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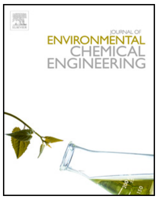

Evaluation of MoS_2 based catalysts for the conversion of syngas into alcohols: A combinatorial approach

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ABSTRACT

72 MoS_2 catalysts were tested in the conversion of syngas to alcohols, using a high-throughput catalyst evaluation unit, to identify the best catalyst, based on CO conversion, both ethanol and higher alcohols and total alcohols selectivity. Catalysts prepared by thermal decomposition of $(NH_4)_2MoS_4$ at low temperature showed a higher selectivity to total alcohols. The highest selectivity to ethanol and higher alcohols was obtained at 300 °C by a catalyst prepared by reacting $Mo(CO)_6$ with sulphur. Catalysts prepared by thermal decomposition of $(NH_4)_2MoS_4$ at high temperature showed very low activity. Catalysts prepared by thermal decomposition of $(NH_4)_2MoS_4$ in tridecane/water with hydrogen atmosphere showed low activity and selectivity. There was no significant difference among the alkaline metal promoters K, Cs and Rb regarding total alcohols selectivities. Incorporation of Co and Ni led to catalysts with activity levels equivalent to catalysts that contain Rh.

Introduction

Increasing awareness about the consequences of global warming and energy dependence has renewed the interest in the development of alternative fuels [1–4]. One option is the production of ethanol from biomass residues through the gasification of biomass and the conversion of the resulting synthesis gas into ethanol and higher alcohols [5–15]. This solution is particularly suited for Brazil, given its growing flex-fuelled (gasoline/ethanol) light vehicle fleet and great availability of sugar cane residues [16,17]. One of the biggest challenges to develop this option is to find a catalyst capable of economically converting syngas into ethanol and higher alcohols. There are various types of catalysts that can be used in this process, but one of the most promising is based on alkali promoted molybdenum sulphide [18–20]. Various studies have examined the performance of alkali promoted molybdenum sulphide based catalysts, prepared by different methods and used under different operating conditions, for the conversion of syngas into ethanol and higher alcohols [21–34].

The thermodynamics of ethanol and higher alcohols formation have been assessed through theoretical calculations with Aspen software [35], and also by calculations with HSC Chemistry Software [18]. Methanol formation is favoured at low temperature and high pressure. At high pressure the formation of higher alcohols increases with increasing temperature [18]. Ethanol formation from syngas is a highly exothermic reaction (Eq. (1)), and heat dissipation may be a problem for scale-up [36].

$$2CO(g)+4H_2(g)\rightarrow C_2H_5OH+H_2O\ (1) \qquad (1)$$

$$\Delta H^{\circ}_{298} = -253.6\ \text{kJ/mol of ethanol}$$

$$\Delta G^{\circ}_{298} = -221.1\ \text{kJ/mol of ethanol}$$

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Alkali promoted molybdenum sulphide catalysts produce linear alcohols and ethanol and higher alcohols are formed via a classical insertion of CO into the corresponding precursor alcohol [21].

CO hydrogenation to methane is a competitive reaction to the alcohol synthesis with such catalysts.

The optimum conditions for this reaction seem to be in the temperature range from 240 to 325 °C, pressure around 7 MPa, and GHSV ranging from 2000 to 5000 h^{-1} [5,6,18,35,37].

MoS_2 catalysts have water gas shift activity [6,38]. As a result, the preferred ratio of hydrogen to carbon monoxide is 1, although several papers reported a ratio of 2 [18].

To find an MoS_2 based catalyst, with high activity and high ethanol and higher alcohols selectivity, capable of economically converting syngas into ethanol and higher alcohols, it is necessary to investigate which is the best preparation procedure and catalyst composition.

In this study a total of 72 molybdenum sulphide catalysts have been prepared using different methods, such as thermal decomposition of ammonium tetrathiomolybdate (ATTM) to yield low or high crystalline material (with two different temperatures, named TH1 and TH2), chemical solution reaction of molybdenum hexacarbonyl with sulphur (named HC) and thermal decomposition of ATTM in the presence of water, tridecane and H_2, (named WTH). The catalysts were loaded with different alkali promoters and transition metals and, finally tested under different operating conditions using a high-throughput catalyst evaluation unit, to identify the best preparation procedure and catalyst composition, based on CO conversion and selectivity to ethanol, higher alcohols and total alcohols.

Briefly, the catalyst preparation procedures were as follows:

In TH1 and TH2 methods, MoS_2 was obtained by thermal decomposition of ATTM in flowing nitrogen at 450 °C and 800 °C, respectively.

In HC methods, MoS_2 was obtained applying a low temperature (140 °C) to a solution of $Mo(CO)_6$ and sulphur in *p*-xylene.

In WTH method, MoS_2 was obtained by decomposing ATTM in tridecane and water at 275 °C, under H_2 pressure (6.9 MPa).

All transition metals and alkaline promoters were loaded in the catalyst's active phase (MoS_2 particles) by physical mixing or wet impregnation.

Material and methods

Catalyst preparation

Around one or two grams of each catalyst were prepared for each phase of this study. All the preparation steps were performed under inert atmosphere and the catalysts were not oxidized. A list of all catalysts can be seen in Table 1.

