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# $CO_2$ hydrogenation to hydrocarbons over alumina-supported iron catalyst: Effect of support pore size

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## ABSTRACT

The effect of support pore size of $FeK/Al_2O_3$ catalysts on the catalytic performance in $CO_2$ hydrogenation reaction was investigated. A total of 8 iron-based catalysts supported on alumina with different pore size were prepared by incipient wetness impregnation where the amount of Fe and K were fixed at 15 and 10 wt%, respectively. $N_2$ adsorption/desorption, XRD, TPR and PZC were used to characterize the supports and catalysts. The results show that the support pore size impacts the size of $Fe_2O_3$ particles formed in the catalyst; increasing pore size of $Al_2O_3$ supports led to increased size of $Fe_2O_3$ particles formed in the pores. Catalyst pore sizes of 7–10 nm and the corresponding $Fe_2O_3$ particle sizes of 5–8 nm were the most active for $CO_2$ hydrogenation to hydrocarbons. Outside this range, larger pore size further decrease the iron dispersion and reduce the number of active sites; smaller pore size is not favorable on account of the too small $Fe_2O_3$ particle sizes and lower reducibility of the small particle.

## 1. Introduction

Rapidly increasing $CO_2$ emission has been regarded as one of the most serious threat to the environment as a result of its contribution to the global climate change. However, $CO_2$, to some extent, is also a potential carbon source in terms of its abundance and renewable character [1]. Provided that renewable or nuclear energy could support the reaction so as to ensure no additional $CO_2$ is released, $CO_2$ utilization can reduce the $CO_2$ content in the atmosphere. Specifically, if hydrogen ($H_2$) could be produced using solar energy which is what numerous research groups focus on, $CO_2$ hydrogenation can be an effective reaction for utilizing the stored or captured $CO_2$ [2,3].

It is widely acknowledged that iron-based catalyst can display good activity in $CO_2$ hydrogenation to hydrocarbons, where $CO_2$ is first reduced to CO via the Reverse Water Gas Shift (RWGS) reaction and then hydrocarbons is generated through Fischer-Tropsch synthesis (F-T synthesis) [4,5]. However, iron catalyst without any promoters could only produce a limited amount of hydrocarbons, especially $C_5^+$ hydrocarbons. The addition of K could decrease $H_2$ chemisorption capacity of Fe based catalyst, but enhance $CO_2$ adsorption and accelerate the generation of $Fe_5C_2$ phase, which might be the active species of the CO hydrogenation [6–9]. Thus, the introduction of proper amount of potassium could enhance the olefin selectivity, $CO_2$ conversion rate and long-chain products selectivity [10]. On the other hand, proper supports are desirable as well. Recent decades have witnessed various types of supports for metal catalysts, such as $SiO_2$, $TiO_2$, $Al_2O_3$, zeolite, and MOFs [11–16]. Among them, alumina, widely used as support material, is believed to be good for the $CO_2$ hydrogenation. Accordingly, in our present work, a typical $FeK/Al_2O_3$ catalyst formulation was selected to study the effect of support pore size.

Support physicochemical variables on $CO_2$ hydrogenation and F-T synthesis has received considerable attention. Ding et al. found surface acidic-basic hydroxyls of alumina affected $CO_2$ conversion and $C_5^+$ hydrocarbons selectivity by changing the dispersion and the particle size of the Fe-based catalysts [17]. According to Shimura et al., pore structure (surface area, pore size) of the support alumina influence the reaction rather than the crystal phase [18]. The effect of support pore size on F-T synthesis has been studied by numerous research groups,

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but the results are not consistent. Song et al. [19] and Saib et al. [20] found the reaction passed through a maximum activity in Co/$SiO_2$ catalysts, while Khodakov et al. [21] found no such optimal point but merely a positive correlation between pore diameter and $C_5^+$ selectivity. For Co/$Al_2O_3$ catalysts, with the increasing pore size, Borg et al. found an increasing trend of $C_5^+$ selectivity [22] while on the other hand, Xiong et al. found a decreasing trend [23]. Such disagreements also exist in Co/CNT catalysts [24,25].

Though some studies about alumina-supported catalysts for $CO_2$ hydrogenation have been reported, the effect of support pore size is still unknown and therefore, this work aims to shed light on this effect. In the present work, a series of 8 alumina-supported iron catalysts were tested for hydrogenation to hydrocarbons. Catalyst activity and product selectivity were evaluated in a fixed-bed reactor. The supports and catalysts were characterized by $N_2$ adsorption/desorption, XRD, $H_2$-TPR and PZC.

## 2. Experimental

### 2.1. Chemicals

Aluminum *sec*-butoxide ($Al(OCH(CH_3)CH_2CH_3)_3$, ASB) and aluminum isopropoxide (AIP) were purchased from Aladdin. Ferric nitrate ($Fe(NO_3)_3·9H_2O$) and potassium nitrate ($KNO_3$) were purchased from Tianjin BODI Co., Ltd. Boehmite (SB powder) was purchased from Sasol (Germany). AEO-7 was purchased from Huize Co., Ltd. Citric acid was obtained from Tianjin TianLi Chemical Reagents Ltd.

### 2.2. Synthesis procedure

Three methods were used to synthesize a series of 8 alumina supports with a wide range of pore size.

The first synthesis method was originally reported by Li et al. [26]. 5 g AEO-7 was dissolved in 100 mL dry ethanol containing 2.5 g citric acid and 8 mL concentrated nitric acid. Then, 10.2 g AIP was added to the solution. After stirring at 303 K for 24 h, the solution was evaporated at 333 K for 48 h. The precursor was calcined at 823 K for 6 h. This support sample was denoted as S1.

