



Fischer Tropsch Synthesis using promoted cobalt-based catalysts



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ABSTRACT

A series of CoMnO_x catalysts with lanthanum and phosphorus promoters were prepared by wet impregnation and investigated for syngas conversion to hydrocarbons activity via Fischer Tropsch Synthesis. The effects of the promoters on the catalyst structure were examined by ICP, XRD, TPR and XPS measurements. The results of the catalytic tests showed that the addition of promoters altered the product selectivities when compared to the unpromoted catalyst.

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1. Introduction

Fischer Tropsch Synthesis (FTS) is an important process for the synthesis of hydrocarbons from syngas mixtures (CO + H₂). Recently interest in FTS has increased as a promising alternative process for the production of low-sulphur fuels from the conversion of syngas.

CoMnO_x catalysts have been extensively studied for the conversion of syngas to light hydrocarbons, due to their relatively low selectivity towards CO₂ and CH₄ [1–3]. Further to this, the addition of rare-earth metals into Co-based catalysts has been reported to be beneficial in FTS [4,5], and the promotional effect of lanthanum on supported metal oxides in particular has been widely studied. Barault et al. [5] reported an increase in specific activity for FTS by the addition of a La promoter to supported Co catalysts. A La/Co/Al₂O₃ catalyst system was studied by Vada et al. [4], and it was observed that low loading of La (La/Co = 0.05) increased the overall catalytic activity in the FTS reaction. The effect of La addition on the properties of precipitated metal oxides, such as Fe-based catalysts, has also been reported [6]. Haddad et al. [7] performed a characterization study of La-promoted Co/SiO₂ systems and showed that La(III) can regulate the strong Co-support interactions and the reducibility of Co oxide.

In addition to the promotional effect of rare earth metals, some studies have also shown a profound promotion effect from the addition of group 15 elements, particularly phosphorus on supported metal oxides for the FTS reaction [8–10]. Bae et al. [11] reported an increase in FTS activity and C₅₊ selectivity by modification of a Co/Al₂O₃ catalyst by the addition of an appropriate amount of phosphorus (1–2 wt%). Other studies have reported an increase in the reducibility of cobalt species, which was shown to have originated from the weak interaction between cobalt and the phosphorus-modified surface. This weak interaction arises from the partial transformation of the Al₂O₃ surface to aluminium phosphate [12]. An increase in catalytic activity and stability has been reported by promotion of a Ru/Co/SiO₂ catalyst with Zr and P. Addition of an appropriate amount of Zr and P into the oxide supported catalyst was postulated to have prevented the cobalt particle aggregation and enhanced the stability of the catalyst [13].

Although a significant amount of work regarding the effect of La and/or P promoter on Co based FTS catalysts has been reported, the main focus has been on Al₂O₃, SiO₂, TiO₂, and activated carbon supported catalysts. However, it appears that no study in the open literature has been devoted to the effect of these promoters on CoMnO_x catalysts. Therefore, it would be interesting to examine the impact of both La and P addition on a CoMnO_x catalyst. In the present study we have compared the effect of addition of La and P dopants on the catalytic activity of CoMnO_x catalysts. Furthermore the effect of sequential addition of both dopants to a CoMnO_x catalyst has also been studied.

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2. Experimental

2.1. Catalyst preparation

2.1.1. CoMnO_x

CoMnO_x catalysts were prepared according to the procedure used previously [8,9]. An aqueous solution was prepared containing equimolar amounts of cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, Sigma Aldrich, 99.999%) and manganese nitrate tetrahydrate (Mn(NO₃)₂·4H₂O, Sigma Aldrich, ≥98%). This solution was heated to 80 °C and aqueous ammonia (28–30% NH₃ 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 dm³, 80 °C), and dried (110 °C, 16 h).

2.1.2. CoMnO_x-La and CoMnO_x-P

The addition of La and P dopants was performed by the wet impregnation method. For the synthesis of CoMnO_x-La, the required amount of lanthanum nitrate (La(NO₃)₃·6H₂O, Sigma Aldrich, 99.999%) was dissolved in 2 cm³ of deionized water and stirred for approximately 15 min until a clear solution was obtained. The dried precursor form of CoMnO_x was added to the solution and stirred at room temperature to form a paste. The paste was subsequently dried (110 °C, 16 h). The resulting material was calcined in static air (500 °C, 24 h, with a ramp rate from ambient of 20 °C min⁻¹).

CoMnO_x-P catalysts were prepared by following the same method, except that ammonium phosphate (NH₄H₂PO₄, sigma Aldrich, 98%) was used as a phosphorus source instead of lanthanum nitrate.