TH1–PM method

This method was based on the thermal decomposition of ATTM at 450 °C, according to Eq. (2) [39] (the name TH comes from thermal and the suffix PM comes from physical mixing):

$$NH4)_2MoS_4 \rightarrow 2NH_3 + S + H_2S + MoS_2 \ (2) \qquad (2)$$

ATTM (Sigma–Aldrich, product No. 323446, lot No. 00810DJ, purity 99.97 mass%) was heated in a tube oven under nitrogen flow (100 ml/min) for 2 h at 450 °C with 2 °C/min ramp rate. To add Co, Ni or Rh to the catalyst, aqueous salt ($Co(NO_3)_2$, $Ni(NO_3)_2$ or $Rh(NO_3)_3$) solutions were added to the powder, then, the catalysts were homogenized on a roller bench for 1 h and treated in a tube oven under nitrogen flow (100 ml/min) for 16 h, at 110 °C, with 1 °C/min ramp rate. The dried catalysts were calcined in a tube oven under nitrogen flow (100 ml/min) for 4 h, at 350 °C, with 2 °C/min ramp rate. To add an alkaline metal, the resulting powder was mixed with K_2CO_3, Cs_2CO_3, or Rb_2CO_3 with the desired atomic ratio (metal/Mo) in a glovebox, by crushing the two powders together, to obtain a homogeneous mixture and dried in a tube oven under nitrogen flow (100 ml/min) for 16 h, at 110 °C, with 1 °C/min ramp rate.

TH2–PM method

This method is similar to TH1–PM, except for the decomposition temperature which is 800 °C.

HC–PM method

This method was based on Eq. (3) [40] (the name HC comes from the precursor's name molybdenum hexacarbonyl and the suffix PM comes from physical mixing):

$$2S + Mo(CO)_6 \rightarrow MoS_2 + 6CO \ (3) \qquad (3)$$

A Schlenk tube containing 100 ml of *p*-xylene (Fluka, product No. 95682, lot No. 1385554 51,408,139, purity 99 mass%) was cooled in liquid nitrogen until the *p*-xylene solidified. Vacuum was applied and the *p*-xylene was warmed up until it returned to liquid phase. This procedure was repeated twice and the tube was filled with nitrogen. An amount of ~1.25 g sulphur (Acros, product No. 199930100, lot No. A0276552, purity 99.999 mass%) was weighed into a 3-necked flask and was transferred to an argon containing glovebox, together with the *p*-xylene containing Schlenk tube. The *p*-xylene was added to the sulphur and the flask was taken to a fume hood where it was connected to nitrogen and a reflux. The temperature was raised to 140 °C in 30 min and this temperature was kept until all sulphur was dissolved (approx. 10 min). Then, the mixture was cooled to room temperature. An amount of 5.15 g of molybdenum hexacarbonyl (Acros, product No. 190390500, lot No. A0282472, purity 98 mass%) was added and the temperature was raised to 140 °C in 20 min. After 150 min at 140 °C the reaction mixture was cooled to room temperature and transferred to the glovebox. The black powder was filtered, dried with acetone in the glovebox and thermally treated in a tube oven under nitrogen flow (100 ml/min) for 1 h, at 550 °C, with 1 °C/min ramp rate.

To add Co, Ni or Rh to the catalyst, the same procedure described for catalyst TH1–PM was used. The resulting powder was mixed with K_2CO_3, Cs_2CO_3 or Rb_2CO_3 using the same procedure described for catalyst TH1–PM.

WTH method

This method was based on Eq. (4) [41] (the name WTH comes from the name of some substances present in the reaction medium: water, tridecane and hydrogen):

$$NH_4)_2MoS_4 + H_2 \rightarrow MoS_2 + 2NH_3 + 2H_2S \ (4) \qquad (4)$$

A 150 ml Premex autoclave was loaded with 2.38 g ATTM (Sigma–Aldrich, product No. 323446, lot No. 00810DJ, purity 99.97 mass%), 100.3 g tridecane (Acros, product No. 139511000, lot No. A0280023, purity 99 mass%) and 4.91 g water. The autoclave was pressurized to 6.9 MPa with hydrogen at room temperature and purged four times. Thereafter, the autoclave was heated to 275 °C and kept at this temperature for 3 h. After reaction, the reactor was cooled to 200 °C and hot vented for 35 min to release water vapour, NH_3 and H_2S. After cooling the reactor to room temperature, the contents (black powder) were washed with 20–30 ml of acetone and filtered through a fine filter paper in an argon containing glovebox. The catalysts were dried overnight in a tube oven at 120 °C (with 2 °C/min ramp rate) under nitrogen flow (100 ml/min). The resulting powder was mixed with K_2CO_3, Cs_2CO_3 or Rb_2CO_3 with the desired atomic ratio (metal/Mo) in a glovebox, by crushing the two powders together, to obtain a homogeneous mixture. After mixing, the catalysts were dried in a tube oven under nitrogen flow (100 ml/min) for 16 h, at 110 °C, with 2 °C/min ramp rate.