Catalysis Communications 25 (2012) 12–17

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Fischer Tropsch synthesis: Deuterium isotopic study for the formation of oxygenates over CeO_2 supported Pt–Co catalysts

Muthu Kumaran Gnanamani, Gary Jacobs, Wilson D. Shafer, Mauro C. Ribeiro, Venkat Ramana Rao Pendyala, Wenping Ma, Burtron H. Davis *

Center for Applied Energy Research, University of Kentucky, 2540 Research Park Dr, Lexington, KY 40511-8410, USA

ARTICLE INFO

Article history:
Received 29 November 2011
Received in revised form 8 March 2012
Accepted 20 March 2012
Available online 28 March 2012

Keywords:
Fischer-Tropsch synthesis
Oxygenates
Cobalt catalyst
Ceria
Deuterium isotope effect

ABSTRACT

The effect of deuterium on Fischer-Tropsch (FT) synthesis was investigated over a Pt promoted Co/CeO_2 catalyst. CeO_2 supported Pt–Co catalyst is more selective towards methane and oxygenates. H_2–D_2–H_2 switching experiments suggest that the hydrogenation of CO is involved in the rate determining step (inverse isotope effect). The suppression of oxygenate formation with deuterium leads to the conclusion that common FT intermediates are responsible for the observed shift in the product spectrum. The deuterium isotopic study supports our previously proposed mechanism for the formation of alcohols in that the Co–CeO_2 interface is involved in the catalysis, such that termination of chain growth occurs at the metal–oxide junction and involves bridging OH groups on partially reduced ceria.

1. Introduction

Fischer-Tropsch synthesis (FTS) is a process that converts synthesis gas (H_2+CO) into a mixture of higher molecular weight hydrocarbons [1–3]. Iron and cobalt are the active elements used in industry for FTS. Iron-based catalysts display higher water-gas shift activities and are more suitable for use with coal– and biomass-derived synthesis gas feeds, which normally have low hydrogen content (i.e., $H_2/CO = 0.7$–1.3) [4,5]. Cobalt catalysts are most suitable for FT synthesis using synthesis gas produced via reforming of natural gas which has high hydrogen content (i.e., $H_2/CO \geq 1.7$). The catalytic activity and selectivity of cobalt catalysts have been shown to depend on several factors such as particle size [6], nature of the support [7], the presence of promoters [8] and pre-treatment conditions [6–10]. Modification of preparation parameters is known to strongly affect the microstructure of cobalt supported catalysts [10].

Direct synthesis of alcohols from syngas has been developed as one of the most promising routes for producing fuels and raw chemicals [11–13]. The driving forces for developing efficient catalysts for producing higher alcohols are their high value and versatile applications as compared to hydrocarbon products [14]. The formation of alcohols from syngas can be performed over a variety of different types of catalyst [15]. However, Cu/Co/ZnO/Al_2O_3 based catalytic systems receive much attention [15]. Earlier results suggest that both copper and cobalt are necessary to give a high selectivity to higher alcohols [16] and cobalt alone was thought to be a catalyst for FT synthesis to produce higher hydrocarbons, but not for the formation of significant fractions of oxygenates.

However, several recent works indicate that cobalt could be suitable for the formation of oxygenates [17–20]. Recently, Spadaro et al. [17] obtained a higher selectivity to oxygenates using CeO_2 supported Co catalysts at low CO conversions (~1.6); however, the authors did not provide an explanation regarding their mechanism of formation. Recently, a plausible pathway for the formation oxygenates using CeO_2 supported Pt–Co bimetallic catalysts was proposed [18].

Even though FT synthesis has been widely studied since 1923, there remains controversy in the literature about the mechanism of CO hydrogenation and the reaction pathway for the formation of hydrocarbons and oxygenates [21–23]. Hindermann et al. [21] supported a view that the range of intermediates (not a unified mechanism operative either for a single reactive intermediate) could exist and become active for the surface polymerization to give carbon–carbon bond formation. The authors further stressed that sensible electronic pairings of suitable nucleophilic and electrophilic surface intermediates could provide many individual pathways for chain propagation to form hydrocarbons and oxygenates. Earlier, Fischer [24,25] proposed a pathway known as the "carbide" mechanism in which CO dissociates on the catalyst surface and the carbon is hydrogenated to CH_2 units. These CH_2 units undergo further polymerization to form longer hydrocarbon chains. However, this mechanism does not support the formation of oxygenates such as linear alcohols. Schulz and co-workers [26] proposed a mechanism known as the "CO insertion" mechanism and Anderson et al. [27] offered

---

* Corresponding author. Tel.: +1 859 257 0253; fax: +1 859 257 0302.
E-mail address: davis@caer.uky.edu (B.H. Davis).

