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Effect of pressure on direct synthesis of DME from syngas over metal-pillared ilerites and metal/metal-pillared ilerites

Sung-Hwan Ahn, Song-Hyoung Kim, Kwang-Bo Jung* and Hyun-Sik Hahm†

Department of Chemical Engineering, Myongji University, San 38-2, Namdong, Yongin, Gyeonggi-do 449-728, Korea
*Department of Chemical Engineering, Han-Seo University, 360 Daegokri, Haemi-myun, Seosansi 360-706, Korea

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Abstract−The effect of pressure on the direct synthesis of dimethyl ether (DME) from syngas over metal (Cu, Zn) pillared ilerites and metal (Cu, Zn) impregnated metal-pillared ilerites was explored. The prepared catalysts were characterized by XRD, BET, ICP-AES, SEM and FT-IR. The direct DME synthesis reaction was carried out in a differential fixed bed reactor with the prepared catalysts at various pressures (10, 20, 30 bar), 250 °C and H_2/CO ratio of 2. The Cu/Zn-pillared ilerite catalyst showed the highest catalytic activity among the prepared catalysts at 20 bar, in which CO conversion was about 62% and DME selectivity was about 89%. CO conversion increased with pressure, and DME selectivity increased with pressure in the range of 10-20 bar, and above the pressure slightly decreased with pressure. The optimum pressure for this reaction was 20 bar.

Key words: Metal-pillared Ilerite, Dimethyl Ether (DME), Direct DME Synthesis, Syngas

INTRODUCTION

DME as an important chemical material and a potential clean fuel substitute for LPG and diesel oil has attracted much more attention in recent years [1-3]. Traditionally, DME has been produced by the high-pressure methanol dehydration process. Direct synthesis of DME from syngas has been known as a potential process compared with the methanol dehydration process for its lower thermodynamic limitation and lower investment [4,5].

There are two processes that have been known as potential processes for the production of DME from syngas. One is the so-called two-step process which produces methanol from syngas over a Cu-based catalyst, followed by a methanol dehydration step over a solid acid catalyst. The other is a single step direct DME synthesis process from syngas over a bifunctional or hybrid catalyst composed of a methanol synthesis catalyst and a methanol dehydration catalyst [6,7].

There are two types of catalyst systems for the single step DME process. The first type, called a hybrid catalyst system, consists of a physical mixture of a methanol synthesis catalyst and a methanol dehydration catalyst. The methanol synthesis catalyst is generally a $Cu/ZnO/Al_2O_3$ (or Cr_2O_3) commercial catalyst, while the methanol dehydration catalyst is generally selected from solid acid materials, including γ-alumina, silica-alumina, zeolites, clays, phosphates, sulfates, metal halides, acidic resins, supported phosphoric acid, and heteropoly acids [8]. In gas phase applications using a fixed or fluidized bed reactor, the powders of the two catalysts can be mixed followed by being formed into pellets or beads, or separate pellets or beads of the each component can be prepared. In liquid phase applications using a slurry bed reactor containing an inert liquid medium, a powder mixture of the two catalysts can be directly used [9,10]. In the second type of catalyst system for the single step DME process, the two functionalities are built into a single catalyst. This has been achieved either by co-precipitating methanol synthesis and dehydration components together to form one catalyst, or by impregnating methanol synthesis components onto a solid acid material.

The direct DME synthesis process, called STD (synthesis gas to DME) process, is claimed to have greater significance than the two-step process because of its higher CO conversion in a single pass [11,12]. The advantage of the single step DME process is the high syngas conversion per pass as compared to the traditional two-step process in which methanol is produced from synthesis gas in a reactor over a methanol synthesis catalyst, then converted into DME in a subsequent reactor over a dehydration catalyst. The catalyst system for the single step DME process possesses two functionalities, that is, a methanol synthesis functionality (methanol synthesis from synthesis gas) and a methanol dehydration functionality (methanol is dehydrated into DME and water). The methanol synthesis catalyst also possesses water-gas shift activity.

Mechanism studies have indicated that the consecutive steps, that is, methanol synthesis step (Eq. (1)) and the methanol dehydration step (Eq. (2)), in the STD process could be compacted with using the hybrid catalyst. The water-gas shift reaction (Eq. (3)) proceeds very fast in this process. The overall stoichiometric reaction in the STD process is shown in Eq. (4). This process is favorable in thermodynamic aspects, and very high CO conversion was reported in earlier papers [7].

$$CO+2H_2 \rightarrow CH_3OH \qquad \Delta H_{298}=-24.0\ \text{kcal/mol: methanol synthesis} \qquad (1)$$

$$2CH_3OH \rightarrow CH_3OCH_3+H_2O \qquad \Delta H_{298}=-5.6\ \text{kcal/mol: methanol dehydration} \qquad (2)$$

$$CO+H_2O \rightarrow CO_2+H_2 \qquad \Delta H_{298}=-9.3\ \text{kcal/mol: water-gas shift reaction} \qquad (3)$$

$$3CO+3H_2 \rightarrow CH_3OCH_3+CO_2 \qquad \text{overall stoichiometric reaction} \qquad (4)$$