The second synthesis procedure of the alumina material was reported by Huang et al. [27]. Typically, ASB were hydrolyzed at room temperature to obtain precursors by adding water with different water to aluminum molar ratios ($H_2O$:Al = 2:1, 7:1, 15:1) while grinding. The precursors were subsequently thermally treated at 973 K for 2 h. The final samples corresponding to $H_2O$:Al ratios of 2:1, 7:1, and 15:1 were denoted as S2, S3, and S4, respectively.

Thirdly, 4 g SB powder were calcined at 823 K, 923 K, 1023 K and 1123 K for 4 h separately and the final $Al_2O_3$ obtained were denoted as S5–S8.

### 2.3. Catalyst preparation

The catalyst samples (C1–C8) containing 15 wt% iron and 10 wt% potassium were prepared by traditional incipient-wetness impregnation of different supports (S1-S8) with aqueous solutions of $Fe(NO_3)_3·9H_2O$ and $KNO_3$. The fresh catalysts were obtained after being dried at 100 °C and then calcined at 773 K for 4 h with the heating rate of 2 °C/min.

### 2.4. Characterization

#### 2.4.1. Nitrogen adsorption/desorption

$N_2$ isotherms were measured using a Quantachrome AUTOSORB sorption analyzer at 77 K. Prior to the measurements, the samples were degassed in vacuum at 300 °C for 8 h.

The Brunauer – Emmauer – Teller (BET) method was used to determine the specific surface area. The Barrett – Joyner – Halenda (BJH) method was applied to evaluate the pore size distribution, and the nitrogen adsorption branch was chosen for pore size analysis. The total pore volume was obtained from the amount of vapor adsorbed at a relative pressure ($P/P_0$) close to unity, where P and $P_0$ are the measured and equilibrium pressure, respectively.

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

X-ray diffraction (XRD) patterns of the supports (S1–S8) and catalysts (C1–C8) were recorded on a Rigaku SmartLab diffractometer with Cu Kα radiation (λ= 1.5406 Å) source. The spectra were recorded from 2θ = 5° to 80° with a step size of 0.02°. The crystallite phases were identified by comparing the diffraction patterns with the data of the Joint Committee on Power Diffraction Standards (JCPDS). The average iron oxide crystallite diameters were calculated with Scherrer's equation using the $Fe_2O_3$ peak located at 2θ = 35.6°. A K factor of 0.89 was used in Scherrer's formula:

$$d = \frac{K\lambda}{B\cos\theta} \times \frac{180^\circ}{\pi}$$

where d is the mean crystallite diameter, λ is the X-ray wave length (1.5406 Å), and B is the full width half maximum (FWHM) of the $Fe_2O_3$ diffraction peak [19,21,28].

#### 2.4.3. Point of zero charge (PZC) of supports

Surface acid-base properties of the alumina supports were estimated by the potentiometric titration method [29,30]. About 200 mg of samples was equilibrated for 40 min in 30 mL of 0.01 M $NaNO_3$ solution with continuous magnetic stirring at 298 K, followed by the addition of 2 mL of 0.01 M $HNO_3$. The suspension was agitated for 30 min, the pH value of the solution was recorded as the initial pH with a pH meter. The suspension was then titrated with 0.2 mL of 0.01 M NaOH, and the pH of the suspension was recorded after every 2 min. The surface charge density was calculated using the formula:

$$\sigma_0 = \frac{[C_A - C_B + [OH^-] - [H^+]]}{mS}F$$

where $C_A$ (mol/dm$^3$) and $C_B$ (mol/dm$^3$) are the concentrations of acid and base added, [$OH^-$] and [$H^+$] are the concentrations of $OH^-$ and $H^+$ ions measured from the pH of the suspension, m is the mass of samples (g) and S (m$^2$/g) is the specific surface area of the samples, F (C/mol) is the Faraday constant.

#### 2.4.4. $H_2$-TPR

$H_2$-temperature-programmed reduction ($H_2$-TPR) was conducted with ChemBET Pulsar TPR/TPD equipment (Quantachrome, USA) to analyze the reducibility of the calcined catalysts. About 100 mg of sample was placed in a quartz tube in the interior of a controlled oven. To remove moisture and other contaminants, the sample was flushed with He at 500 °C for 1 h prior to the reduction, and then cooled down to room temperature. The sample was reduced with a gas mixture containing 5% $H_2$/Ar at a flow rate of 30 mL/min and heating rate at 10 °C/min up to 800 °C. For removal of the water formed during the reduction process, a cooling trap was placed between the sample and the TCD detector, the temperature and TCD signals were continuously recorded during the $H_2$-TPR analysis.

### 2.5. $CO_2$ hydrogenation reaction

The reaction was carried out in a pressurized fixed-bed flow reactor (inner diameter 8 mm), where 0.5 g catalyst (powder, mixed with inert quartz sand to 1.0 mL) was loaded for each test. Prior to the reaction, the catalyst was pretreated by reduction with $H_2$ at 673 K overnight. After the reduction, the feed gas was switched to the mixture of $CO_2$ and $H_2$ with a $H_2/CO_2$ molar ratio of 3.0 under the reaction conditions: P = 3.0 MPa, T = 673 K, and space velocity = 3600 mL/(gcat·h).

Products were analyzed by an on-line FULI GC97 gas chromatograph. CO, $CO_2$ and $CH_4$ were analyzed on a carbon molecular sieve