina catalysts and report methyl chloride formation, reaction (I), to be dominant and reactions (II) and (III), which consider dimethyl ether production, negligible. It was demonstrated however, that dimethyl ether is present in the reaction mixture in a considerable amount at low methanol conversions [2,3]. With increased reaction time however, the dimethyl ether concentration decays due to reaction (III).

The influence of zinc modification on the heat of adsorption of HCl and methanol on alumina, $ZnCl_2$/alumina and $ZnCl_2$ was studied in an early study to characterize the catalyst [8]. Three different adsorption sites on $ZnCl_2$ modified alumina were suggested: alumina surface sites, $ZnCl_2$ monolayer sites and bulk $ZnCl_2$ sites (≥ 2 layers). In the case of methanol adsorption an optimum zinc content was found, i.e. a loading at which the heat of adsorption for methanol was maximal. This was the case for the catalyst with the highest number of $ZnCl_2$ monolayer sites (60 wt%). Although the heat of adsorption was maximal at a $ZnCl_2$ loading of 60 wt% the surface area was decreased from 180 to 79 m^2/g. At even higher $ZnCl_2$ loadings, the heat of adsorption decreased again due to the appearance of bulk $ZnCl_2$ sites. Thus, a too high $ZnCl_2$ loading is not desirable, due to the surface area decrease and formation of $ZnCl_2$ sites less suitable for methanol adsorption. On the contrary, the heat of adsorption of HCl was only weakly dependent on the $ZnCl_2$ loading.

In this work, a range of known and new catalysts was applied for methyl chloride synthesis. In addition to alumina and $ZnCl_2$/alumina, both neat and $ZnCl_2$ modified zeolites were also studied. The zeolite catalysts were of special interest due to their high acidity and tunable acid properties. Two zeolite structures were compared: Beta-zeolite with a high Brønsted activity with three different Si/Al ratios (25, 150 and 300) was used and compared to H-ZSM 5 (Si/Al 23, 80 and 280), which was reported to be highly stable in the presence of chlorinated compounds and HCl [9]. Furthermore, a high surface area mesoporous silica (MCM 48) was modified with $ZnCl_2$ as a benchmark for the highly siliceous zeolites.

For the zinc chloride modified catalysts, 5 wt% zinc with respect to the mass of support was used. Although the activity of the catalysts is enhanced with increasing $ZnCl_2$ loading up to a point where the loss of surface area due to pore blocking and formation of bulk $ZnCl_2$ on the catalyst leads to a decrease in activity again [8,10], a low zinc loading was preferred to avoid the pore blockage. To observe the impact of the $ZnCl_2$ modification on the catalyst properties, selectivity and activity, a zinc content of 5 wt% was considered to be sufficient.

To understand the catalytic properties of the catalysts modified with $ZnCl_2$, it is important to know the chemical state of zinc on the catalyst surface. The mechanisms for interaction of zinc with alumina and zeolites are still discussed in the literature and the main results are presented in the following paragraphs.

In the case of $ZnCl_2$ modified alumina, the nature of Zn species on the catalyst surface is unclear, as catalysts have not been characterized in depth. According to a recent study of Pillai et al. [11] applying XPS analysis, the Zn–Cl bond is retained. Zinc species were suggested to replace the terminal basic hydroxide groups on the alumina surface. In other studies it has been reported that the chlorine-to-zinc ratio was reduced compared to the expected value for $ZnCl_2$, suggesting the formation of an S–O–Zn–Cl species, where S stands for the support [12–14].

More detailed characterization has been performed for $ZnCl_2$ modified zeolites, but due to the more complex nature of zeolites, the state of zinc on the catalyst is still under debate. Different kinds of zinc species formed by ion exchange have been suggested [13,15–17] alongside reaction of zinc with extra framework aluminum (EFAL) [18] and the formation of extra crystalline ZnO at higher zinc loadings [19,20].

The following main conclusions have been drawn for the interaction of zinc ions with zeolites:

(i) Mainly strong Brønsted acid sites (BAS) are involved in ion exchange, while weak BAS are retained [21].
(ii) In the case of divalent ions, such as Zn^{2+}, vicinal BAS are preferred for ion exchange, isolated BAS remain [19,22].
(iii) In the case of Zn/Al < 0.26, zinc species are isolated or of molecular size (see Fig. 1); at higher loading the formation of ZnO nanocrystals is proposed [19,21,22].
(iv) Reaction with extra framework aluminum is possible [18].

An overview of probable Lewis acid sites according to Iglesia and co-workers [19] and Lercher and co-workers [22] are shown in Fig. 1. These types of ion-exchange sites have been validated as well in a work by Bell and co-workers for a range of divalent cations, including Zn^{2+}, on ZSM 5 using density functional theory [23]. The first two structures shown are a dimeric structure with a bridging oxygen atom and a zinc exchanged on two aluminum sites. These two structures can be formed if the two sites are in proximity, as in four to six membered rings [23]. Furthermore, zinc species can be exchanged on a single site and carry a negatively charged ligand as e.g. a hydroxyl group. The last structure represents neutral ZnO that is located at the pore walls of the zeolites.

This work aims to provide information on novel catalysts for methyl chloride synthesis and give insight into the influence of the catalyst properties, such as the acidity and chemical state of zinc, on the catalyst activity and selectivity.

2. Experimental

2.1. Catalyst preparation

As catalysts and supports for $ZnCl_2$ (Fluka, $\geq$98%) the following materials were applied: H-Beta 25 (from NH_4-Beta 25, Zeolyst, CP814E), H-Beta 150 (Zeolyst, CP811E) H-Beta 300 (Zeolyst, CP811C-300), H-ZSM 5 80 (from NH_4-ZSM 5 80, Zeolyst, CBV8014), H-ZSM 5 280 (from NH_4-ZSM 5 280, Zeolyst, CBV2814) and γ-alumina (UOP Versal VGL-25). H-Beta 150 and alumina were used as received. The NH_4-zeolites were transformed to their proton form by calcination at 450 °C for 3 h. H-Beta 300 was calcined as well to remove traces of remaining template used for its preparation. H-MCM 48 was synthesized as described in [24], where the detailed procedure can be found. NaOH, cetyl trimethyl ammonium chloride (CTMACl) and tetraethyl orthosilicate (TEOS) was added and the solution was stirred in an open vessel at room temperature for 1 h. The resulting gel was transferred into a 300 mL autoclave, and the synthesis was carried out at 373 K for 75 h.