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†To whom correspondence should be addressed.
E-mail: hahm@mju.ac.kr

According to the reaction mechanism in the STD process, the methanol synthesis step and methanol dehydration step should be matched completely in order to achieve a higher DME yield. It is widely known that active alumina shows high catalytic performance for alcohol dehydration in points of selectivity and life, while HZSM-5 and HY zeolites show higher activity for methanol dehydration to DME than the active alumina [13], and the direct synthesis of DME via CO hydrogenation on active alumina supported Cu-Mn-Zn catalysts must be carried out at a higher temperature [14]. Zeolites, HZSM-5 and HY, were recommended as a favorable dehydration catalyst [15,17].

In this study, several metal (Cu, Zn) pillared ilerites and metal/metal-pillared ilerites were prepared and used as a bifunctional catalyst for direct DME synthesis from syngas. The effect of pressure on catalytic activity was also explored.

EXPERIMENTAL

Na-ilerite was synthesized by a hydrothermal method, and H-ilerite was prepared by an acid titration of the Na-ilerite. Metal-pillared ilerites were prepared by an intercalation method [5]. Na-ilerite was synthesized with hydrothermal method at 110 °C for 14 days from a gel composed of 1.0 Na_2O : 2.0 SiO_2 : 20 H_2O. H-ilerite was prepared by 0.1 N HCl acid titration of the prepared Na-ilerite. The solid product was recovered by filtering, washed, and dried at 40 °C. Metal-pillared ilerite catalysts were prepared by the intercalation method using octylamine as a swelling agent. The pillaring procedure is as follows: (i) Octylamine-ilerite gel was formed by the reaction of H-ilerite with octylamine at room temperature for 72 h; (ii) metal precursor was slowly added to the octylamine-ilerite gel and the mixture was stirred for 48 h at room temperature; (iii) the resultant product was washed twice, filtered, and dried at 100 °C; (iv) finally, the product was refluxed overnight with 1 M NH_4NO_3 solution at 80 °C, followed by calcination in air at 700 °C for 1 h to remove octylamine.

The bifunctional catalysts for direct DME synthesis, Cu/Zn-ilerite and Zn/Cu-ilerite, were prepared by the impregnation of Cu or Zn onto the metal-pillared ilerites.

XRD analysis was performed with a Rigaku automated powder X-ray diffractometer system (Cu Kα radiation). The specific surface areas of the catalysts were measured by a BET apparatus. Chemical analysis was performed with an ICP spectrometer. The morphologies and crystal sizes of the catalysts were examined by HITACHI S-4100 scanning electron microscope (SEM). FT-IR spectra were recorded with a BOMEM, MB104 spectrometer. The acidic properties of the catalysts were examined through NH_3-TPD analysis. NH_3-TPD measurements were carried out with a PCI-3135 TPD/TPR analyzer.

The reaction was carried out in a differential fixed-bed high-pressure reactor. The products were analyzed with an on-line gas chromatograph with TCD and FID detectors using Porapak Q and Carbosphere columns. For the STD process, the prepared catalysts were reduced in a 5% H_2/He gas at 300 °C for 2 h. After the reduction, the reactant gas mixture composed of H_2 and CO (H_2/CO=2) was introduced into the reactor at a pressure of 10-30 bar and the temperature of 250 °C. The reactant gas ratio was fixed to be 2, because with the ratio of 2, maximum catalytic activity was obtained in our previous work [16].

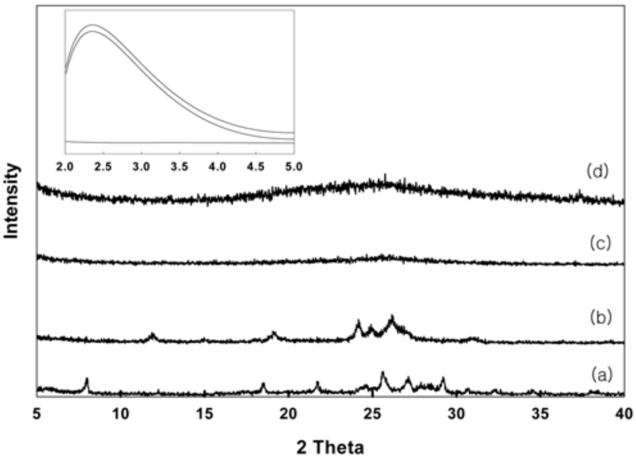

Fig. 1. XRD patterns of prepared ilerite catalysts: (a) Na-ilerite, (b) H-ilerite, (c) Cu-ilerite, (d) Cu/Zn-ilerite.

