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Development of Core-Shell Catalysts for Fischer-Tropsch Synthesis in 3D Printed SS Microchannel Microreactors

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ABSTRACT

Chemical conversion of syngas, a mixture of carbon monoxide (CO) and hydrogen (H_2) from biomass gasification to long chain hydrocarbons and liquid fuels through Fischer-Tropsch synthesis (FTS) is an excellent route for fuels from renewable sources. Our research group has been focusing on the development of stable catalysts for FTS using CO_2 enriched syngas in stainless steel 3D printed microchannel microreactors.

In this work, synthesis of different core-shell catalysts for FTS is proposed. Core-shell nanostructures are nanoparticles encapsulated and protected by an outer shell that isolates the nanoparticles, prevents their migration and coalescence during the catalytic reactions. Iron, cobalt and ruthenium based catalysts are conventionally used in FTS. The suitable core-shell catalysts made up of Co, Fe and Ru will be synthesized and their efficiencies will be compared with the results obtained from theoretical calculations studies. The major focus of this work is to investigate the structural effects of core-shell morphology on the FTS performance. We have mainly focused on the engineering of shell structures to create mesoscale porosity in the shells, to allow the diffusion of reactant species to the surface of the core, typically the catalytically active phase, where they can adsorb and react.

We have prepared various catalysts with core-shell structure, namely Fe_3O_4@ZSM-5, $Fe_3O_4@SiO_2$, and $Fe_2O_3@SiO_2$.These catalysts were characterized by a series of techniques including N_2 physisorption, XRD, SEM, and H_2-TPR. The expected phase was confirmed and the core-shell structure was observed. The effect of outer shell type on the properties of the catalysts were also investigated. Herein, we prepared two types of iron-based core as the active component of the catalysts, hematite and magnetite, respectively, to study the effect of iron valence state and the particle size of the core particles on their performance in FTS. In comparison with the core-shell composite's mechanical mixture counterpart, the benefits of introducing the core-shell structure can be revealed.

INTRODUCTION

Fischer-Tropsch synthesis is a catalyzed chemical reaction in which synthesis gas (syngas), including H_2 and CO, is converted to gaseous, liquid and solid hydrocarbons. The feedstock of the syngas is mainly from the gasification process of various solid carbonaceous resources like coal and biomass. Current catalysts used for FTS are cobalt, iron, and ruthenium loaded on various supports. Cobalt-based catalysts are highly active, but also sensitive to poisoning even when trace amount of sulfur-containing compound is present. The reaction conditions for ruthenium catalysts are mild due to its considerable high activity. But its high price and limited resource hinder its industrial application. Iron-based catalysts are attractive owing to its low price, abundant resources, tunable properties and controllable selectivity toward various hydrocarbons. Various technologies have been investigated to engineer the conventional iron-based catalyst for FTS to promote the activities and manipulate the product distribution, including modification of the support properties, employing favorable composites, introducing various promoters, and altering the activation methods, etc.

