KMo alumina supported catalysts for the direct synthesis of methyl mercaptan from syngas and H₂S under industrial reactions conditions

Hélori Salembier,a,b Carole Lamonier,a,* Pascal Blanchard,a Christine Lancelot,a Georges Frémyb

aUniv. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
bARKEMA, Groupement de Recherches de Lacq, BP 34, 64170 Lacq, France
*Corresponding author: carole.lamonier@ed.univ-lille1.fr

Abstract: Methyl mercaptan (CH₃SH) is a precursor to methionine whose worldwide demand is steadily growing. The direct synthesis of CH₃SH from syngas (CO/H₂) and H₂S appears as an attractive industrial process. KMo supported catalytic systems efficient for this reaction and the study focuses here on the effects of molybdenum loading and calcination procedure on KMo alumina supported catalysts. Correlations are made between catalytic performances and characterizations of the oxide and sulfide catalysts, evidencing the potassium intercalated 1T-MoS₂ phase as the active phase.

Keywords: Methyl mercaptan (CH₃SH), 1T-MoS₂, KMo sulfide catalysts.

1. Introduction

The synthesis of CH₃SH is currently produced by a catalytic reaction between H₂S and methanol, involving multiple reaction steps due to the production of methanol. Direct synthesis from CO/H₂/H₂S gas mixture (also called syngas route) can be effective by tuning the supported catalysts composition. Few literature deals with this one-step reaction even if it has been studied since 1980s. KMo and KW supported catalysts were reported for this synthesis, with SiO₂ and Al₂O₃ as the most frequently used carriers. This study focuses on the KMo alumina supported system prepared from K₂MoO₄ precursor. The effects of the Mo content as well as the preparation procedure (with or without calcination before activation) have been studied. Catalytic performances have been evaluated. Characterizations performed before activation together with the quantification of the K⁺ intercalated 1T-MoS₂ phase obtained after activation have been performed explaining the catalytic results.

2. Experimental

Catalysts were prepared by incipient wetness impregnation method using γ-Al₂O₃ (“Al” noted) (pellets, SSA = 254 m².g⁻¹, water pore volume V_p = 0.85 cm³.g⁻¹) as support. For all solids, the molar ratio K/Mo was fixed to 2 by using solutions of K₂MoO₄ (Aldrich, purity 98.0 %) with different concentrations in order to obtain various Mo loading, wt% Mo = 8.0 ; 9.3 ; 10.6 ; 12.0 ; 14.0 ; 15.0 ; 16.7 % (“xKMoAl” noted, x = wt% Mo). The resultant solids were matured under a steamy atmosphere for 2.5 h and dried overnight at 100 °C. Optionnally, a calcination procedure was performed under air (500 °C at 2 °C.min⁻¹ for 3 h). CH₃SH synthesis was carried out using a fixed-bed reactor placed in a temperature-controlled oven supplied by the feed gases (CO, H₂, H₂S, and N₂). Performances were estimated for 30 mL of catalysts at three different temperatures, 280, 300, and 320 °C, at 10 bar of pressure, CO/H₂/S gas molar ratio equal to 1/2/1, gas hourly space velocity equal to 1333 h⁻¹. Catalysts were characterized using XRD, Raman spectroscopy and XPS, and textural characteristics were measured using N₂ adsorption-desorption experiment at -196 °C.

3. Results and discussion

The catalytic performances of KMo/Al catalysts with various Mo loading have been evaluated showing differences in terms of CH₃SH selectivity (between 35 and 39%) together with the formation of the main by-products as CO₂ (the main one) and CH₄. CO conversion reached its maximum at wt% Mo = 15.0 (Fig.1.(a)) which is confirmed by the CH₃SH productivity per volume of catalyst at three different
temperatures: 280, 300, and 320 °C as shown in Figure 1(a). In Figure 2.(a), no diffraction peak (except those for alumina) are observed for wt% Mo ≤ 15.0 while K₂MoO₄ diffraction peaks appear at wt% Mo = 16.7 % (PDF 00-022-0835) indicating that no crystalized species are observed for Mo loading up to 15.0 %. Whatever the catalyst Raman spectra (Figure 2.(b)) showed lines at 317, 851 and 893 cm⁻¹ characteristics of K₂MoO₄ species. The Raman line at 911 cm⁻¹ only observed at low Mo loading (wt% Mo = 8.0) is related to isolated adsorbed MoO₂²⁻ species. CH₃SH productivity was correlated with the quantity of K₃MoS₂ (the intercalated K⁺ 1T-MoS₂ phase) determined by XPS (Figure 1.(b)) until to 15.0 wt% Mo that was demonstrated by XRD as the limit of the detection of crystallized particles of K₂MoO₄.

![CH₃SH Productivity vs wt% Mo](image1)

Figure 1. (a) CH₃SH productivity per volume of catalyst as a function of wt% Mo and temperature and (b) total CH₃SH productivity as a function of the quantity of K₃MoS₂ in the reactor (Reaction conditions: CO:H₂:H₂S = 1:2:1, 1333 h⁻¹, 10 bar).

![XRD and Raman Spectra](image2)

Figure 2. (a) XRD patterns of K₃MoO₄/Al₂O₃ dried and calcined catalysts (▲) K₃MoO₄; (○) alumina and (b) Raman spectra of K₂MoO₄/Al₂O₃ dried and calcined catalysts

4. Conclusions

K₂MoO₄ catalysts precursors supported on alumina have been prepared at different Mo loading with a K/Mo ratio equal to 2 by incipient wetness impregnation. After activation, these catalysts have been evaluated in the direct reaction of syngas with hydrogen sulfide to produce methyl mercaptan. The optimum of the Mo loading for the best catalytic activity was found at 15.0 wt% Mo which corresponds to the limit of the detection of crystallized particles of K₂MoO₄ on the oxidic form. Catalytic performances and then CH₃SH productivity are correlated with the amount of the active phase, the K intercalated 1T-MoS₂ phase until a molybdenum content of 15.0%, showing that the formation of active sites is favored starting from dispersed Mo entities.

References