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Impact of Cr, Mn and Zr addition on Fe Fischer–Tropsch synthesis catalysis: Investigation at the active site level using SSITKA

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ABSTRACT

Recently, we reported that Cr, Mn, or Zr promotion of a precipitated Cu-promoted Fe Fischer–Tropsch synthesis (FTS) catalyst significantly improves its catalytic activity. In this study, we used steady-state isotopic transient kinetic analysis (SSITKA) of methanation to investigate the activity of these catalysts at the site level, providing insight into how this promotion enhances catalyst activity. We found that the activity of the base Fe catalyst was enhanced by promotion with Cr, Mn, and Zr in varying degrees, depending on the type and concentration of metal added. The addition of these third metals promoted the dispersion of Fe but did not significantly affect either the BET surface area or reducibility. The activities of the reaction sites (estimated by $1/\tau_{CH_4} = TOF_{ITK}$) were found to be similar regardless of the type of third metal added, suggesting that the active sites for Fe catalysts with or without third-metal promotion were essentially identical. The higher catalyst activities observed for the Cr-, Mn-, and Zr-promoted Fe catalysts were found to be due primarily to an increased number of active surface intermediates leading to hydrocarbon products.

1. Introduction

Due to the limited supply and unpredictable price of crude oil, increasing attention has focused on other energy sources, including coal, natural gas, and biomass. The U.S. has 25% of the world's coal reserves, which is sufficient to supply most of the U.S. liquid transportation fuel needs for more than 100 years with the use of Fischer–Tropsch synthesis (FTS) [1]. FTS is an excellent method for upgrading low-value coal and biomass to high-value, environmentally friendly liquid fuels with no sulfur contamination [2,3]. A catalyst with high water–gas shift (WGS) activity is needed to use the low-H_2/CO ratio syngas derived from coal or biomass.

Fe-based catalysts have great potential to convert low-H_2 source syngas to fuels via FTS due to their high WGS activity and low cost compared with Co-based catalysts. Development of Fe catalysts with high FTS activity, low methane selectivity, and long-term stability is of great importance. It has been shown that the addition of some transition metals to Fe-based FTS catalysts improves these catalysts' activity and selectivity. Increases in chain growth probability and catalyst activity from the addition of Cr to a precipitated Fe catalyst have been reported [4]. Very stable activity and high selectivity to light olefin formation have been observed for Mn-promoted Fe catalysts [5–8]. A positive affect of other transition metals, such as Mo, Ta, V, and Zr, on the catalyst activity for both CO hydrogenation and WGS activity also has been reported [8].

Previous studies have explored how the addition of Cr [4], Mn [5,6,9], or Zr [10] affects the activity of Fe FTS catalysts. Recent work by us in a comparative study of third-metal promotion also has demonstrated that the addition of Cr, Mn, and Zr significantly enhances the activity of a typical precipitated Cu- and SiO_2-promoted Fe catalyst [8]. Little is known about how Cr, Mn, or Zr promotion affects the kinetic nature of the Fe catalyst active sites, however. Most investigations to date have used *ex situ* characterization techniques to evaluate catalysts' physicochemical properties under conditions far different than reaction conditions. Speculation on the nature of the active sites during reaction based on the findings of such studies has the potential for significant error. Steady-state isotopic transient kinetic analysis (SSITKA) can provide *in situ* surface kinetic information about a reaction on a catalyst under actual reaction conditions. In the present study, we used SSITKA to determine the concentration of active surface intermediates leading to products and the intrinsic site activities of the catalysts, with the aim of gaining insight into how Cr, Mn, and Zr influence the activity of Fe catalysts. We also explored the effect of varying Cr, Mn, and Zr concentrations on the catalyst activity for both CO hydrogenation and the WGS reaction.

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2. Experimental

2.1. Catalyst preparation

Catalysts were prepared using a pH precipitation technique [11] according to the general formulations of 100Fe/5Cu/17Si (base catalyst) and (100 − x)Fe/xMe/5Cu/17Si (on an atomic basis), where Me is Cr, Mn, or Zr and x is $\leqslant 20$. The details of the catalyst preparation method used in this study can be found elsewhere [8]. In brief, a mixed aqueous solution containing $Fe(NO_3)_3{\cdot}9H_2O$, $CuN_2O_6{\cdot}3H_2O$, and $Si(OC_2H_5)_4$ without a third metal species for 100Fe/5Cu/17Si and with a third metal species [$Cr(NO_3)_3$, $Mn(NO_3)_2$, or $ZrO(NO_3)_2$] for (100 − x)Fe/xMe/5Cu/17Si was precipitated with NH_4OH at 83 °C to achieve a pH of 8–9. The precipitate was aged at room temperature for 17 h (overnight) to allow it to cool completely, and then thoroughly washed with deionized water. The washed precipitate was dried at 110 °C for 18–24 h and calcined in air at 300 °C for 5 h. The catalysts were sieved to <90 µm. The catalyst nomenclatures used are 100Fe, 97Fe3Cr, 95Fe5Cr, 93Fe7Cr, 90Fe10Cr, 95Fe5Mn, 93Fe7Mn, 90Fe10Mn, 80Fe20Mn, 97Fe3Zr, 95Fe5Zr, 90Fe10Zr, and 86Fe14Zr for the benchmark and Cr-promoted Fe catalysts at 3, 5, 7, and 10 at% of Cr, Mn-promoted Fe catalysts at 5, 7, 10, and 20 at% of Mn, and Zr-promoted Fe catalysts at 3, 5, 10, and 14 at% of Zr, respectively. Metal at% is based on 100Fe for the benchmark catalyst. Total (Fe + the third metal) at% is 100. General catalyst nomenclatures for Cr-, Mn-, Zr-, and third metal-promoted Fe catalysts are FeCr, FeMn, FeZr, and FeMe, respectively.

