Fischer Tropsch synthesis using cobalt based carbon catalysts

Sarwat Iqbal[a], Thomas E. Davies[b], David J. Morgan[a], Khalid Karim[c], James S. Hayward[a], Jonathan K. Bartley[a], Stuart H. Taylor[a], Graham J. Hutchings[a,*]

[a] Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK
[b] Stephenson Institute for Renewable Energy, Chemistry Department, The University of Liverpool, Crown Street, Liverpool L69 7ZD, UK
[c] SABIC T&I, P.O Box 42503, Riyadh 11551, Saudi Arabia

ABSTRACT

The catalytic activity of a series of carbon-supported cobalt manganese oxide ($CoMnO_x$) catalysts was investigated for the Fischer Tropsch synthesis reaction. The catalysts were compared with an unsupported $CoMnO_x$ catalyst under the same reaction conditions, and it was shown that the use of an activated carbon support increased both the catalyst activity and the selectivity to C_{2+} hydrocarbons, whilst lowering the selectivity to CH_4 and CO_2. Additionally, the effects of varying heat treatment temperatures and increasing the precursor ageing times were also investigated. Increasing the heat treatment temperature of the catalyst precursor between 300 and 500 °C led to an increase in activity, as well as an increase in selectivity to C_{2+} hydrocarbons, but it also increased the selectivity to CO_2. At 600 °C there was a marked decrease in activity, and the main product was C_{5+} hydrocarbons. Ageing the initial precipitate led to a decrease in activity and also decreased the selectivity towards hydrocarbons.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Fischer Tropsch synthesis (FTS) is valuable for the production of clean liquid fuels from syngas ($CO + H_2$). The product distribution in FTS is, however, typically very broad and a major part of the extensive current research is focussed on controlling the selectivity to the desired products. Fe, Co, and Ru are active catalysts for FTS, but only Fe and Co are used extensively. Although ruthenium exhibits excellent activity for this reaction, its limited availability and cost prohibits its use on an industrial scale. Iron based catalysts have been shown to be active for the formation of hydrocarbons at higher reaction temperatures, but suffer from complex phase formation and deactivation by water. Cobalt catalysts are active at lower temperatures than Fe and tend to produce light hydrocarbons, particularly when promoted with manganese oxide. A range of studies have been published on $CoMnO_x$ catalysts for the synthesis of light hydrocarbons, and they demonstrate lower selectivity to methane [1–4]. It has been observed that Co in combination with manganese oxide can produce high yields of alkenes with increasing CO conversion, whereas this is not observed with cobalt only catalysts [5]. The use of partially reducible oxides such as MnO_2 and TiO_2 [4] has been shown to improve the selectivity towards

light alkenes in FTS using cobalt as the active metal component. There are reports showing the structure–performance relationship of $CoMnO_x$ catalysts which supports the hypothesis that it is necessary for Co and Mn to be in close proximity to observe the enhanced catalytic performance [6].

It is well-established that the catalytic activity depends on the number of surface metal sites available for reaction. A common method of increasing the dispersion and stability of metal is supporting the particles on a stable metal oxide, such as Al_2O_3 or SiO_2. However, it has been observed that the strong metal–support interaction can lead to the formation of undesirable phases such as $CoAl_2O_4$, and these mixed oxides are believed to be a cause of deactivation that is generally observed with these catalysts. The utilization of inert supports can present an alternative approach, in this way it might be possible to improve the dispersion and stability of the active metal sites without risking the formation of the inactive mixed metal oxide. Materials based on activated carbon have been reported to be promising supports because they are relatively chemically inert [7–9]. Carbon provides a stable platform for the deposition of the active species [10] and carbon has been shown to enable the reduction of metal oxides in an inert atmosphere, as a result of auto-reduction [11]. To date there has been a growing trend for the use of activated carbon as a support for the FTS reaction [7,12–16].

In the present study we have investigated the effect of two parameters, namely the heat treatment temperature and the

* Corresponding author.
  E-mail address: hutch@cardiff.ac.uk (G.J. Hutchings).

precipitate ageing time on the catalytic activity of $CoMnO_x$ catalysts supported on carbon. Both of these factors have been shown to effect catalytic activity and the product selectivity previously [17,18].

2. Experimental

2.1. Catalyst preparation

2.1.1. Co-precipitation

$CoMnO_x$ catalysts were prepared according to the procedure given in the patent literature [16,19]. An aqueous solution was prepared containing equimolar amounts of cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma–Aldrich, 99.999%) and manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, Sigma–Aldrich, ≥98%). This solution was heated to 80 °C and aqueous ammonia (28–30% NH_3 in water, Sigma–Aldrich) was added to raise the pH from 2.9 to 8.30 ± 0.01. The resulting precipitate was recovered by filtration, washed with distilled water (1 dm^3, 80 °C), dried (110 °C, 16 h) and calcined in static air (500 °C, 24 h).

