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Comparative study on the support properties in the total oxidation of dichloromethane over Pt catalysts

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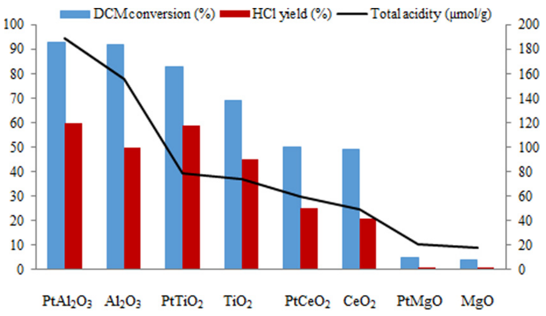
HIGHLIGHTS

- Total conversion of dichloromethane was reached at 450 °C over Al_2O_3 and $PtAl_2O_3$.
- Formation of by-products over $PtTiO_2$ and $PtCeO_2$ is smaller than over $PtAl_2O_3$.
- Dichloromethane oxidation is influenced by the nature and quantity of acid sites.
- By-products formation is influenced by acid sites and catalyst reducibility.
- Pt/Al_2O_3 showed good activity even after 55 h of stability test.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to study the influence of the support oxide properties on the total oxidation of dichloromethane in moist conditions. The support materials γ-Al_2O_3, TiO_2, CeO_2 and MgO were synthesized by a sol-gel method followed by wet impregnation of Pt and characterized by different physico-chemical techniques. The conversion of DCM was higher than 90% at 500 °C over impregnated and non-impregnated Al_2O_3, TiO_2 and CeO_2, even at high GHSV. CO, CH_3Cl and CH_2O were the major by-products observed and their amounts decreased after Pt impregnation. The CH_3Cl formation was higher when Lewis acid sites were present while the existence of Brønsted sites promoted the CH_2O formation. The complete conversion of DCM was achieved at around 450 °C over the Al_2O_3 and Pt/Al_2O_3 and at 500 °C for Pt/TiO_2. These two catalysts exhibited the highest total acidities among the materials tested. The activity of Pt/Al_2O_3 remained the same also after 55 h of testing, however, increase in Pt particle size and decrease in acidity were observed. Pt/CeO_2 while being less active showed smallest amount of by-product formation during the whole temperature range used in light-off tests. This is most probably due to its easy reduction ability. The textural parameters of the supports did not appear to be the key parameters when considering the activity and selectivity of the catalysts.

1. Introduction

Dichloromethane (methylene chloride, CH_2Cl_2, DCM) is widely used in industry in paint strippers and removers, as propellants

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in aerosols, in the manufacture of drugs, decaffeination of coffee, etc. [1,2]. Majority of DCM detected in the environment is due to human actions. However, DCM is not very persistent in the environment. It is quite easily photochemically oxidized by hydroxyl radicals and it does not contribute significantly to the ozone depletion nor to the photochemical smog formation [3]. The volatility increases the health effects of DCM due to facility of inhalation. Long contact with DCM causes problems with skin, central nervous system and liver. Even deaths of the employees are reported to be caused by use of DCM in US [8]. DCM is also considered as a human carcinogen [4]. Several authorities have set the exposure limits for the DCM, which are for example in Europe, 100 ppm (8 h) and 200 ppm (15 min) [5].

Catalytic oxidation is an economic and environmentally sound abatement method, since it is effective in destroying even diluted streams of volatile organic compounds (VOCs) as well as chlorinated volatile organic compounds (CVOCs) at a low temperature range (200–500 °C) [6]. In addition, CVOC oxidation in the presence of efficient catalysts leads selectively to the desired reaction products CO_2, H_2O and HCl, and the harmful and toxic by-products such as dioxins can be avoided [7]. DCM is one of most frequently used model compound for CVOCs, since it constitutes a significant fraction of CVOCs' industrial emissions [8–15].

Different noble metals (Pd, Pt, Rh) supported on various metal oxides such as Al_2O_3, TiO_2, MgO and CeO_2 alone or as mixed oxides are mostly studied catalysts in CVOC oxidation. Brink et al. [16] have studied DCM oxidation over γ-Al_2O_3. During the DCM oxidation, they observed CO and CH_3Cl as the major by-products in addition to HCl. Padilla et al. [8] and Corella et al. [9] studied various CVOCs, including DCM, over different aluminium and titanium oxides and shaped (monoliths, sphere, pellet) catalysts containing Cu, Cr, Pt and Pd. They obtained higher than 80% conversion of DCM with the formation of $CHCl_3$ and CCl_4 as the major by-products. They also observed that Pt based catalysts are more active than the other metal based catalysts studied. Pitkäaho et al. [10] studied γ-alumina supported Pt, Pd, Rh and V_2O_5 monolith catalysts. The formation of CH_2O, CO and CH_3Cl was seen to decrease when platinum and/or ceria was added to the catalyst. Pt/Al_2O_3 was found to be the most active and selective catalyst: 100% conversion was reached at 420 °C and the HCl yield detected was 92%.