RESULTS AND DISCUSSION

1. Characterization of Metal-pillared Ilerites

In order to examine the structure, acidity and surface area of the synthesized catalysts, XRD, BET, FT-IR, ICP-AES, and SEM analyses were carried out. Fig. 1 shows the XRD patterns of Na-, H-, Cu- and Cu/Zn-ilerite catalysts. The XRD patterns of Na-ilerite and H-ilerite (Fig. 1(a) and (b)) agree well with those reported elsewhere [8,10]. As shown in Fig. 1(c)-(d), Cu- and Cu/Zn-ilerite catalysts exhibit the XRD patterns of amorphous-like materials in the wide-angle region, but they have a new peak in the small-angle region (Fig. 1(c), (d)). This new peak must stem from the intercalation of Cu or Zn into the layers of the ilerite [10]. By the intercalation of the metals, the spacing between the layers becomes widened. The interlayer spacing of H- and Na-ilerites is 7.1 and 12 Å, respectively. The interlayer spacing of Cu- and Cu/Zn-ilerites is widened to values larger than those of H- and Na-ilerites. The peaks of the Cu- and the Cu/Zn-ilerites appear around 2.5 in 2θ in Fig. 1(c) and (d), which corresponds to the interlayer spacing of 38-40 Å.

The BET surface areas of the Cu- and Cu/Zn-ilerites are 500 and 450 m^2/g, respectively. These values are larger than those of H- and Na-ilerites whose surface areas are 20 and 40 m^2/g, respectively. These surface area increases of Cu- and Cu/Zn-ilerites can be explained by the intercalation of the ilerites by the metals.

The metal contents of Cu-, Zn-, Cu/Zn-, Zn/Cu-ilerite samples, determined by the ICP spectroscopy, were 1.972.0 wt% for Cu and 1.721.8 wt% for Zn as listed in Table 1.

The scanning electron micrographs of Na-, H- and Cu-ilerite are

Table 1. ICP-AES data for prepared ilerite catalysts

Catalyst	Cu metal [%]	Zn metal [%]
Cu-ilerite	2.0	-
Zn-ilerite	-	1.8
Cu/Zn-ilerite	1.98	1.72
Zn/Cu-ilerite	1.97	1.8

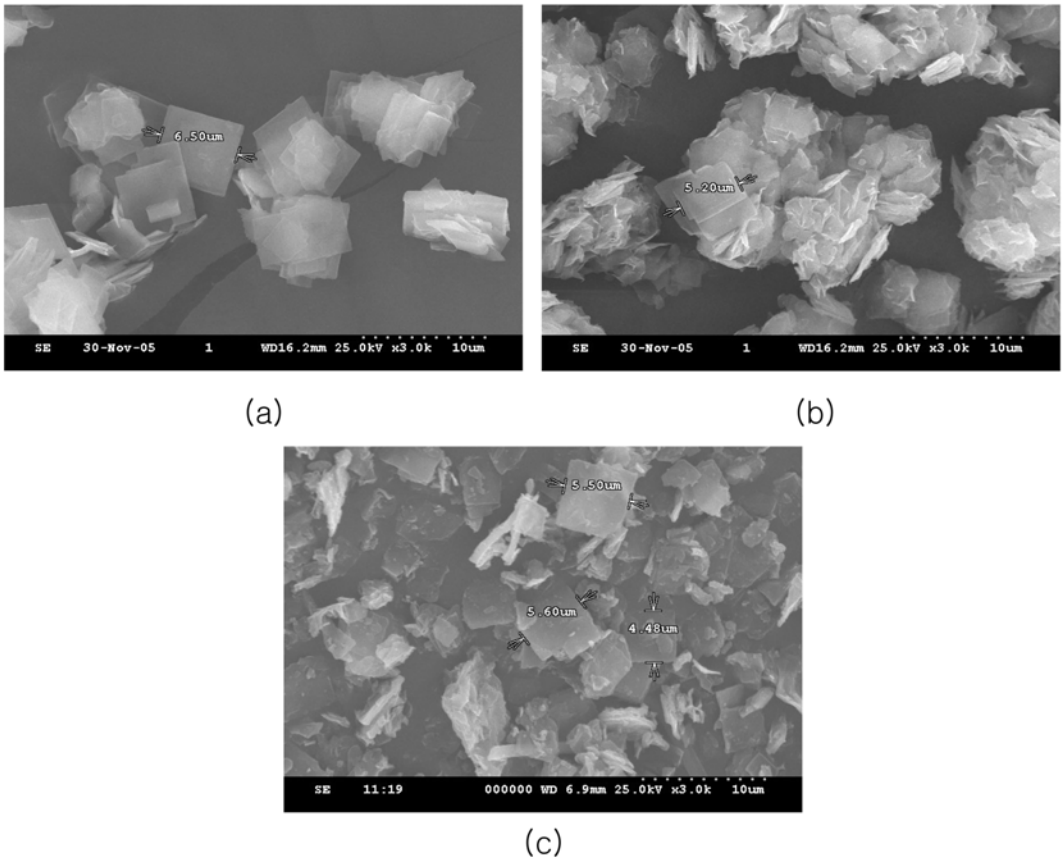

Fig. 2. Scanning electron micrographs of prepared ilerites: (a) Na-ilerite, (b) H-ilerite, (c) M-ilerite.