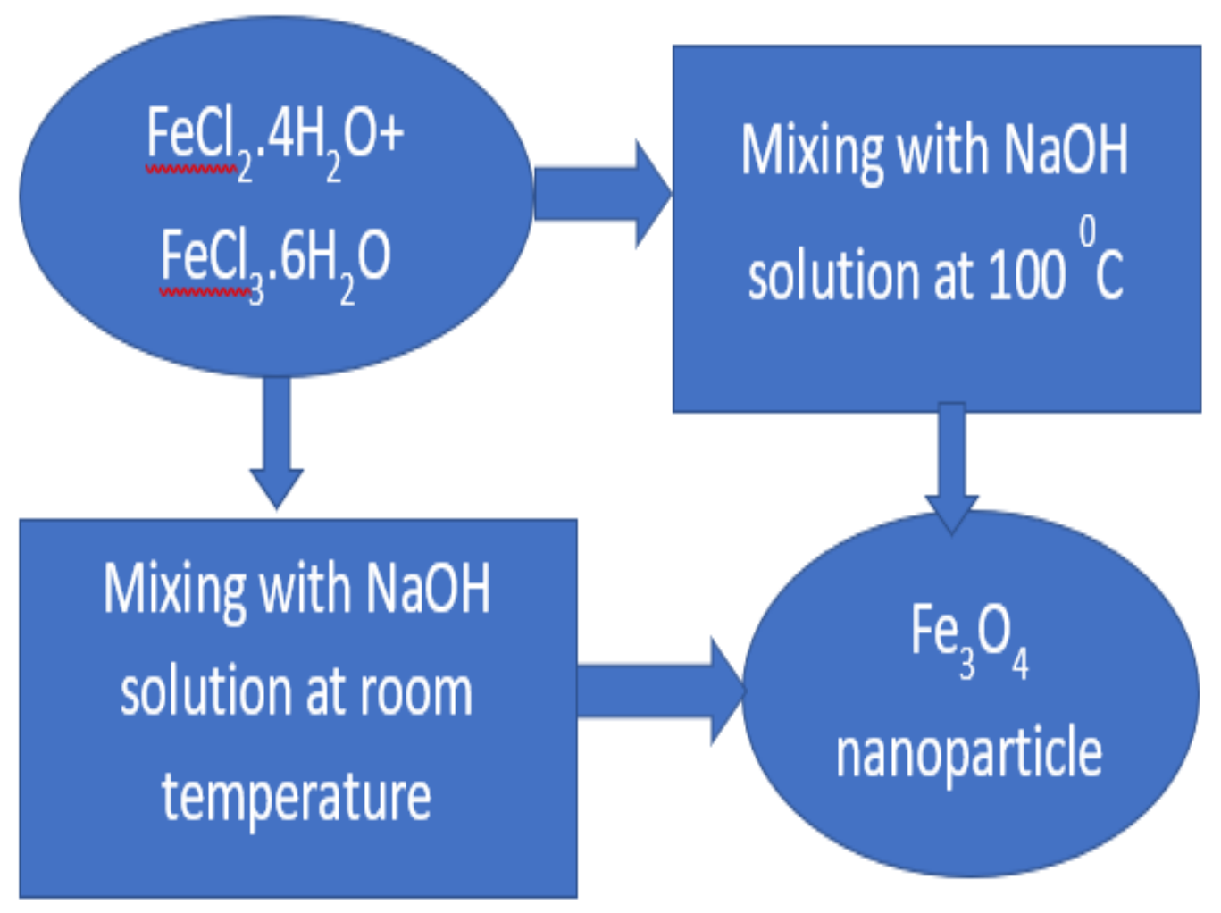
In this work, we synthesized iron-based catalysts with core-shell structure, altering physical and chemical properties of the catalyst in nano scale, and investigated the novel material's positive effect on the production of liquid hydrocarbons via FTS.

OBJECTIVE

- Design and synthesize core-shell nanostructure materials to be used as catalysts for FTS; more specifically, the novel materials include: Fe_3O_4@ZSM-5, $Fe_3O_4@SiO_2$, and $Fe_2O_3@SiO_2$.
- Characterize the core-shell materials using various techniques to confirm its composition, morphology and physical and chemical properties.
- Evaluate the novel material's feasibility as the catalyst for FTS and test their performances in 3-D printed SS microchannel reactors.