Pinard et al. [11,12] and Maupin et al. [13] investigated the DCM oxidation over different zeolite (NaY, HFAU and FAU) and alumina (Al_2O_3 and Pt/Al_2O_3) based catalysts. They concluded that the first step of DCM conversion occurs on the support in the presence of steam with the formation of by-products, the nature and quantity of which depend on the nature of the acidic sites present on the support surface: CH_3Cl is formed on the Lewis acid sites (LAS) whereas CH_2O is formed on the Brønsted acid sites (BAS). Then, these by-products are transformed to final products (HCl and CO_2) on the noble metal sites (Pt). Wang et al. [17] studied the oxidation of DCM over a platinum catalyst supported on an anodic alumite plate. They also observed the formation of by-products, the amount of which decreased with the addition of Pt on the surface of the support.

Based on the earlier studies, it seems that the support properties have a crucial role in the initiation of the DCM reaction on the catalyst. In this study, we selected four different types of supports to compare their properties in more detail. Al_2O_3, having both Lewis and Brønsted acid sites on its surface, was selected to represent acidic support. The good activity of MgO in CCl_4 conversion and its interesting selectivity towards HCl and CO_2 formation were pointed out earlier by Weiss et al. [18]. This is why we decided to choose MgO as a material representing basic properties. Furthermore, a good oxygen storage and oxygen activator [19–21], CeO_2, was selected to check the effect of improved oxidation properties of the support material. TiO_2 was studied as it has shown good selectivity towards H_2O, CO_2 and Cl_2 formation and high stability [22]. To summarize, four oxides Al_2O_3, TiO_2, MgO and CeO_2, with and without Pt impregnation, representing different acido-basic and physico-chemical properties were characterized and tested in DCM oxidation aiming at to find out more information on the role of the support in DCM oxidation.

2. Materials and methods

2.1. Catalyst preparation

The γ-Al_2O_3 support was prepared from aluminium-tri-sec-butoxide (AB, $Al(O$-$C_4H_9)_3$, Sigma-Aldrich, 97 wt.%) precursor using a sol-gel method proposed by Yoldas [23]. The molar ratio of 1:100:0.1 for AB:H_2O:HCl was used in the preparation. The mixture of AB and ultrapure water were kept under stirring at 60 °C for 60 min followed by the addition of HCl in order to catalyse the condensation process. Then, the mixture was kept at 80 °C under vigorous stirring for 2 h after which a viscous sol was obtained. During the preparation, the beaker was covered to minimize evaporation of water.

The preparation of TiO_2, CeO_2 and MgO supports is described in detail in our previous study [24]. Briefly, it consists of a sol-gel preparation using alkoxide precursors for titanium and magnesium and an ionic salt for cerium (cerium (III) nitrate hexahydrate). In the preparation, the precursors were dissolved in alcohol and after water addition the sol-gel formation occurs.

All the prepared viscous sols were dried on a sand bath at 60 °C (formation of gel during drying) overnight followed by drying in a ventilated oven at 120 °C, and finally calcined at 500 °C for 6 h after the temperature had been increased from room temperature to the final calcination temperature with the heating rate of 5 °C min^{-1}.

The hexachloroplatinic acid ($H_2PtCl_6{\cdot}xH_2O$, Johnson-Mattey, 99.9%) was used as a precursor of platinum in wet impregnation to obtain 0.5 wt.% of metallic platinum on the final catalyst. The precursor solution was mixed with the support and maintained under mechanical stirring overnight and then dried at 60 °C on a sand bath. The catalysts were calcined at 500 °C for 2 h followed by a reduction step under a hydrogen flow diluted in N_2 (1/3 H_2 and 2/3 N_2) at 500 °C for 2 h. Heating rate used in both cases was 5 °C min^{-1}. PtAl, PtTi, PtCe and PtMg are used as acronyms for the impregnated catalysts, i.e. Pt/γ-Al_2O_3, Pt/TiO_2, Pt/CeO_2, Pt/MgO, respectively.

2.2. Catalyst characterization

TGA and DTA curves of the non-calcined supports were obtained using SDT2960 TA and SDTQ600 analyzers. Prior to experiments the samples were dried at 120 °C after which they were packed into a Pt crucible. The weights of the samples were between 20 and 30 mg. Samples were analysed in the temperature range of 25–1000 °C with a heating rate of 10 °C min^{-1} under an air flow (100 mL min^{-1}). The information achieved was used in the selection of the correct calcination temperature for the supports.

XRD data were collected at room temperature, using a Bruker D8 diffractometer, equipped with a Cu Kα radiation ($\lambda K_{\alpha 1} = 0.15406$ nm) anode X-ray tube and Nickel filter monochromator. Diffractograms were recorded in the 5–90° range of 2θ with a step of 0.05° and a dwell time of 2 s. For sample identification, diffraction patterns were compared to the JCPDS database (Joint committee on powder diffraction standards). The crystallite sizes were calculated using the Debye–Scherrer Eq. (1):

$$D = k\lambda/(\beta \cos \theta) \quad (1)$$