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Effect of K promotion of Fe and FeMn Fischer–Tropsch synthesis catalysts: Analysis at the site level using SSITKA

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ABSTRACT

Promoting a precipitated $FeCuSiO_2$ catalyst with Mn has been shown to significantly improve its catalytic activity for Fischer–Tropsch synthesis (FTS). Although the impact of K promotion on the activity of Fe catalysts with and without Mn addition has been studied previously, no one has previously delineated how K influences the concentration of active surface intermediates and the intrinsic site activities of Fe and, more specifically, Mn-promoted Fe catalysts. This paper addresses that issue using steady-state isotopic transient kinetic analysis (SSITKA). Adding K at relatively low concentrations to the base Fe and Mn-promoted Fe catalysts improved the catalyst activity, but the activity of the catalysts declined with the addition of an excess amount. The percentage of light olefins (C_2–C_4 fraction) and chain growth probability (α) were enhanced, as expected with the presence of K, regardless of Mn addition. The addition of K decreased the BET surface area and the concentration of surface exposed Fe^0 atoms (as determined by CO chemisorption). The intrinsic site activities (TOF_{ITK}) of all of the Fe catalysts determined using SSITKA were essentially identical, regardless of the concentration of added K or Mn promotion. This indicates that adding K to unpromoted or Mn-promoted Fe catalysts did not greatly affect the activity of the active sites. Rather, the higher catalyst activities observed for the Fe and Mn-promoted Fe catalysts with K addition were due primarily to an increase in the number of active surface intermediates leading to hydrocarbon products.

1. Introduction

Fischer–Tropsch synthesis (FTS) is a well-known reaction and has been used commercially for more than 70 years. The synthesis involves the hydrogenation of CO to high-value liquid hydrocarbon fuels and chemical products [1]. The use of biomass and coal as raw materials for FTS is of great interest due to CO_2 (a greenhouse gas) recycling and the existence of large coal reserves in the United States, respectively [2]. However, syngas derived from biomass or coal has a H_2/CO ratio significantly below 2 (the ratio needed for hydrocarbon synthesis); thus, a high water–gas shift (WGS) activity catalyst is required to provide additional H_2 for the reaction. Bulk Fe catalysts are particularly useful for syngas with low H_2/CO ratios due to their high WGS activity and low cost, although they are less active for FTS than Co-based catalysts [3].

A number of studies have indicated an improved activity and/or selectivity on the addition of transition metals to Fe-based FTS catalysts [4–7]. Our previous work showed that the addition of various transition metals besides Cu, such as Zr, Cr, Mo, Mn, Ta and V, greatly increased the catalyst activities for both CO hydrogenation and WGS activity in varying degrees [8]. The addition of moderate amounts of Mn has been found to promote the activity of Fe catalysts [8,9], the formation of low-molecular weight olefins [4,5,8,9], higher hydrocarbon formation [10], and catalyst stability [4]. In addition, promotion of an Fe catalyst with small amounts of Mn has been shown to improve the surface basicity and carburization of Fe [9,10].

The impact of K addition on the performance of Fe FTS catalysts has been studied extensively and is well established. K is known to promote the formation of olefins and longer-chain hydrocarbon molecules, the carburization of surface Fe, and the suppression of CH_4 formation [1,3,11–13]. K promotion strengthens the Fe–C bond by increasing the electron density on Fe while weakening Fe–H and C–O bonds [13–15]. The positive impact of K addition on the activity of Fe catalysts depends on the level of promotion [1,3,11–13]. Enhanced WGS activity of Fe catalysts on K promotion also has been observed [11,12]. A similar impact of K promotion has been reported for FeMn catalysts [10,11,16].

To date, no study has investigated the impact of K on the surface kinetic properties (at the site level) of Fe and Mn-promoted Fe catalysts for CO hydrogenation. In the present study, steady-state isotopic transient kinetic analysis (SSITKA) was carried out to determine the surface kinetic parameters at the site level of K-promoted $FeCuSiO_2$ bulk catalysts with and without Mn addition.

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In a previous study [8], an Fe catalyst promoted with Mn with a formulation of $80Fe/20Mn/5Cu/17SiO_2$ was reported to give rise to the highest catalyst activity among various Fe catalysts with added transition metals; thus, this formulation was used in the present study for the Mn-promoted Fe catalyst. The impact of varying K concentration on the activity of the Fe and Mn-promoted Fe catalysts also was investigated.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared using a pH precipitation technique [17], according to the general formulation $100Fe/5Cu/17Si/xK$ and $80Fe/20Mn/5Cu/17Si/xK$ (on a relative atomic basis, where $Fe + Mn = 100$), with $x \leqslant 9$. The details of catalyst preparation used in this study can be found elsewhere [8]. In brief, a solution containing $Fe(NO_3)_3{\cdot}9H_2O$, $CuN_2O_6{\cdot}3H_2O$, $Si(OC_2H_5)_4$ with and without $Mn(NO_3)_2$ for Mn-promoted Fe (FeMn) and unpromoted Fe (100Fe) catalysts, respectively, was precipitated with NH_4OH at 83 °C until the precipitate had a pH of 8–9. The precipitate was aged at room temperature for 17 h, then washed thoroughly with deionized water to eliminate excess NH_4OH. The washed precipitate was dried at 110 °C for 18–24 h and then sieved to <90 µm before being calcined in air at 300 °C for 5 h. In the case of K promotion, after sieving, the Fe catalysts were impregnated to incipient wetness with a $KHCO_3$ solution to give the desired K content. Subsequently, the catalysts were dried at 110 °C for 4 h before calcination at 300 °C.