METHODOLOGY AND EXPERIMENTATION

Different Size of (125nm) Fe_3O_4 Core Nanoparticles Preparation



$FeCl_2.4H_2O$+ $FeCl_3.6H_2O$

Mixing with NaOH solution at 100 ^0C

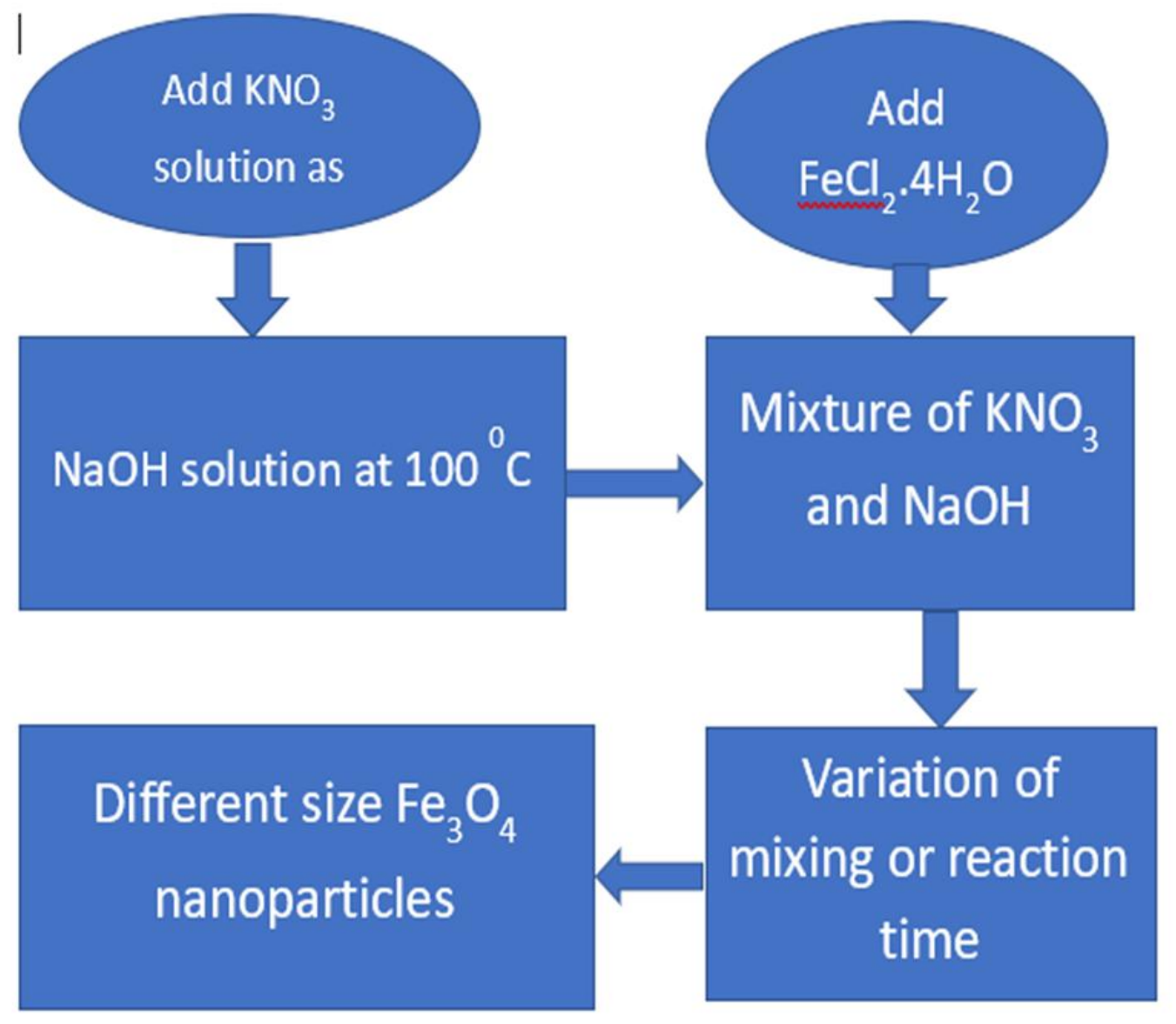
Mixing with NaOH solution at room temperature

Fe_3O_4 nanoparticle

ZSM-5 Shell Preparation

TEOS (Tetraethyl orthosilicate)
↓
TPAOH (Tetrapropylammonium hydroxide)
+
NaOH
+
DI Water
↓
The solution stirred in a polypropylene bottle for 10 h @ room temperature.
↓
Aluminum isopropoxide added slowly and the solution stirred 24 h @room temperature
↓
Teflon-lined stainless-steel autoclave @ 60h @ 100 C
↓
Centrifugation at 4700 rpm for 40 min
↓
Dried at 95 °C overnight & Calcined 6 h @550 C