2.1.3. CoMnO_x-La-P

In order to prepare the CoMnO_x-La-P catalysts, CoMnO_x-La was first prepared by wet impregnation as reported above, followed by a drying step (110 °C, 16 h). In the next step the P dopant was added by wet impregnation. The resulting slurry was dried (110 °C, 16 h) and calcined in static air (500 °C, 24 h, and 20 °C min⁻¹).

2.2. Catalytic activity

The catalysts were pelleted and sieved (0.65–0.85 mm), before samples (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) before being allowed to cool to room temperature. The reactor was subsequently pressurized to 6 barg with syngas (CO:H₂ = 1:1 molar ratio). All catalysts were tested under the same reaction conditions, (240 °C, 6 barg, 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 3800 GC. Hydrocarbons were analysed using a CP-Al₂O₃/KCl column and a flame ionisation detector. Permanent gases and C₁–C₄ hydrocarbons were analysed using molecular sieve 13X and Poropak Q columns with TCD and FID detectors in series. The product stream was cooled in a wax trap (~25 °C) to retain the liquid products. Calibrations were performed with standard samples (C₁–C₅ hydrocarbon mixture diluted with nitrogen, BOC certified) for data quantification. Nitrogen was used as an internal standard to correct for contraction of the gas volume following reaction.

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 operating

Table 1

ICP elemental analysis of La and P content in the catalysts.

Catalysts	La content (wt%)		P content (wt%)	
	Theoretical	Measured	Theoretical	Measured
La _{0.05}	0.05	0.03	0	0.00
La _{0.1}	0.10	0.08	0	0.00
La _{0.5}	0.50	0.20	0	0.00
La ₁	1.0	1.10	0	0.00
P _{0.03}	0	0.00	0.03	0.01
P _{0.05}	0	0.00	0.05	0.06
P _{0.1}	0	0.00	0.10	0.08
La _{0.1} -P _{0.03}	0.1	0.07	0.03	0.01
La _{0.1} -P _{0.05}	0.1	0.13	0.05	0.02

at 144 W (12 mA × 12 kV). 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 284.8 eV, and quantified using CasaXPS v2.3.17, utilizing sensitivity factors supplied by the manufacturer.

2.3.2. Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) was performed on a X'Pert Pro diffractometer with a monochromatic Cu-Kα source (λ = 0.154 nm) operated at 40 kV and 40 mA. Data were collected over a 2θ range from 10° to 80°, and phases identified by matching with the ICDD database.

2.3.3. Temperature programmed reduction (TPR)

Temperature programmed reduction/oxidation was carried out using a TPDRO 1100 series analyser. Samples (25 mg) were pre-treated for 1 h at 130 °C (20 °C min⁻¹) in a flow of Argon (20 cm³ min⁻¹). Following this the gas flow was changed to 10% H₂/Ar and the temperature was ramped to 800 °C (10 °C min⁻¹) with a 5 min hold at the T_{max}. H₂/O₂ consumption was monitored using a TCD detector.

2.3.4. Inductively Coupled Plasma (ICP-AES)

Catalyst bulk elemental composition was determined by Inductively Coupled Plasma (ICP) (ICPE-9000, Shimadzu). 25 mg of the calcined catalyst was dissolved in 0.5 cm³ of *aqua regia* at room temperature overnight. The solutions obtained were diluted with distilled water up to 10 ml. The prepared solutions were subjected to ICP analysis. For calibration, standard solutions of 1000 ppm of La and 1000 ppm of P were mixed and diluted to 0.2, 0.5, 1.0, 2.5, and 5.0 ppm.

Analysis showed that the amounts of dopant were in general agreement with the theoretical amounts. The error in P content was consistently within ± 0.03 wt%, and the error in La content was within ± 0.02 wt%. One exception to this was La_{0.5}, which had an error of –0.3 wt%. The full data are shown in Table 1.

3. Results and discussion

3.1. CoMnO_x-P

The catalysts doped with various loadings of P were tested for FTS activity under identical conditions and the results are presented in Table 2. A comparison of the CoMnO_x and CoMnO_x-P catalyst performance indicates that all the P doped catalysts showed a lower CO conversion and CO₂ selectivity. The addition of phosphorus increased the selectivity to alkenes particularly propene and butene. It was apparent that increasing the phosphorus content decreased the selectivity to alkenes, and increased the CH₄ selectivity. All of these catalysts required around 90 h to stabilize and no deactivation was observed after the stabilization was achieved during the period of our investigation. The deactivation of the catalyst

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