Catalyst nomenclatures used are 100Fe, 100Fe*x*K, FeMn, and FeMn*x*K for the benchmark catalyst, the K-promoted Fe catalyst at *x* at% (relative to the amount of Fe), the Mn-promoted Fe catalyst with 20 at% (relative to the amount of Fe + Mn) of Mn, and the K-promoted FeMn catalysts with 20 at% of Mn and *x* at% (relative to the amount of Fe + Mn) of K, respectively. General catalyst nomenclatures for K-promoted Fe and K-promoted FeMn catalysts are 100FeK and FeMnK, respectively.

2.2. Catalyst characterization

2.2.1. BET surface area

The BET surface areas of catalysts were analyzed by N_2 physisorption using a Micromeritics ASAP 2020 automated system. A 0.3-g sample was degassed under a vacuum of 10^{-3} mm Hg at 100 °C for 1 h, after which the temperature was ramped to 300 °C (at 10 °C/min) and held for 2 h before N_2 physisorption at 77 K.

2.2.2. Catalyst composition

The metal composition of the freshly calcined catalysts and carbon content of spent catalysts were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) and a combustion method, respectively, by Galbraith Laboratories Inc. (Knoxville, TN). Carbon content of the spent Fe catalysts was determined after the catalyst was passivated with 40 cm^3/min of 2% O_2 in He at room temperature. During passivation, the temperature increased about 7 °C before decreasing back to room temperature, indicating completion of passivation.

2.2.3. X-Ray diffraction (XRD)

The crystallinity of prepared catalysts was studied using a Scintag 2000 X-ray diffractometer with monochromatized CuK_α radiation (40 kV, 40 mA) and a Ge detector. A step scan mode was used with a scan rate of 0.02° (2θ) per second from 10 to 90°.

2.2.4. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The catalyst morphologies were studied using SEM. The elemental distributions on the surface of catalyst particles were determined using EDX. SEM and EDX were performed using a Hitachi FESEM-S4800 in the scanning electron (SE) mode. The accelerating voltage was 20 kV, with a working distance of 15 mm.

2.2.5. Temperature-programmed reduction

The reducibility of Fe was determined by H_2 temperature-programmed reduction (TPR) using an Altamira AMI-1 system. A 0.1-g sample of the calcined catalyst was reduced in 5% H_2/Ar (30 cm^3/min) as the temperature was increased from 35 to 800 °C at a rate of 2 °C/min. A thermal conductivity detector (TCD) was used to measure H_2 consumption, and the detector output was calibrated based on 100% reducibility of Ag_2O powder. A H_2O trap was placed before the TCD.

2.2.6. CO chemisorption

CO chemisorption was performed using a Micromeritics ASAP 2010 automated system to determine the number of active surface metal atoms. Before CO chemisorption, 0.1 g of the calcined catalyst was first evacuated to 10^{-6} mm Hg at 100 °C for 30 min, and then reduced under flowing H_2 at 280 °C for 12 h (at a ramp rate of 2 °C/min). The catalyst was evacuated at 280 °C for 60 min to desorb any H_2. The analysis was carried out at 35 °C. An average $CO{:}Fe_s$ stoichiometry of 1:2 was assumed [18].

2.3. Kinetic measurements

Catalytic measurements were carried out in a quartz microreactor (8 mm i.d.). The reaction conversion was kept below 10% (differential reaction conditions) to minimize temperature and concentration gradients. A 10–50 mg catalyst sample was reduced *in situ* at 280 °C (after heating to that temperature at a rate of 2 °C/min) under 30 cm^3/min of H_2 (National Specialty Gases, Zero Grade) for 12 h. Then 30 cm^3/min of He (National Specialty Gases, UHP) was used to purge the catalyst for 15 min before the reaction at 280 °C and a constant pressure of 1.8 atm. The total flow rate of the reaction mixture was kept constant at 60 cm^3/min (STP) and contained 5 cm^3/min of 95% CO + 5% Ar (National Specialty Gases), 10 cm^3/min of H_2, and balance He to obtain a $H_2{:}CO$ ratio of 2:1. The reaction line and sampling valves were maintained at 200 °C with heating tapes to avoid condensation of higher hydrocarbon products. The effluent samples were analyzed using a Varian 3700 gas chromatograph equipped with a AT-Q 30 m × 0.53 mm Heliflex capillary column with a flame ionization detector (FID) for hydrocarbon detection and with a Carbosphere 80/100 $6' \times 1/8'' \times 0.085''$ SS packed column with a TCD for CO and CO_2 detection. All experiments were reproducible within a maximum error of ±5%.

2.4. Steady-state isotopic transient kinetic analysis

During SSITKA measurements, a switch between 95% ^{12}CO + 5% Ar (National Specialty Gases) and ^{13}CO (Isotec, 99%) was made by using a Valco 2-position valve with an electric actuator without disturbing any other reaction conditions (i.e., the total flow rate and reaction pressure of these 2 feed streams were kept identical during the switch). The gas-phase holdup for the reaction system was measured by the presence of a small amount of Ar in the unlabeled ^{12}CO stream. The reaction was carried out at the same conditions as stated above, but with a $H_2{:}CO$ ratio of 20:1 to obtain CH_4 as the primary product (i.e., the total flow rate of the reaction mixture was 1 cm^3/min of 95% CO + 5% Ar, 20 cm^3/min of H_2, and 39 cm^3/min of He). The effluent gas was analyzed online