

# Fe-based Fischer–Tropsch synthesis catalysts containing carbide-forming transition metal promoters

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## Abstract

Surprisingly, although the impacts of promoters such as K and Cu on the activity of Fe catalysts have been studied extensively, the effects of many other potential promoters for Fe catalysts similar to the commercial Ruhrchemie catalyst have not been significantly investigated or compared directly in a comprehensive study reported in the literature. In this study, the impact of adding various different transition metals (Cr, Mn, Mo, Ta, V, W, and Zr) on the catalytic properties of precipitated bulk Fe-based catalysts was investigated using the same preparation method and reaction conditions. All of the Fe catalysts prepared in this study exhibited high BET surface areas with excellent metal distributions. The addition of the third metal in addition of Fe and Cu (all except W) increased the activity of the Fe catalyst for CO hydrogenation and for the water–gas shift (WGS) reaction, with Cr-, Mn- and Zr-promoted Fe-based catalysts exhibiting the highest catalytic activities. However, hydrocarbon selectivity was not affected by the presence or type of added third metal. The enhanced activity of the Fe catalyst by third metal promotion (with the exception of Mn and Zr) appears to have been primarily due to a higher degree of Fe dispersion on the surface of catalyst whereas the higher activities observed for Mn- and Zr-promoted Fe catalysts were especially due to higher  $\text{TOF}_{\text{chem}}$  values based on CO chemisorption.

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**Keywords:** Fischer–Tropsch synthesis (FTS); CO hydrogenation; Cr promotion; Mn promotion; Mo promotion; Ta promotion; V promotion; W promotion; Zr promotion; Water–gas shift (WGS); Fe-based FTS catalysts

## 1. Introduction

Gasification followed by Fischer–Tropsch synthesis (FTS) is an established technological route for upgrading natural gas, coal, and biomass to liquid fuels and other chemical products. Fe and Co catalysts are currently used in industrial practice. Although Fe catalysts are not as active as Co-based catalysts, they show high water–gas shift (WGS) activity, which makes Fe catalysts more suitable for the conversion of low  $\text{H}_2/\text{CO}$  ratio syngas derived from coal or biomass [1–3]. Commercial-grade Fe catalysts for FTS typically consist initially of bulk Fe oxide promoted with Cu (a reduction promoter), K (a chemical promoter), and  $\text{SiO}_2$  (a structural promoter). Adding Cu to Fe catalysts facilitates reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  or metallic Fe [1,2,4–6]. The addition of  $\text{SiO}_2$  is used to increase the surface area of the catalyst and to improve its attrition resis-

tance, which is needed for FTS in a slurry phase reactor [5,7]. Longer-chain hydrocarbon products and better olefin selectivities are promoted by the addition of K [2,3].

Numerous studies have shown that the addition of transition metals can result in an enhancement of the activity of Fe-based FTS catalysts. For instance, Mn-promoted Fe catalysts (FeMn where Mn <15%) demonstrated higher light olefin ( $\text{C}_2\text{--C}_4$ ) formation compared to unpromoted Fe catalysts [8–11]. Mo-promoted Fe supported on activated carbon also showed significant catalytic stability [12]. Increased catalytic activity has been observed for FeOOH supported on  $\text{ZrO}_2$  [13]. Adding Cr enhanced the selectivity of precipitated Fe catalysts for longer-chain hydrocarbon products [14].

Several research groups have suggested, based on evidence, that Fe carbides, not metallic Fe, play a critical role in the activity of Fe-based catalysts for FTS [15–19]. If this is so, then the active sites of Fe-based FTS catalysts likely should exist in a carburized state on the surface. Therefore, it seems that the ability of the Fe catalyst to maintain a carburized surface may

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be the key to increasing and maintaining its long-term activity. The addition of another transition metal to bulk Fe catalysts could result in improved catalyst activity if it helped maintain or gave rise to the formation of more active carbide species.

Surprisingly, to date there appears to have been little or no study of the impact of a wide variety of different transition metals, such as Cr, Mn, Mo, Ta, V, W, and Zr, on the catalytic properties of bulk Fe-based catalysts having similar preparation methods and reaction conditions. Although the impact of added Mo [12] or Mn [8,10,11,20,21] on the activity of Fe catalysts has been studied, to the best of our knowledge, no study has been done on an Fe-based catalyst containing Cu and SiO<sub>2</sub> similar to a commercial Ruhrchemie catalyst, a standard in the FTS area. The study of the effect of added Zr on Fe FTS catalysts also has been studied only modestly [22]. Most of these studies focused on catalyst systems in which Zr was used as a support (ZrO<sub>2</sub>) [23,24]. In addition, fundamental studies of the impact of the addition of Cr, Ta, V, or W on the activity of Fe-based FTS catalysts have not been reported to date, although some patents have claimed the use of Cr and V as promoters for Fischer–Tropsch synthesis catalysts [14,25].

