KMo alumina supported catalysts for the direct synthesis of methyl mercaptan from syngas and H_2S under industrial reactions conditions

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Abstract: Methylmercaptan (CH_3SH) is a precursor to methionine whose worldwide demand is steadily growing. The direct synthesis of CH_3SH from syngas (CO/H_2) and H_2S 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-MoS_2 phase as the active phase.

Keywords: Methyl mercaptan (CH_3SH), 1T-MoS_2, KMo sulfide catalysts.

1. Introduction

The synthesis of CH_3SH is currently produced by a catalytic reaction between H_2S and methanol, involing multiple reaction steps due to the production of methanol. Direct synthesis from $CO/H_2/H_2S$ 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 SiO_2 and Al_2O_3 as the most frequently used carriers [1,2]. This study focuses on the KMo alumina supported system prepared from K_2MoO_4 precursor. The effects on 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-MoS_2 phase obtained after activation have been performed explaining the catalytic results.

2. Experimental

Catalysts were prepared by incipient wetness impregnation method using γ–Al_2O_3 ("Al" noted) (pellets, SSA = 254 $m^2.g^{-1}$, water pore volume $V_p = 0.85$ $cm^3.g^{-1}$) as support. For all solids, the molar ratio K/Mo was fixed to 2 by using solutions of K_2MoO_4 (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. Optionally, a calcination procedure was performed under air (500 °C at 2 $°C.min^{-1}$ for 3 h). CH_3SH synthesis was carried out using a fixed-bed reactor placed in a temperature-controlled oven supplied by the feed gases (CO, H_2, H_2S, and N_2). Performances were estimated for 30 mL of catalysts at three different temperatures, 280, 300, and 320 °C, at 10 bar of pressure, $CO/H_2/H_2S$ 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 N_2 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 CH_3SH selectivity (between 35 and 39%) together with the formation of the mainby-products as CO_2 (the main one) and CH_4. CO conversion reached its maximum at wt% Mo = 15.0 (Fig.1.(a)) which is confirmed by the CH_3SH 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 K_2MoO_4 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 K_2MoO_4 species[3]. The Raman line at 911 cm^{-1} only observed at low Mo loading (wt% Mo = 8.0) is related to isolated adsorbed MoO_4^{2-} species. CH_3SH productivity was correlated with the quantity of K_xMoS_2 (the intercalated K^+ 1T-MoS_2 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 K_2MoO_4.

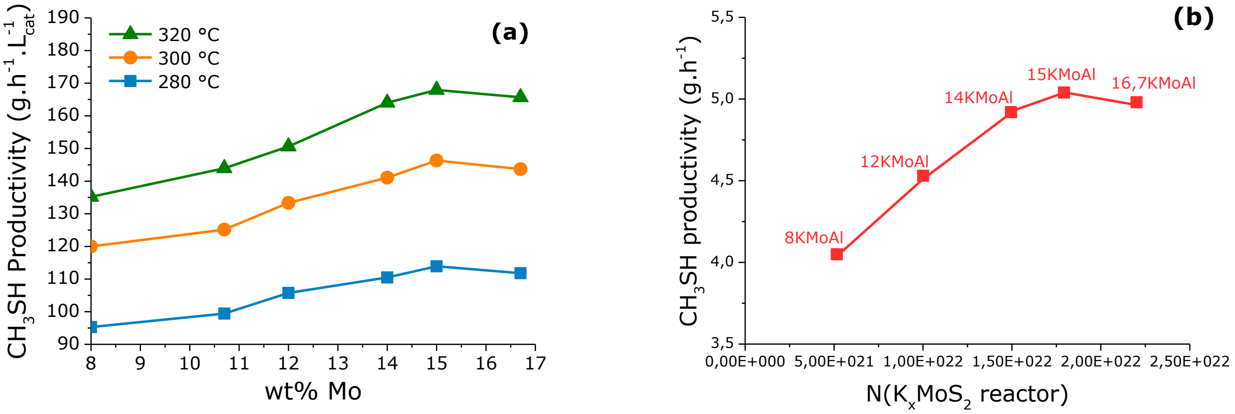

Figure 1. (a)CH_3SH productivity per volume of catalyst as a function of wt% Mo and temperature and **(b)**total CH_3SH productivity as function of the quantity of K_xMoS_2 in the reactor (Reaction conditions: CO:H_2:H_2S = 1:2:1, 1333 h^{-1}, 10 bar).

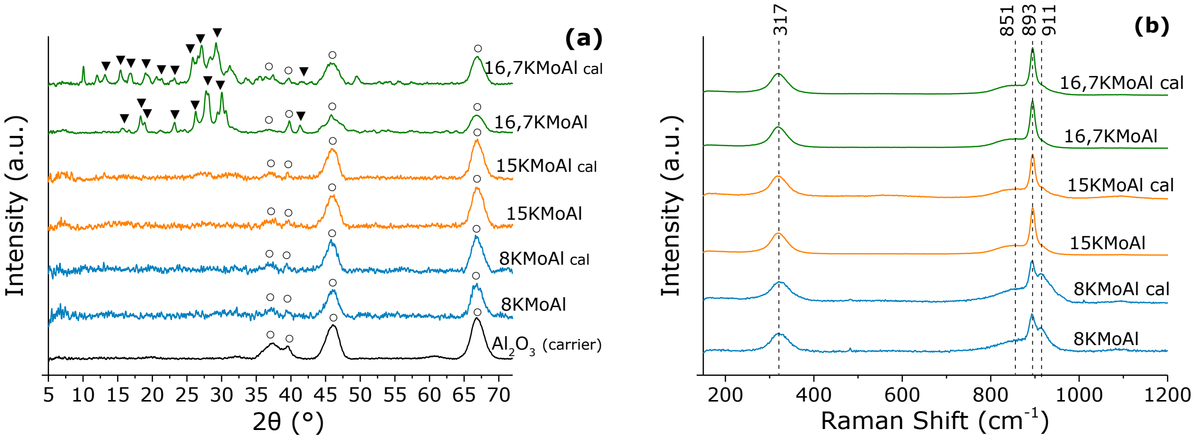

Figure 2. (a)XRD patterns of K_2MoO_4/Al_2O_3 dried and calcined catalysts (▲) K_2MoO_4 ; (○) alumina and **(b)**Raman spectra of K_2MoO_4/Al_2O_3 dried and calcined catalysts

4. Conclusions

K_2MoO_4 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 K_2MoO_4 on the oxidic form. Catalytic performances and then CH_3SH productivity are correlated with the amount of the active phase, the K intercalated 1T-MoS_2 phase until a molybdenum content of 15.0%, showing that the formation of actives sites is favored starting from dispersed Mo entities.

References

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