1566-7367/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2012.03.028

Table 1
Effect of deuterium on CO conversions and rate of products formation.

Catalyst 0.5% Pt–5% Co/CeO_2	H_2–CO	D_2–CO	H_2–CO	H/D
TOS (h)	68.7	172.0	259.7	
CO conversions (%)	18.5	23.0	17.6	0.82
CH_4 rate (mol/h g. cat) $\times 10^{-3}$	5.75	9.97	7.79	0.79
CO_2 rate (mol/h g. cat) $\times 10^{-3}$	3.15	2.24	3.98	1.41
HC rate(C_2–C_{15}) (mol/h g. cat) $\times 10^{-3}$	0.37	0.56	0.47	0.66
Oxygenates rate (C_1–C_{10}) (mol/h g. cat) $\times 10^{-5}$	8.36	6.97	7.86	1.20

Reaction conditions: 503 K, 1.98 MPa; SV = 0.375 (syngas) slh^{-1} g^{-1} cat; H_2 (D_2)/CO = 2.0.

Table 2
Effect of H_2–D_2 switch on FT products obtained over 0.5%Pt–5%Co/CeO_2 catalyst.

Feed mixture (TOS, h)	Product distribution (C-%)				
	CH_4	C_2–C_4	C_5^+	CO_2	Alcohols
H_2–CO (68.7)	23.7	20.3	23.3	13.0	19.6
D_2–CO (172.0)	37.9	20.5	21.0	9.8	10.8
H_2–CO (259.7)	28.8	22.6	13.3	17.6	17.7

Reaction condition: 503 K, 1.98 MPa; SV = 0.375 (syngas) slh^{-1} g^{-1} cat; H_2 (D_2)/CO = 2.0.

Table 3
Effect of deuterium on product distributions (Paraffin, olefins, and oxygenates).

TOS (h)	Sample ID	Product distribution in organic layer (oil + wax, mol%)		
		Paraffin	Olefins	Oxygenates
45.2	2 (H_2–CO)	40.6	12.4	47.0
68.7	4 (H_2–CO)	34.8	10.8	54.4
141.2	8 (D_2–CO)	64.2	22.6	13.2
172.0	9 (D_2–CO)	61.8	18.9	19.3
259.7	11 (H_2–CO)	40.9	12.3	46.8
288.8	12 (H_2–CO)	40.0	10.8	49.2

Reaction conditions: 503 K, 1.98 MPa; SV = 0.375 (syngas) slh^{-1} g^{-1} cat; H_2 (D_2)/CO = 2.0.

a “hydroxyl-carbene” mechanism; both these mechanisms explain the formation of oxygenates through an oxygen containing intermediate. Dry [28] argued that there may be two kinds of intermediates which are generated by the addition of CH_2 and CO at the carbon–metal bond and desorption or subsequent hydrogenation of these two species accounts for the formation of alkenes, alkanes, aldehydes and alcohols as the primary products of the FT reaction.

With the aim of providing further insights into the mechanism of oxygenate formation, this paper describes the effect of deuterium on the product distribution obtained for the hydrogenation of carbon monoxide over CeO_2 supported Pt–Co FT catalysts. The observed inverse isotope effect for hydrogenation of CO ($r_{CO}^{(H)}/r_{CO}^{(D)} = 0.82$) reveals that hydrogen addition to CO is likely involved in a kinetically relevant step. The deuterium isotopic study supports the previously proposed mechanism [18] for the formation of oxygenates over Pt promoted Co–CeO_2 catalysts where the surface hydroxyl groups (−OH) on ceria at the Co–CeO_2 interface likely will play an important role in determining the selectivity of cobalt FT synthesis.