In this work, transition metals such as Cr, Mn, Mo, Ta, V, W and Zr, which are all known to form metal carbides [2], were added to a series of Fe-based catalysts with the general formulations of 100Fe/5Cu/17Si and 95Fe/5*Me*/5Cu/17Si, where *Me* was the third metal present in addition of Fe and Cu (i.e., Cr, Mo, Mn, Ta, V, W or Zr). Metals able to form carbides were hypothesized to have the potential for interesting interactions with Fe since Fe carbide formation occurs during FTS. The formation of mixed metal carbides could even be possible. To distinguish more clearly the effects of *Me*, K promotion was not used for any of the catalysts here. The catalysts were investigated using CO hydrogenation and various characterization techniques. Catalytic activities and selectivities for hydrocarbon products were compared to those for the benchmark catalyst, 100Fe/5Cu/17Si, without third metal promotion.

## 2. Experimental

### 2.1. Catalyst preparation

Catalysts for FTS were prepared according to the general formulations of 100Fe/5Cu/17Si (benchmark catalyst) and 95Fe/5*Me*/5Cu/17Si (third metal-promoted Fe catalysts) where *Me* indicates the third transition metal (Cr, Mn, Mo, Ta, V, W or Zr). Compositions are all given on a relative atom basis.

The catalysts (100Fe/5Cu/17Si and 95Fe/5*Me*/5Cu/17Si) were prepared using a pH precipitation technique [26]. For the 100Fe/5Cu/17Si catalyst, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (~0.6 M) and CuN<sub>2</sub>O<sub>6</sub>·3H<sub>2</sub>O were first dissolved together in 60 ml of H<sub>2</sub>O, whereas tetraethylorthosilicate (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, TEOS) was dissolved in 40 ml of propanol. The solutions were mixed together and 100 ml of final solution was obtained. The final solution was then heated to 83 ± 3 °C. Subsequently, aqueous NH<sub>4</sub>OH (~2.7 M) preheated to 83 ± 3 °C was continuously added into the solution containing Fe, Cu, and Si precursors under vigor-

ous stirring until precipitation. The resulting pH after formation of a precipitate was 8–9. The precipitate was aged in a vessel at room temperature for 17 h and then thoroughly washed with 1.3–1.5 l of deionized water to remove excess NH<sub>3</sub> until the pH of the washed H<sub>2</sub>O was 7–8. The washed precipitate was dried in an oven for 18–24 h at 110 °C to remove excess water. After drying, the catalyst precursor was calcined in static air at 300 °C for 5 h, then cooled to room temperature over a 2-h period in a muffle furnace. The fresh calcined catalyst was sieved <90 μm before reaction testing and other characterizations.

Similarly, 95Fe/5*Me*/5Cu/17Si catalysts were prepared using the same procedure as the 100Fe/5Cu/17Si catalyst except that Cr(NO<sub>3</sub>)<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>, MoO<sub>3</sub>, Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub>, V(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>, WCl<sub>6</sub>, or ZrO(NO<sub>3</sub>)<sub>2</sub> (as the precursor for Cr, Mn, Mo, Ta, V, W, or Zr, respectively) was dissolved in either the solution of Fe and Cu (in 60 ml of H<sub>2</sub>O) or the solution of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (in 40 ml of propanol), depending on its solubility properties. Then the two solutions were mixed to obtain the final solution of 100 ml which was then heated to 83 ± 3 °C. The following steps were then the same as those for the preparation of the 100Fe/5Cu/17Si catalyst. For the W-promoted Fe catalyst, the catalyst was washed 4 times with hot deionized water (90 °C) after calcination to remove any remaining Cl<sup>-</sup> impurity from the precursor [27]. Catalyst nomenclatures used are 100Fe, FeCr, FeMn, FeMo, FeTa, FeV, FeW, and FeZr for the benchmark and Cr-, Mn-, Mo-, Ta-, V-, W- and Zr-promoted Fe catalysts, respectively.

### 2.2. Catalyst characterization

#### 2.2.1. Physical adsorption

BET surface areas, pore volumes and average pore diameters were determined by N<sub>2</sub> physisorption at 77 K using a Micromeritics ASAP 2020 automated system. A 0.3 g catalyst sample was degassed at 100 °C for 1 h and then heated at 10 °C/min to 300 °C and held for 2 h before analysis.

#### 2.2.2. Catalyst composition

Elemental analysis was performed to determine the elemental composition of the fresh calcined catalysts and the carbon content of the catalysts after reaction using inductively coupled plasma optical emission spectrometry (ICP-OES) and the combustion method, respectively. These analyses were done by Galbraith Laboratories Inc. (Knoxville, TN). Elemental compositions of the prepared Fe catalysts as determined by ICP-OES were found to be the expected values within an error of ±10%.

#### 2.2.3. X-ray diffraction (XRD)

The XRD spectra of the catalysts were collected using a Scintag 2000 X-ray diffractometer with monochromatized CuK<sub>α</sub> radiation (40 kV, 40 mA) and a Ge detector with a step scan mode at a scan rate of 0.005° (2θ) per second from 10°–90°.

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