Different Size of (3-4 µm) Fe_3O_4 Core Nanoparticles Preparation



Add KNO_3 solution as

Add $FeCl_2.4H_2O$

NaOH solution at 100 ^0C

Mixture of KNO_3 and NaOH

Variation of mixing or reaction time

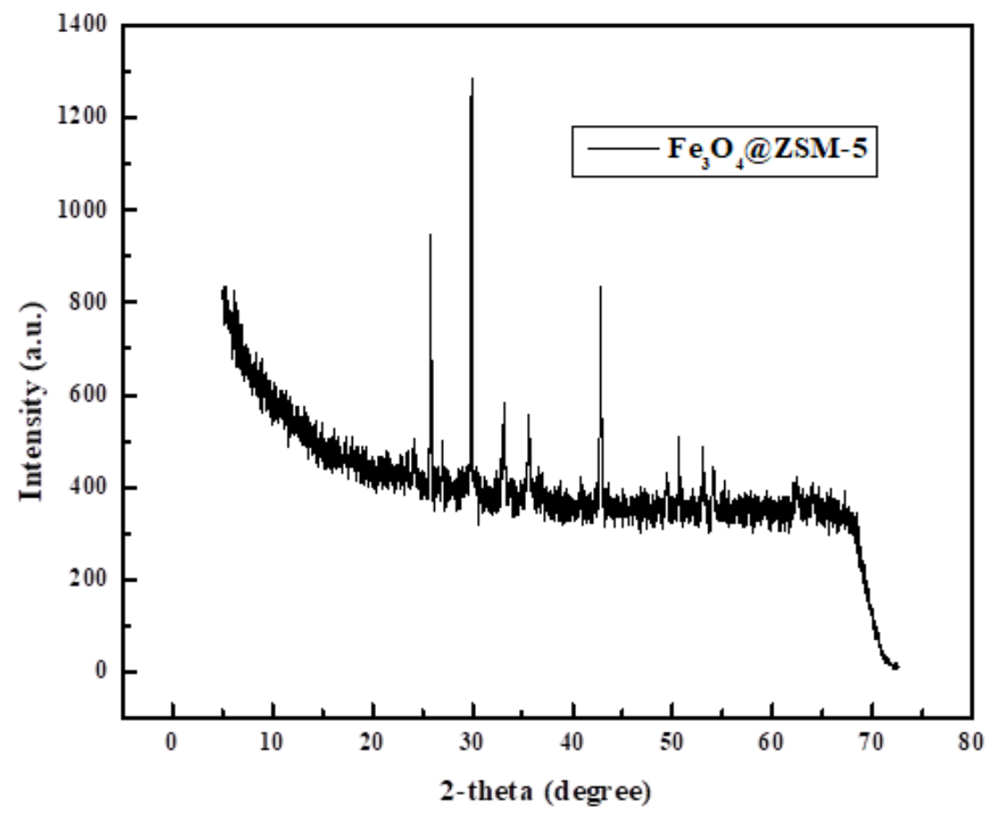
Different size Fe_3O_4 nanoparticles

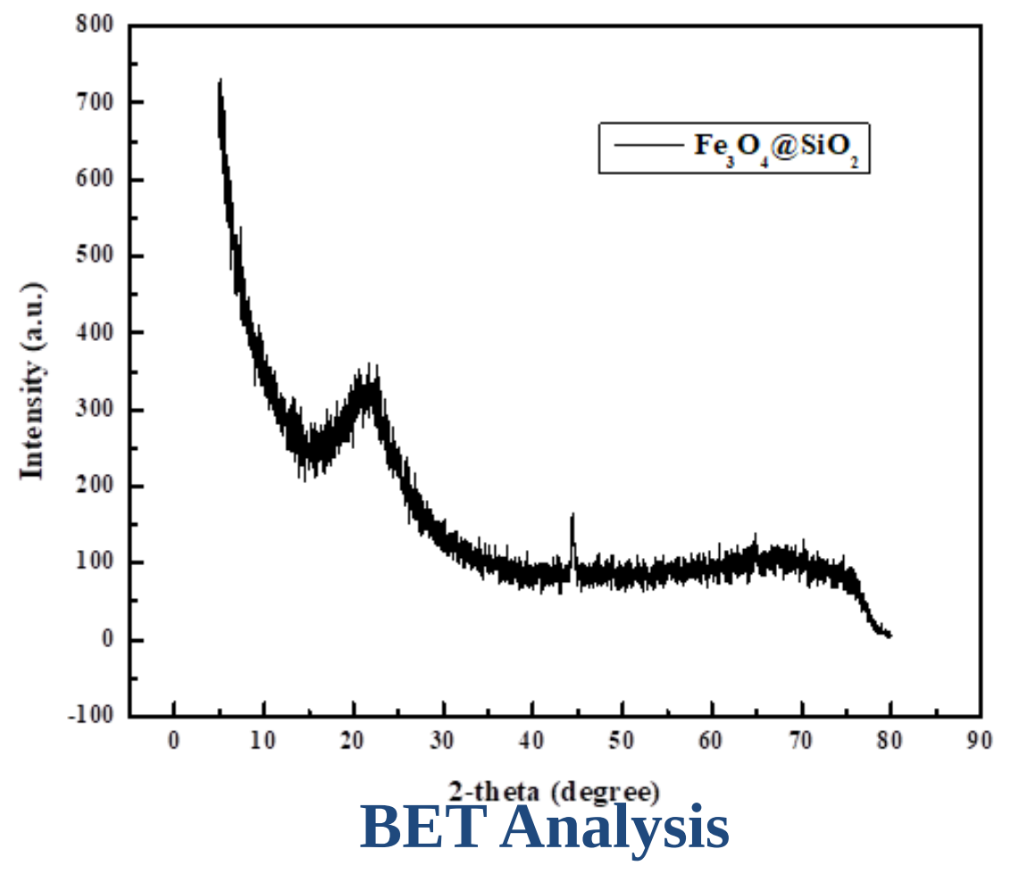
SiO_2 Shell Preparation

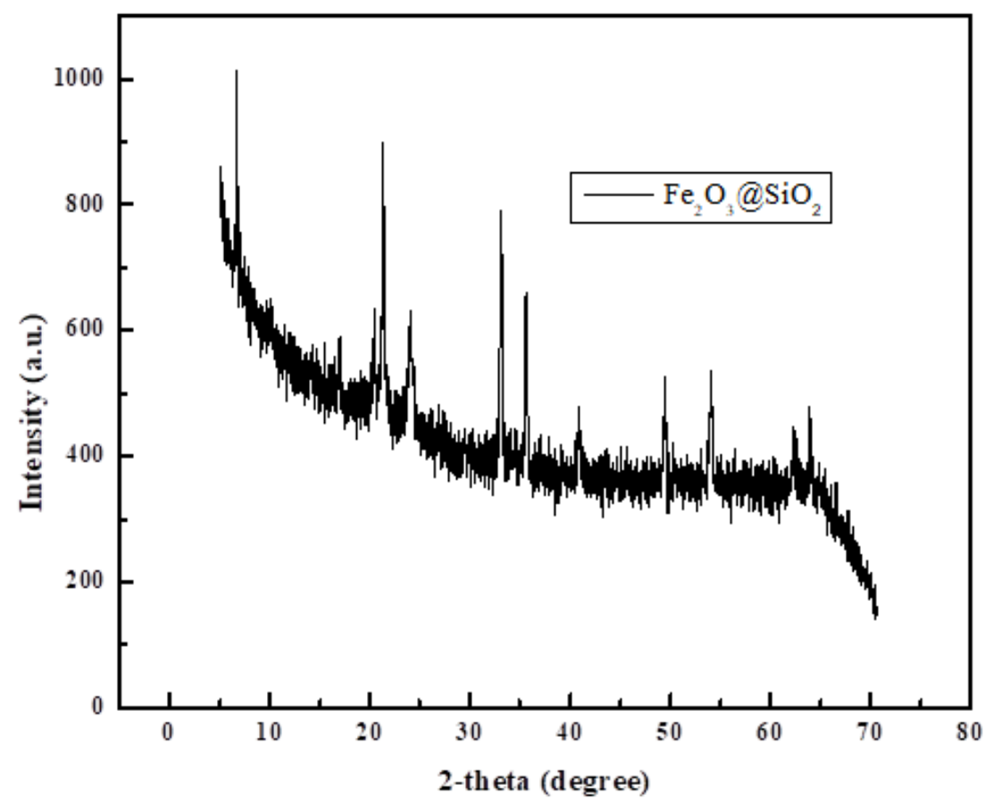
Fe_3O_4 mix with Oleic Acid
↓
Add Chloroform
+
Mix DI Water
↓
CTAB (Cetyl Trimethyl Ammonium Bromide) mix with DI Water and heat @ 65C
↓
Add NaOH (Sodium Hydroxide)
↓
Add TEOS (Tetraethyl Orthosilicate)
Add EtOAc (Ethyl Acetate) and heat @70⁰C
↓
After 2 Hours Fe_3O_4 & SiO_2 core-shell particles collected by centrifugation and washed with Ethanol

