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Synthesis gas conversion over a Rh–K–MoP/SiO_2 catalyst

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ABSTRACT

Synthesis gas conversion over a 1 wt% Rh–5 wt% K–10 wt% MoP on SiO_2 catalyst was investigated at different temperatures, synthesis gas H_2/CO ratios and space velocities. Compared to a 5 wt% K–10 wt% MoP on SiO_2 catalyst, addition of Rh increased the stability of the catalyst and the selectivity to hydrocarbons. The highest C_{2+} oxygenate selectivity of 44 C atom% was achieved at 598 K and H_2:CO = 1. Power law kinetics were used to describe the space–time yield (STY) of the major products. The apparent activation energies for ethanol (77.7 kJ/mol) and acetaldehyde (81.9 kJ/mol) formation suggested that both originated from the same surface intermediate whereas, a higher activation barrier was identified for methanol (114.5 kJ/mol).

1. Introduction

Interest in the development of new technologies that convert renewable resources to alternative transportation fuels, and thereby address issues of air quality, CO_2 emissions and energy security, are increasing. Biomass, especially agricultural and forest residue, has potential as a renewable energy resource and is expected to play an important role in the synthesis of clean and sustainable fuels [1,2]. One route to clean fuels from biomass is through the thermocatalytic conversion of synthesis gas ($CO + CO_2 + H_2$) that is produced by biomass gasification. The synthesis of alcohols from synthesis gas (syngas) has been known since the 1930s [3,4] and the production of methanol is practiced industrially using Cu/ZnO catalysts [5]. Higher alcohols, especially iso-butanol, are produced when high temperature Zn/Cr and low temperature Cu/ZnO methanol catalysts are promoted with alkali metals. These catalysts produce C_1–C_6 linear and branched alcohols [6,7] primarily via an aldol condensation or methanol homologation reaction mechanism [1,8]. However, they have very low selectivity toward ethanol because of the fast C–C chain growth of the C_2 surface intermediate [8,9].

Many other catalysts for the synthesis of ethanol or mixed alcohols have been reported in the literature, and these can be categorized as (i) modified Fischer–Tropsch (FT) catalysts (ii) Rh-based catalysts and (iii) Mo-based catalysts. Alkali-doped FT catalysts produce mainly hydrocarbons from syngas, with a ratio of hydrocarbon to alcohol equal to one or more [10], and among the alcohols, C_{2+} alcohols predominate. A high yield of alcohols has also been reported on Cu–Co catalysts, but these catalysts produce significant amounts of hydrocarbons which have a negative effect on the overall process feasibility, especially if the CH_4 selectivity is above about 10% [1]. Rh-based catalysts have the highest reported ethanol selectivity among the various synthesis gas catalysts investigated to date [1,11–16]. Hu et al. reported 44.5 C atom% selectivity to ethanol with a considerable amount of CH_4 (48 C atom%) in the product [11] when synthesis gas was reacted over a Rh catalyst, promoted with Li and Mn, at 573 K, 3 MPa and a syngas H_2:CO ratio of 2. Recently, Rh supported on carbon nanotubes was reported to have good selectivity (52.4 C atom%) towards C_{2+} oxygenates as well [12].

The high hydrocarbon selectivity reported on Rh-based catalysts, especially toward CH_4, means that these catalysts would be difficult to implement in a commercial process. Furthermore, because of cost and supply issues associated with Rh, there is significant interest in less expensive synthesis gas conversion catalysts with high alcohol selectivity. Several researchers have reported that Mo sulphides, phosphides, nitrides and carbides have catalytic

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properties similar to some precious metal [17], and that they resist sulphur poisoning [1]. These two characteristics have led to several studies of Mo-based catalysts for syngas conversion to alcohols. Synthesis gas conversion at 568 K, 7.2 MPa and a H_2:CO ratio of 1 was reported with high selectivity to ethanol (40 C atom%) over a K-promoted MoS_2 [18,19], but later researchers only achieved 10–30 C atom% ethanol selectivity on K–MoS_2 catalysts promoted with Rh, Co, Ni, and Mn [20–23]. Recently, syngas conversion over β-Mo_2C at 573 K and 8 MPa was reported to produce hydrocarbons and alcohols, and among the liquid products, ethanol predominated [24,25]. On alkali doped Mo catalysts (both Mo_2C and MoS_2), the higher alcohol synthesis followed the Anderson–Schulz–Flory distribution, with a high selectivity to methanol. Addition of FT metals (Ni, Co, Rh) increased the selectivity to ethanol and enhanced the performance of MoS_2 and Mo_2C catalysts [20–23,25].

The kinetics of synthesis gas conversion to alcohols has also been reported in the literature. The activation energy of synthesis gas conversion on Rh catalysts promoted with Mn has been reported by several researchers [13–16], with values of 90–140 kJ/mol reported for the activation energy of methane formation and 40–70 kJ/mol for ethanol formation. Kinetic models for higher alcohol synthesis over MoS_2 have also been developed by several researchers [26–28] and it is now well established that the alcohol chain growth occurs via a CO insertion mechanism on MoS_2 catalysts, although recent theoretical studies have shown that CO does not dissociate on MoS_2 [29]. There is very limited information on the kinetics of synthesis gas conversion over Mo_2C catalysts, although Xiang et al. [25] has reported the activation energies for linear alcohols (C_1–C_5) over several alkali-promoted Mo_2C catalysts. For K–Mo_2C the ethanol activation energy was 74 kJ/mol, and with the addition of Co, the activation energy decreased to 71 kJ/mol [25].