2.1.2. Deposition precipitation

$CoMnO_x/C$ catalysts were prepared as according to the procedure given in the patent literature [16,19]. An aqueous solution was prepared containing equimolar amounts of cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma–Aldrich, 99.999%) and manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, Sigma Aldrich, ≥98%). Coconut shell-derived activated carbon (GCN3070, NORIT) was added to the mixed nitrate solution to give a final catalyst with a composition of 20% Co, 20% Mn and 60% activated carbon. The slurry was stirred for 10 min at 80 °C before aqueous ammonia (28–30% NH_3 in H_2O, Sigma–Aldrich) was added drop wise to the nitrate solution to raise the pH from 4 to 8.30 ± 0.01. The resulting precipitate was recovered by filtration, washed with distilled water (1 L, 80 °C), dried (110 °C, 16 h) and heated in flowing He.

To study the effect of heat treatment, one batch of catalyst was divided into four portions which were heated in flowing He separately at 300, 400, 500, and 600 °C for 5 h.

To study the effect of ageing the precipitate was left in the mother liquor for the specific time intervals of 1, 2, and 3 h followed by heat treatment in He at 500 °C for 5 h.

2.2. Catalytic activity

The catalysts were pelleted and sieved (0.65–0.85 mm) and 0.5 g were loaded into stainless steel fixed bed reactors (internal diameter 8 mm). Catalysts were reduced in situ at 400 °C for 16 h in pure hydrogen (GHSV = 600 h^{-1}) then cooled to room temperature and pressurized to 6 bar with syngas (CO:H_2 = 1:1 molar ratio). All catalysts were tested under identical reaction conditions, 240 °C, 6 bar, and GHSV = 600 h^{-1}.

A stabilization period of ~100 h was allowed before catalyst data was collected and the mass balance determined. Analysis of gas products was performed by on-line gas chromatography using a Varian GC-3800. Hydrocarbons were analyzed using a CP-Al_2O_3/KCl column and a flame ionization detector. Permanent gases and C_1–C_4 hydrocarbons were analyzed using molecular sieve 13× and Poropak Q columns with TCD and FID detectors in series. Nitrogen was used as an internal standard. The product stream was cooled in a wax trap (~25 °C) to retain the liquid products. Calibrations were performed with standard samples (C_1–C_5 hydrocarbon mixture diluted with nitrogen, BOC certified) for data quantification.

2.3. Catalyst characterization

2.3.1. X-ray photoelectron spectroscopy (XPS)

XPS was performed using a Kratos Axis Ultra-DLD photoelectron spectrometer, using monochromatic Al Kα radiation, at 144 W. High resolution and survey scans were performed at pass energies of 40 and 160 eV, respectively. Spectra were calibrated to the C (1s) signal at 284.5 eV, which is typical for graphitic carbon as measured for HOPG, and quantified using CasaXPS v2.3.15, utilizing sensitivity factors supplied by the manufacturer.

2.3.2. Powder X-ray diffraction (XRD)

XRD measurements were performed using a Bruker AXS Company, D8 Advance diffractometer. Scans were taken with a 2θ step size of 0.02° and a counting time of 1.0 s using Cu Kα radiation source generated at 40 kV and 30 mA. Specimens for XRD were prepared by compaction into a glass-backed aluminium sample holder. Data was collected over a 2θ range from 4° to 80° and phases identified by matching with the ICDD database.

3. Results and discussion

3.1. Comparison of catalyst performance of $CoMnO_x$ and $CoMnO_x/C$ catalysts

The unaged catalysts were tested for the FTS reaction under identical conditions and the data are presented in Table 1. A comparison of the $CoMnO_x$ and $CoMnO_x/C$ catalyst performance indicates the selectivity to carbon dioxide and methane was decreased markedly with the carbon-supported catalyst. CO conversion and the selectivity to C_{5+} hydrocarbons were higher compared with the pure $CoMnO_x$ catalyst. The effect of time-on-line is presented in Fig. 1 and this shows that the carbon-supported catalyst attained steady state after 45 h, whereas the unsupported $CoMnO_x$ catalyst achieved steady state only after 90 h. Neither catalyst showed deactivation over the time period studied.

3.2. Effect of preparation variables on the performance of $CoMnO_x/C$ catalysts

3.2.1. Pre-treatment temperature

Pretreatment of the catalyst precursor, particularly the heat treatment temperature is a critical parameter in catalyst preparation which can affect the activity and selectivity of the catalysts [17]. In order to study the effect of the pretreatment, one batch of $CoMnO_x/C$ was heated at different temperatures in He. Intervals of 100 °C were selected and although relatively large they are considered to be appropriate for this initial screening study. CO conversion and product selectivity data are presented in Table 2 and it is apparent that there was a steady increase in CO conversion with increasing heat treatment temperatures from 300 to 500 °C. An

Table 1
Comparison of the catalytic activity of $CoMnO_x$ with $CoMnO_x/C$ catalyst.

	$CoMnO_x$	$CoMnO_x/C$
CO conversion (%)	36.0	48
	Product selectivity (%)	
CH_4	22.1	7.0
C_2	4.5	4.3
C_3	11.5	16.1
C_4	1.2	7.6
C_{5+}	17.0	43.4
CO_2	37.0	20.4
Alcohols	6.7	2.2

Reaction conditions: Catalyst 0.5 g, data collected at 135 h, 240 °C, 6 bar, CO:H_2 1:1 mol ratio, GHSV 600 h^{-1}.