2. Experimental

The CeO_2 support (HSA-10, Rhodia) containing 5 wt.% Co was prepared by following the incipient wetness impregnation (IWI) method using an aqueous solution of cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$, Sigma Aldrich, 99.95%]. Pt (0.5 wt.%) was introduced to the above dried catalyst by following the same IWI technique using tetraammine platinum (II) nitrate. Details about the preparation are described elsewhere [29].

The H_2–D_2 switching experiment was performed using a 1 L CSTR. In a typical experiment, 20 g of calcined catalyst (80–140 mesh) was reduced *ex situ* using H_2:He (1:3) mixture at 623 K for 10 h. The reduced catalyst was transferred to the 1 L CSTR which contained 310 g of melted Polywax-3000 under flowing nitrogen. The catalyst was reduced *in situ* using pure H_2 (20 slph) for 24 h at 503 K. Three Brooks mass flow controllers were used to control the flow rates of CO, H_2, and D_2. The hydrogenation of CO was conducted at 503 K, 1.99 MPa and a constant space velocity of 0.375 SL/h/g cat. at a H_2:CO ratio of 2.0. The deuterium switch was made after reaching a pseudo-steady-state CO conversion. The exit gas stream was passed

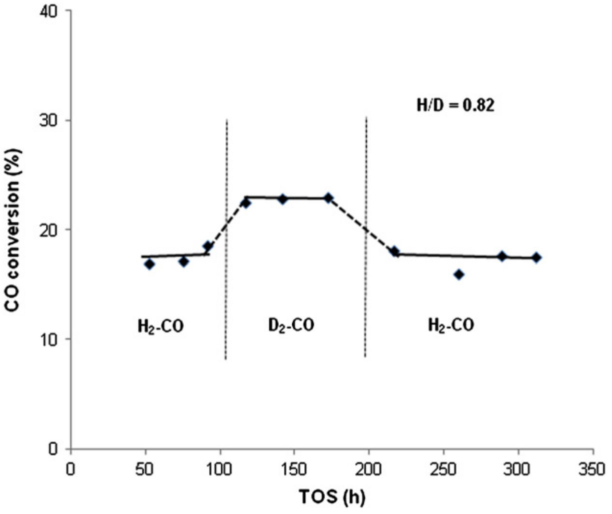

Fig. 1. Effect of deuterium on CO conversions with TOS over 0.5% Pt–5% Co/CeO_2 catalyst.

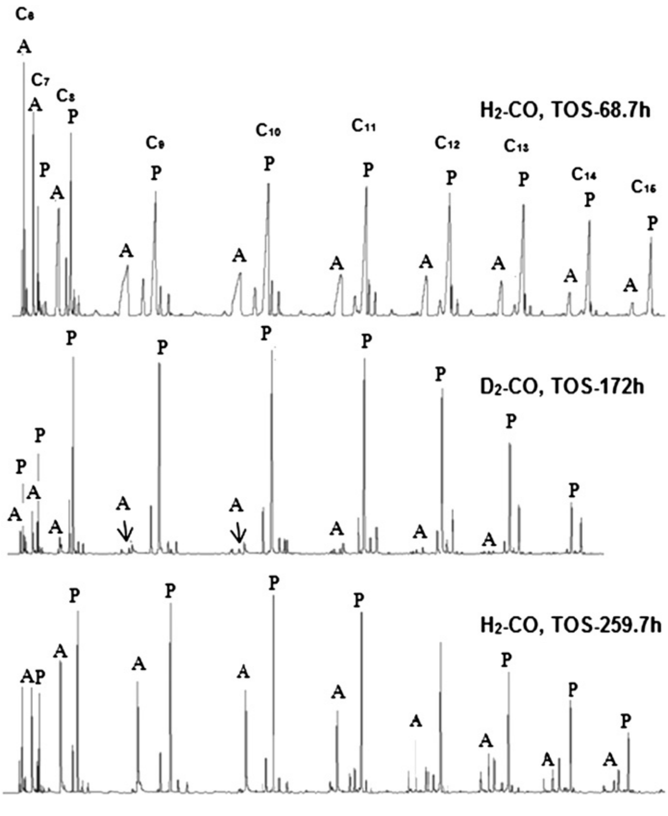

Fig. 2. A typical GC-FID chromatogram for the H_2–D_2–H_2 switch experiment for CO hydrogenation over 0.5% Pt–5% Co/CeO_2 catalyst (A-alcohols; P-paraffins).