An Interaction Study Between CO and H\textsubscript{2} with Fibrous Silica KCC-1 by \textit{in situ} FTIR

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\textbf{ABSTRACT} In this study, fibrous silica KCC-1 was prepared by a modified microemulsion system with microwave assisted hydrothermal method to study its properties as a supported catalyst. Then, its physicochemical properties were further examined to discover its potential as a catalyst support. Characterization results of fibrous silica KCC-1 by FESEM-EDX and N\textsubscript{2} physiosorption analysis revealed that the material possessed a spherical morphology dendrimeric silica fiber with a high surface area of 634 m\textsuperscript{2}/g. Furthermore, \textit{in situ} FTIR spectroscopy was carried out to study the interaction of fibrous silica KCC-1 with reagents such as H\textsubscript{2} and CO to understand the interaction on it. Based on the study, it can be observed that there is a significant change in fibrous silica KCC-1 while interacting with both reagents suggesting a role of KCC-1 as support catalyst in CO methanation.

1. Introduction

The discovery of mesoporous silica such as MCM 41 and SBA 15 with highly uniform porous solid materials and the high surface area was commonly used as a supported catalyst. This material was normally synthesized by surfactant micelle template method \cite{1}. Since the discovery of mesoporous materials in 1992, a new category of porous materials has applied in many applications such as catalyst, sensor and separator. The most interesting mesoporous materials is MCM-41 which exhibit high specific area (~1000 m\textsuperscript{2}/g), high crystallinity, high thermal stability, uniformity of hexagonal cylindrical pores, narrow pore distribution and regulated pore diameter. In the past research, it has been a proven that MCM-41 is nontoxic, easy to be modified and functionalized \cite{2}. Unfortunately, MCM-41 shows low mechanical and hydrothermal stability due to its hydrolysis thin (1-2 nm thickness) pore wall \cite{3}.

In recent times, mesoporous silica nanoparticles (MSN) have been effectively utilized in the fields of adsorption, drug delivery and catalysis due to their highly ordered hexagonal structure, highly uniform pore distribution, tunable pore size and unique hosting properties \cite{4}. MSN has become an important porous material since it can be easily functionalized with a functional group to the surface of mesoporous silica material, for example, mesoporous silica nanoparticle (MSN) was granulated with calcium alginate and act as an adsorbent for BTX (benzene, toluene and xylene) \cite{1}. However, these materials did not give a good metal dispersion due to low surface accessibility, which consequently leads to the formation of larger metal particles of metal agglomeration.

In recent years, fibrous silica (KCC-1) have been effectively utilized in the fields of adsorption, drug delivery and catalysis due to their unique dendrimer morphology, high surface area, large pore volume and good thermal stability. The development of silica-based fibrous material was first reported by Poleshstiwar \textit{et al} in 2010 under the name KCC-1 \cite{5}. Fibrous KCC-1 is one of the modified silica catalysts that provides higher accessibility through its dendrimer that allows reactant to pass through the active sites. The formation of fibrous morphology involved microemulsion formation from surfactant. The morphology of this material depends upon the equilibrium between hydrophobic-hydrophilic interaction

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among the surfactant, precursor, hydrolyzing agent, and solvent.

Considering all the factors mentioned before, an attempt to explore the fibrous silica KCC-1 is an imperative task due to it has high potential as a supported catalyst in CO methanation. Besides, further study on fibrous silica KCC-1 was expected to open a new field of research based on silica nanoparticles base fibrous materials.

2. Experimental procedure

2.1 Preparation of fibrous silica KCC-1

Fibrous silica KCC-1 was prepared via modifying microemulsion system with microwave assisted hydrothermal technique. Firstly, 15 mL of tetraethyl orthosilicate (TEOS) was dissolved in a mixture of cyclohexane and 1-pentanol. Then, mixture which consists of 5 g of cetylpyridinium bromide (CPB), 3 g urea and 150 ml distilled water was prepared. After that, both mixtures were stirred for 30 min at room temperature before it was transferred into a Teflon-sealed microwave (MW) reactor. The solution was exposed to intermittent MW irradiation (400 W) for 4 hours at 393 K. The solid product was centrifuged followed by washing with distilled water and acetone. Finally, the sample was dried at 373 K overnight in the oven, followed by calcined at 823 K in air for 6 h to obtain a fibrous silica KCC-1.

2.2 Characterization

Field Emission Scanning Electron Microscopy (FESEM) (Zeiss Supra 35 VP) is the instrument that was used to study morphology and the size of the sample solid. While Electron Dispersive X-Ray (EDX) was used to analyse simultaneously the trace element in the sample. Nitrogen adsorption technique was used to analyse the specific surface area of the catalyst by using SA3100 Beckman Coulter. The pore size distribution was calculated automatically by using Barret-Joy-Halenda (BJH) from nitrogen adsorption data. Furthermore, in situ FTIR spectroscopy was carried out to study the ability of fibrous silica KCC-1 catalyst to interact with the reactant. In this study, CO and H2 gas were used as a reactant. The interaction of CO and H2 were done by exposing 60 and 20 torr, respectively at room temperature before subsequent heating to 623 K with the increment of 50 K.