Recently, the present authors reported on the product distribution obtained from synthesis gas conversion over a new series of K–MoP catalysts supported on SiO_2 [30,31]. Within the investigated range of compositions, a 5 wt% K–10 wt% MoP supported on SiO_2 catalyst showed the highest selectivity towards liquid oxygenates and C_2 oxygenates, i.e. ethanol (16 C atom%) and acetaldehyde (18 C atom%). Although the MoP catalysts showed promising selectivity to oxygenates and ethanol, the catalysts deactivated during the first 20 h of operation before stabilizing at a lower level of conversion. In the present study, we demonstrate that addition of 1 wt% Rh to the 5 wt% K–10 wt% MoP-SiO_2 catalyst stabilizes the CO conversion. The space–time–yield data for the Rh–K–MoP/SiO_2 catalyst, measured at similar CO conversions (10–25%), have been used to develop simplified power law kinetic models of the synthesis of the oxygenated compounds and the apparent activation energies obtained for the Rh–K–MoP/SiO_2 catalyst have been compared to those obtained over other Mo catalysts.

2. Experimental

2.1. Catalyst preparation

The silica supported Rh–K–MoP catalyst was prepared by stepwise impregnation of a SiO_2 support, followed by calcination and temperature-programmed reduction (TPR). Approximately 10 g of the SiO_2 (Sigma–Aldrich, Grade 62, 60–200 mesh, BET area = 330 m^2/g, pore volume = 1.2 cm^3/g) was impregnated with a solution of potassium nitrate (1.77 g KNO_3, BDH Chemicals, 99.97% dissolved in 15 ml of de-ionized water). After aging at room temperature for 12 h, the impregnated SiO_2 was dried at 373 K for 12 h followed by calcination at 773 K for 5 h. Stoichiometric amounts (Mo:P = 1) of ammonium heptamolybdate (1.39 g of $(NH_4)_6Mo_7O_{24}$ $4H_2O$, BDH Chemicals, 99%) and diammonium hydrogen phosphate (1.04 g of $(NH_4)_2HPO_4$, Sigma–Aldrich, 99%) were dissolved in 15.7 ml of de-ionized water and impregnated drop-wise onto 10 g of the K–SiO_2 with continuous mixing. The impregnated support was held at room temperature for 12 h before being dried at 373 K for 12 h and calcined at 773 K for 5 h. To add the 1 wt% Rh, 0.215 g of rhodium (III) acetate (Sigma–Aldrich, 99%) was dissolved in 15 ml of de-ionized water. A few drops of HNO_3 were added to make a translucent solution (light brown-yellow in color). The Rh solution was then added to the calcined K–MoP–SiO_2, aged for 12 h at room temperature and dried at 373 K for 12 h. A final calcination was conducted at 773 K for 5 h. The calcined catalyst precursor was subjected to TPR in a H_2 (Praxair, 99.99%) flow of 120 cm^3 (STP) min^{-1} g^{-1}, at a temperature ramp of 1 K/min to a final temperature of 923 K. The final temperature was maintained for 2 h. After reduction, the catalyst was cooled in He to the desired reaction temperature. For samples prepared for EDX, XPS and BET area analysis, the catalyst was cooled to room temperature in He and then passivated in 2 vol% O_2 in He for 2 h at room temperature prior to removal from the reactor.

Details of the preparation of the MoP/SiO_2 and K–MoP/SiO_2 catalysts used herein for comparison, have been reported previously [30,31].

2.2. Catalyst characterization

The chemical composition of the prepared catalysts was done by CANTEST Laboratories (Burnaby, BC) using ICP-AES. Prior to analysis about 0.1 g of the passivated catalyst was mixed with 0.7 g of $LiBO_2$ and fused at 1273 K before being dissolved in 100 ml of 4% nitric acid.

The catalyst single point BET surface areas were measured using a Micromeritics FlowSorbII 2300 analyser. About 0.1 g of the passivated catalyst was degassed at 473 K for 2 h and the measurement was made using 30% N_2 and 70% He. Temperature-programmed reduction experiments were carried out using a Micromeritics AutoChem 2920 apparatus, following the procedure of Zuzaniuk and Prins [33]. The calcined, catalyst precursor (160–180 mg) was placed in a quartz U-tube and reduced in a flow of a 9.5% H_2/Ar mixture (50 ml min^{-1}). The temperature was increased at a ramp rate of 5 K min^{-1} up to 1023 K, the final temperature being maintained for 4 h. Prior to the analysis, the temperature-programmed reduction of a reference material (silver oxide) was carried out using the same procedure. The peak area of the reference material was correlated to the known volume of consumed H_2 and these data were used to calculate H_2 consumption during the reduction of the phosphide precursors.

EDX analysis was performed using a Hitachi S-3000N electron microscope operated with a 20 kV electron beam acceleration voltage. The average composition, from at least 10 data points, was determined for each catalyst sample. A Leybold Max200 X-ray photoelectron spectrometer with an Al Kα photon source was used for the XPS analysis. After reduction and reaction the catalyst was cooled to room temperature in He and prior to removal from the reactor, the catalyst was passivated in 2 vol% O_2 in He for 2 h at room temperature. Exposure of the samples to ambient atmosphere was minimized by transferring the samples from the reactor to the spectrometer either in vacuum or under N_2. No further treatment of the catalysts was done in the XPS chamber. All XPS spectra were corrected to the C1s peak with a binding energy (BE) of 284.6 eV.

2.3. Catalyst assessment

Catalyst activities were measured in a laboratory fixed-bed micro-reactor (copper lined stainless steel tube with o.d. = 9.53 mm and i.d. = 6.35 mm), operated at low conversion to investigate the