CATALYST CHARACTERIZATION

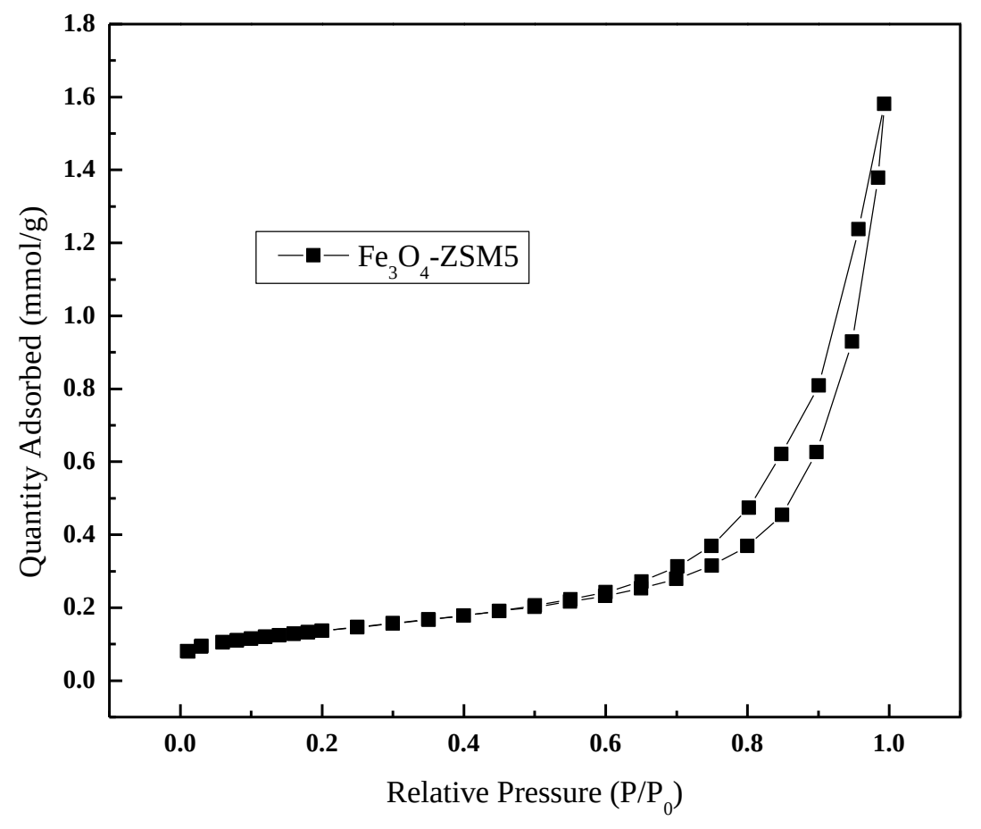
XRD Analysis

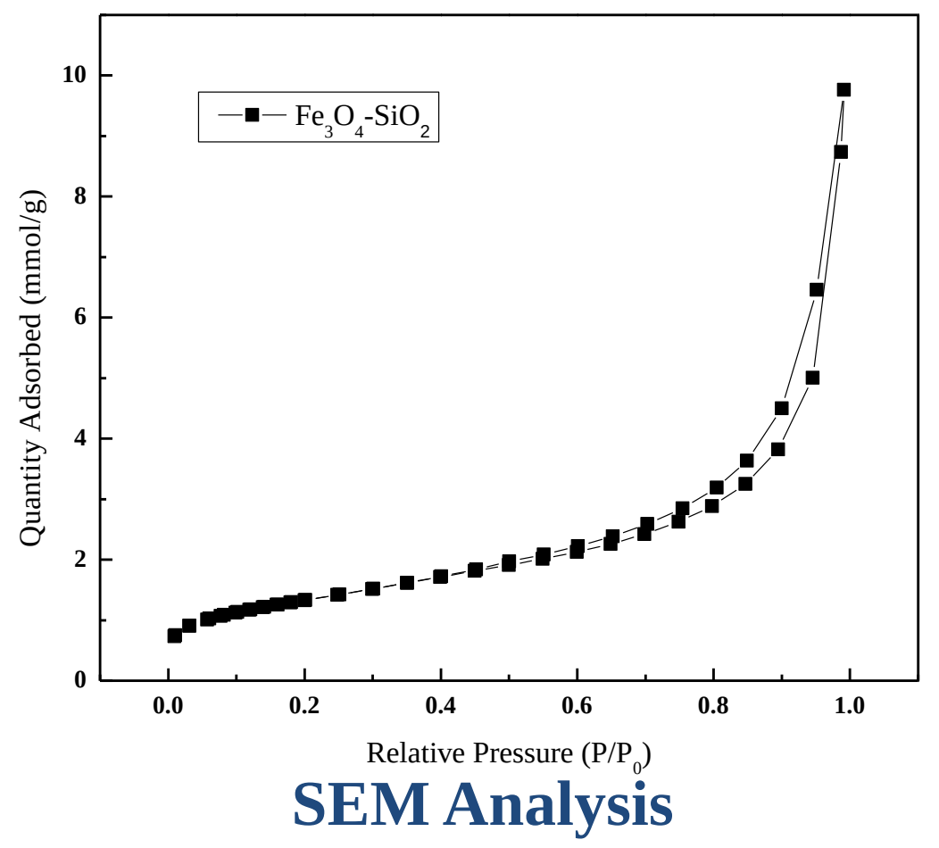


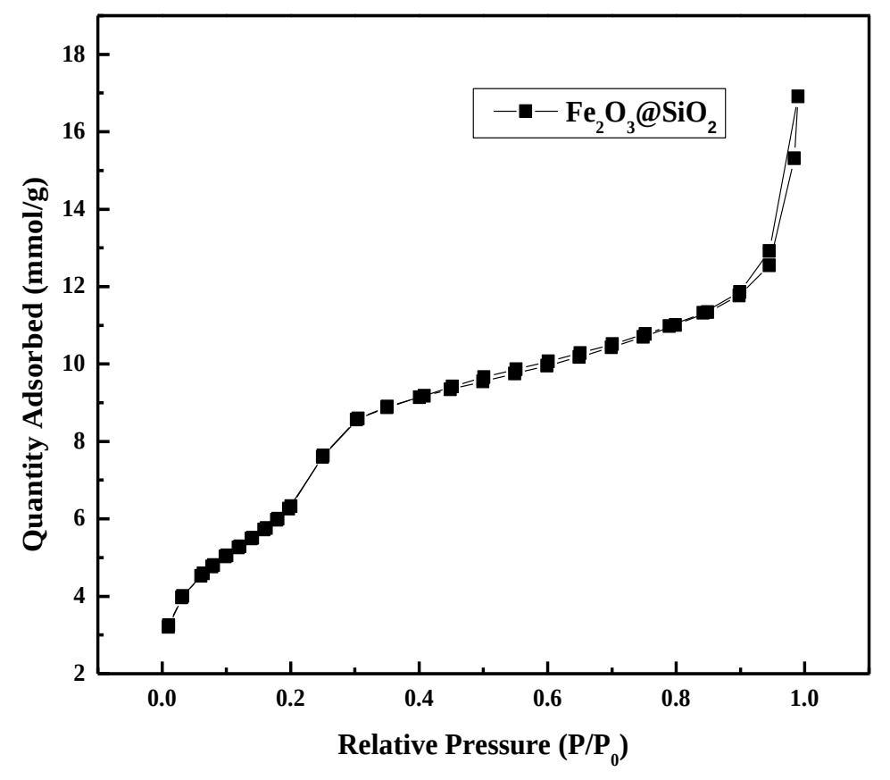




BET Analysis

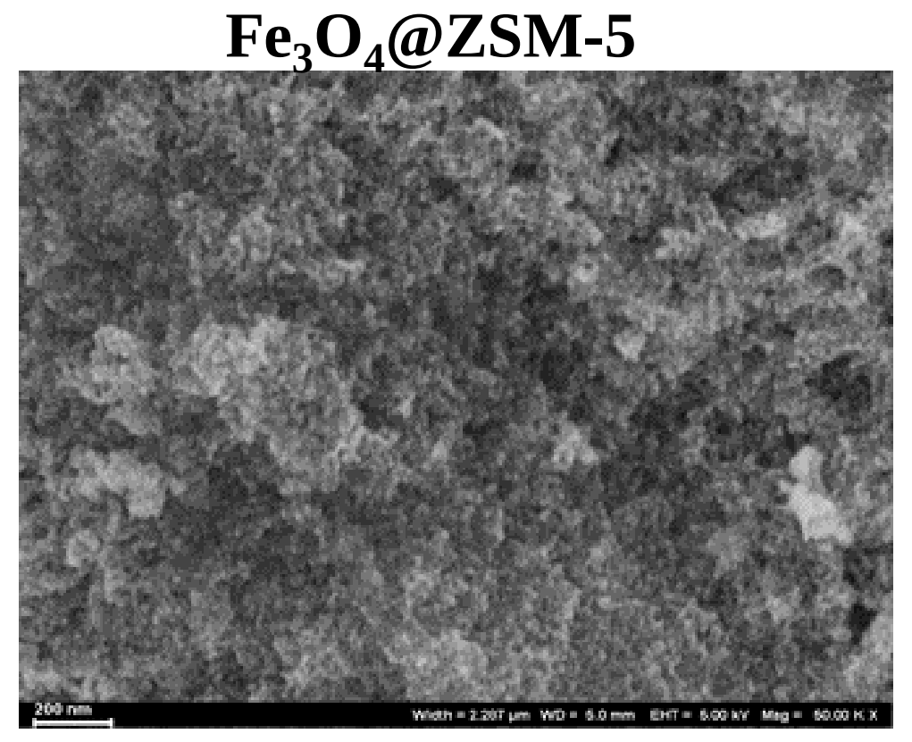




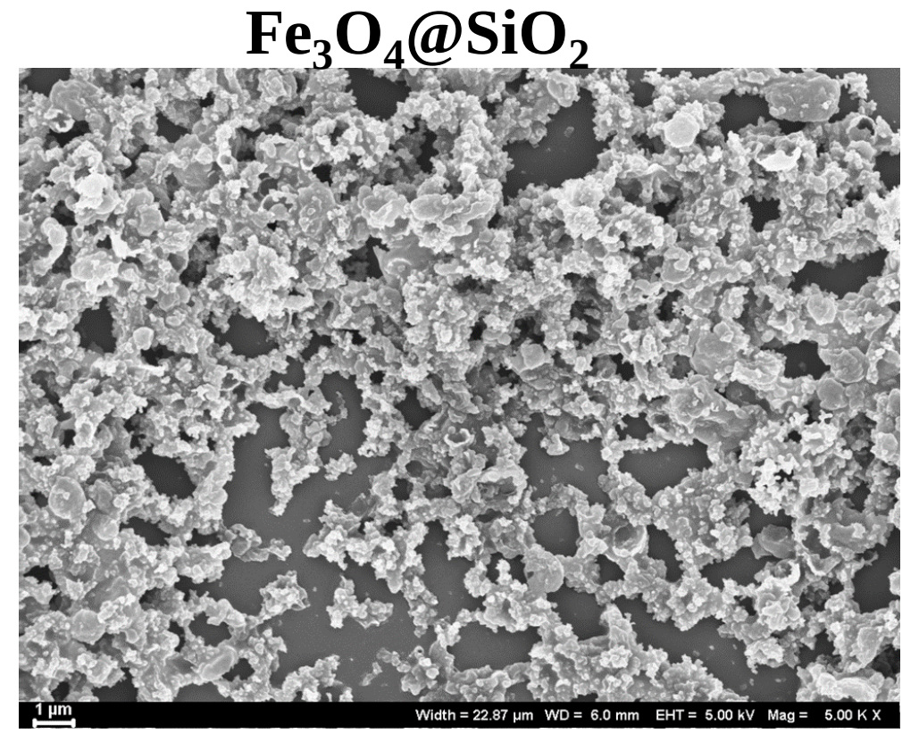


SEM Analysis

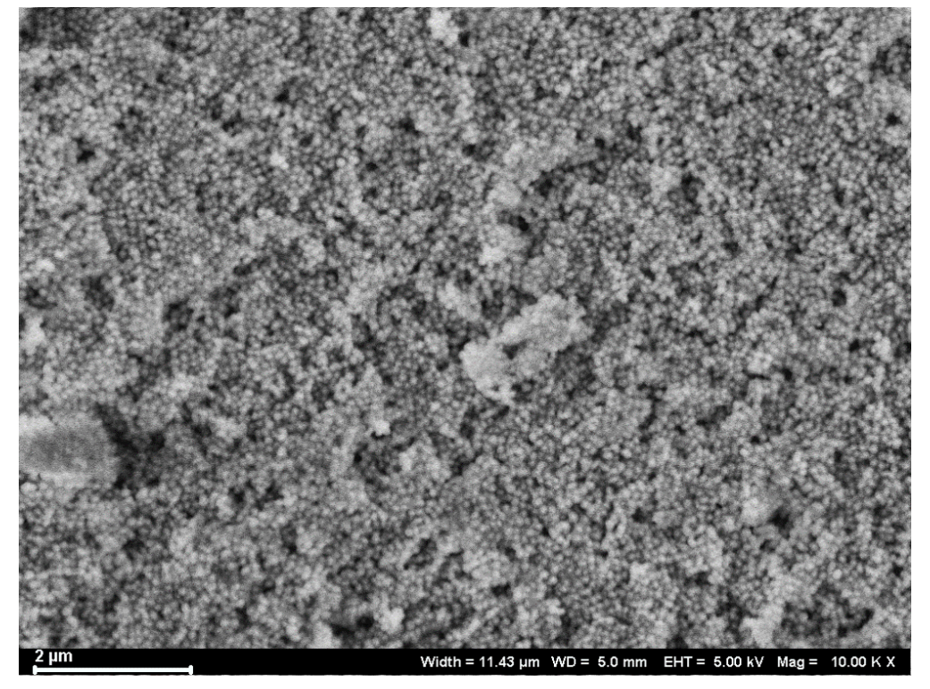
Fe_3O_4@ZSM-5



$Fe_3O_4@SiO_2$



$Fe_2O_3@SiO_2$



Catalyst	Sp. surface Area (m^2/g)	Pore volume (cc/g)	Pore diameter (nm)
Fe_3O_4@ZSM-5	11.0103	0.053945	19.5981
$Fe_3O_4@SiO_2$	106.3203	0.335898	12.6372
$Fe_2O_3@SiO_2$	617.9110	0.587170	3.8010

RESULTS

- XRD analyses:
  (1) in Fe_3O_4@ZSM-5, main feature peaks for Fe_3O_4 and ZSM-5 were detected;
  (2) in $Fe_3O_4@SiO_2$, peaks for Fe_3O_4 and orthorhombic silica were observed;