2.2. Catalyst characterization

2.2.1. BET surface area

N_2 physisorption at 77 K was used to determine the BET surface areas 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 raised to 300 °C (at a rate of 10 °C/min) and held there for 2 h before N_2 adsorption.

2.2.2. Catalyst composition

The carbon content of catalysts after reaction and the elemental composition of the fresh calcined catalysts were analyzed using a combustion method and inductively coupled plasma optical emission spectrometry (ICP-OES), respectively, by Galbraith Laboratories Inc. (Knoxville, TN). Passivation was performed for spent catalysts before they were removed from the reactor, to prevent rapid oxidation on exposure to air, by introducing a flow of 40 cc/min of 2% O_2 in He to the catalyst bed at ca. 35 °C. A ca. 5–7 °C increase in catalyst temperature was observed during passivation. Passivation was considered complete once the temperature of the catalyst bed dropped back to the original temperature.

2.2.3. X-ray diffraction

Powder XRD was conducted to determine the crystallinity of fresh calcined catalysts 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 at a scan rate of 0.02° (2θ) per second from 10–80°.

2.2.4. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

The morphologies of the catalyst samples and the elemental distributions and concentrations of the exterior catalyst particle surfaces were studied by SEM and EDX, respectively, using a Hitachi FESEM-S4800 under the scanning electron (SE) mode. The accelerating voltage was 20 kV with a working distance of 14 mm.

2.2.5. Temperature-programmed reduction

H_2 TPR (ambient to 800 °C at 2 °C/min) was performed using an Altamira AMI-1 system to measure the reducibility of Fe. A 0.1-g sample of a freshly calcined catalyst was reduced in a flow of 30 cc/min of 5% H_2/Ar. A variation of TPR was also performed in which the temperature was increased to 280 °C (2 °C/min) and held there for 12 h, to mimic the reduction conditions before the reaction. Then the temperature was increased to 800 °C at 2 °C/min, and the additional H_2 consumed was measured. The H_2 consumption was determined by a thermal conductivity detector (TCD) calibrated based on 100% reducibility of Ag_2O powder using the same heating rate. A cold trap was placed before the TCD to trap H_2O produced during the TPR process.

2.2.6. CO chemisorption

The concentration of surface metal atoms was determined using CO chemisorption in a Micromeritics ASAP 2010 automated system. A 0.1-g sample of a freshly calcined catalyst was first evacuated to 10^{-6} mm Hg at 100 °C for 30 min and then reduced under flowing H_2 by ramping at 2 °C/min to 280 °C and holding there for 12 h. The catalyst was then evacuated at 280 °C for 60 min to desorb H_2. CO chemisorption was carried out at 35 °C. An average CO:Fe_s stoichiometry of 1:2 was assumed [12].

2.3. Reaction kinetic measurements

The reaction was carried out in a differential quartz microreactor (8 mm i.d.). The reaction conversion was kept below 10% to minimize temperature and concentration gradients. A 35- to 100-mg catalyst sample was reduced *in situ* at 280 °C (after ramping at 2 °C/min) under 30 C/min of H_2 (National Specialty Gases, zero grade) for 12 h. Then 30 cc/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 cc/min (STP) containing 5 cc/min of 95% CO + 5% Ar (National Specialty Gases) and 10 cc/min of H_2 in He balance, to obtain a H_2:CO ratio of 2:1. The reaction effluent line and the sampling valves were maintained at 200 °C with heating tape, to avoid condensation of higher hydrocarbon products. The effluent samples were analyzed using a Varian 3700 gas chromatograph equipped with an AT-Q 30 m × 0.53 mm Heliflex capillary column with a flame ionization detector (FID) for hydrocarbon detection and a Carbosphere 80/100 $6' \times 1/8'' \times 0.085''$ SS packed column with a TCD for CO and CO_2 detection.

2.4. Steady-state isotopic transient kinetic analysis

SSITKA was performed by switching ^{12}CO (containing 5% Ar) and ^{13}CO (Isotec, 99%) without disturbing the other reaction conditions, using a Valco 2-position valve with an electric actuator. The total flow rate and reaction pressure of these two feed streams were identical during the switch. A small trace of Ar was present in the unlabelled ^{12}CO stream, to measure the gas-phase holdup for the reaction system. The reaction was carried out at the same conditions as described above but with a H_2:CO ratio of 20:1, to obtain CH_4 as the primary product. Thus, the reaction mixture comprised 1.5 cc/min of 95% CO + 5% Ar, 30 cc/min of H_2, and 28.5 cc/min of He. The effluent gas was analyzed online with a Varian 3700 gas chromatograph and a Balzers–Pfeiffer Prisma 200 amu quadrupole mass spectrometer (Pfeiffer Vacuum) via a 1/16-inch capillary tube with differential pumping. The gas inlet line to the mass spectrometer was designed to be as short as possible, to minimize gas-phase holdup in the system, and was heated to 150 °C to avoid the deposition of heavy hydrocarbon products. The mass spectrometer was equipped with a high-speed data-acquisition system interfaced