3. Results and discussion

Figure 1 shows the structural morphology and elemental mapping of KCC-1 observed using FESEM-EDX. KCC-1 types catalyst possessed a porous and uniform spherical structure with a unique dendrimeric morphology that exhibits the high surface area of parent catalysis [5]. Besides, the distance between each unique dendrimer is expected to allow the reactant to diffuse and facilitate the high reaction performance [6]. The particle size distribution of the KCC-1 was determined by measuring the diameter of projected areas of 100 individual particles in the FESEM image. The particle size was mainly distributed in the range from 400-1200 nm. The elemental mapping showed that the Si-atoms and the O-atoms were widely distributed on the core of each sphere. The elemental composition of the O atoms is 3.23% while for Si atoms is 96.77%.

N2 physisorption analyses is a widely used technique to estimate textural properties of solid materials. Figure 2 shows the N2 adsorption-desorption isotherms and pore size distribution of fibrous silica KCC-1. According to the IUPAC classification, fibrous silica KCC-1 exhibited type IV isotherm curve with H1-type hysteresis loop, which is typical for mesoporous materials [7,8]. These hysteresis loops are found on solids consisting of slit shape pores, with uniform size and/or shape [9]. The sharp inflections at P/P0 = 0–0.03, 0.3–0.4 and 0.85–1 observed in the isotherm indicate the presence of micropores, mesopores and interparticle voids in the catalysts, respectively. The fibrous silica KCC-1 shows the high surface area of 634 m²/g with the average pore diameter of 4.7 nm.
which obtained from NLDFT method. Besides, the BJH method revealed that fibrous silica KCC-1 possessed a total pore volume of 1.72 cm$^3$/g.

Figure 2: Nitrogen physisorption isotherms and pore size distribution for Fibrous silica KCC-1

Figure 3 shows FTIR study carried under blank condition (without catalyst) of gaseous CO, H$_2$ and CO$_2$ on fibrous silica KCC-1. The important of the blank reaction is its give an important information that the adsorbed species needs a supporting material such as fibrous silica KCC-1 to confirm on the formation of intermediate needed in CO methanation. Based on this figure, it was observed that each absorbed species formed its own specific adsorption peaks. After the flowing of CO gas, two peaks were observed at 2170 and 2110 cm$^{-1}$ which can be assigned to the peaks of gaseous CO. No peaks were observed when flowing with the H$_2$ gas. Meanwhile, two peaks at 2350 and 2310 cm$^{-1}$ were observed by addition of gaseous CO$_2$.

Figure 3: Evaluation of FTIR spectra of blank reaction at room temperature.

Figure 4 showed the adsorption of gases H$_2$ on fibrous silica KCC-1. Based on this figure, one sharp and narrow peak at 1625 cm$^{-1}$ which can be deduced as atomic hydrogen peak was observed. The intensity of this peak centred at 1625 cm$^{-1}$ was slightly increased with the increasing of temperature up to 623 K. This might due to the high ability of the catalyst to dissociate H$_2$ molecule to form atomic H [10]. Besides, another peak was observed at 1870 cm$^{-1}$ which were assigned to the peak for Si-O-Si vibration of the supported KCC-1 [11]. Meanwhile, the existent of the peak at 1970 cm$^{-1}$ indicated the linearly adsorption band for atomic H on the surface of catalysts sites [12].

Figure 4: Evaluation of FTIR spectra of adsorbed H$_2$ on fibrous silica KCC-1. The samples were (a) outgasses at 673 K, followed by (b) adsorption of H$_2$ at room temperature and heating up to (c) 323 K, (d) 373 K, I 423 K, (f) 473 K, (g) 523 K, (h) 573 K and (i) 623 K

Figure 5 showed the adsorption of gases CO on fibrous silica KCC-1. Two peaks were observed at 2170 and 2110 cm$^{-1}$ indicating that there were remaining of gaseous CO which not adsorbed on the surfaced of catalyst and remained as a CO gas. The peak at 1625 cm$^{-1}$ also observed when the addition of gas CO on fibrous silica KCC-1 which due to the symmetric stretching mode of carbonyl which acts as intermediate in CO methanation [13]. As increasing the temperature to 623 K, the peak mention was slightly decreased as the increasing the peaks at 2360 and 2340 cm$^{-1}$ which can be assigned to gaseous CO$_2$ [14]. At high temperature, the gas CO$_2$ started to appear due to the water gas shift (WGS) might take placed [15].

Figure 5: Evaluation of FTIR spectra of adsorbed CO on fibrous silica KCC-1. The samples were (a) outgasses at 673 K, followed by (b) adsorption of CO at room temperature and heating up to (c) 323 K, (d) 373 K, (e) 423 K, (f) 473 K, (g) 523 K, (h) 573 K and (i) 623 K.
Fibrous mesostructured silica KCC-1 was successfully prepared by microwave assisted hydrothermal method from urea, cetylpyridium bromide and water with microwave assisted hydrothermal method. The physical and chemical properties of the catalysts were characterized using FESEM-EDX and N₂ physisorption and in situ FTIR analyses. Based on the FESEM image, fibrous silica KCC-1 type catalysts exhibited a porous and uniform spherical structure with a unique silica dendrimeric morphology. Elemental analysis performed by EDX confirmed the presence of well dispersed Si and O in the framework. Besides, based on N₂ physisorption analyses, fibrous silica KCC-1 possessed a mesoporous structure and high surface area of 634 m²/g with the average pore diameter of 4.7 nm. Based on in situ FTIR, it can be observed that while the absence of support catalyst, the reactant was in the form of the gaseous phase. However, in the presence of support catalyst, there is a formation of an intermediate which was a well-known influence on CO methanation activity.

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Reference