  (3) $Fe_2O_3@SiO_2$ also exhibits the peaks for iron, indicating the successful synthesis of desired phases.
- All the N_2 adsorption isotherms are Type III isotherm with hysteresis loop Type 3, suggesting the adsorption of N_2 on the catalysts occur in multilayers. It might be due to the mesopores of the materials. The hysteresis loop confirms the presence of mesopores in the catalysts.
- The mesopores ensure the improvement of diffusion of reactants and products as well as enhanced heat transfer, which is significant for exothermic Fischer-Tropsch reactions.
- Morphology obtained from SEM shows that the catalyst particles with core-shell structure have nano scale features. They either aggregate in clusters ($Fe_3O_4@SiO_2$), or exist as isolated particles (Fe_3O_4@ZSM-5, $Fe_2O_3@SiO_2$). The tiny size is the basis of high reactivity for nano-sized catalysts.

FUTURE WORK

- Alter the shell thickness and study the effect of shell thickness on porosity, the diffusion efficiency and the catalyst performance in FTS.
- Investigate effect of iron valence state (Fe_2O_3 ,Fe_3O_4) and the particle size of the core phase on their performance in FTS.
- Incorporate other active component, such as Co, Ni, and Ru, and promoters to enhance the activity and modify the selectivity towards formation of various hydrocarbons.
- Further development of dual core-shell nanocomposites could potentially show combined advantages of both active components.

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