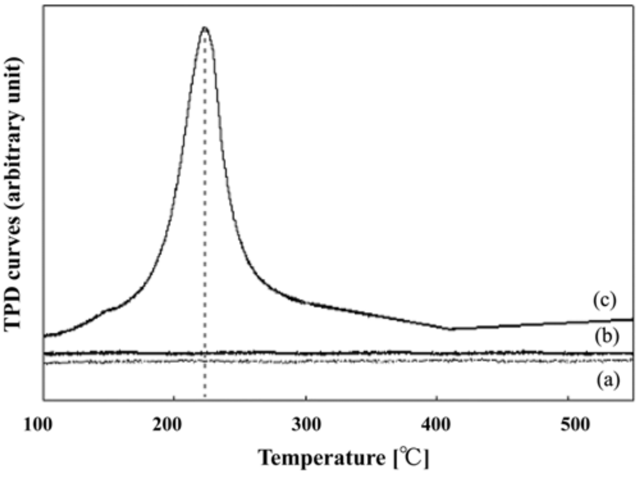

Fig. 3. NH_3-TPD profiles of prepared ilerite catalysts: (a) Na-ilerite, (b) H-ilerite, (c) Cu-ilerite.

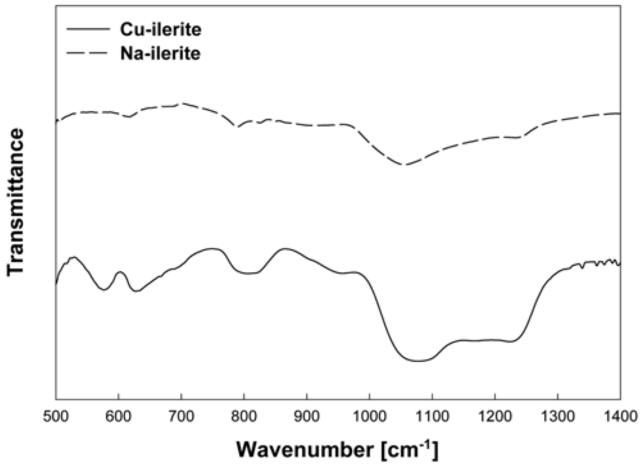

Fig. 4. FT-IR spectra of Na-ilerite and Cu-ilerite catalysts.

shown in Fig. 2. H-ilerite exhibits thin rectangular plate crystallites similar to Na-ilerite. This plate structure still remains after Cu metal pillaring (Cu-ilerite).

Fig. 3 shows the NH_3-TPD profiles of Na-ilerite, H-ilerite and Cu-ilerite. There were no remarkable NH_3-TPD peaks for Na-ilerite and H-ilerite, but for Cu-ilerite a peak was observed around 220 °C, which implies that the metal-pillared ilerite has weak acidity. It may stem from a certain function of the intercalated metal, or from the structural differences between the layers of ilerite [3]. And this result indicates that the Cu-ilerite possesses a large number of weak acidic sites.

Cu metal pillaring into the layers of ilerite is also confirmed by the FT-IR spectrometer. As shown in Fig. 4, the IR spectrum of Cu-ilerite exhibits a new peak at 965 cm^{-1}. Since this band is not present in the IR spectrum of Na-ilerite, it must be due to the metal pillaring into the layers of ilerite. As for metal-substituted zeolites, the peak around 960 cm^{-1} was assigned to the stretching Si-O vibration mode perturbed by a heavy metal in a neighboring position [10]. A similar peak was found in the vibration spectra of silicalite-1 containing metal ions in the framework [6,18]. This proves that the new peak at 965 cm^{-1} is attributed to the intercalation of Cu metal into the layers of the H-ilerite.

2. Effect of Pressure on Catalytic Performance of Metal-pillared Ilerites and Metal Impregnated Metal-pillared Ilerites

To test the effect of pressure on catalytic performance of Cu-, Zn-, Cu/Zn- and Zn/Cu-ilerite catalysts, the direct DME synthesis reaction was carried out at various pressure (10-30 bar), with 250 °C and reactant ratio (H_2/CO) of 2. The results of the direct synthesis of DME from syngas over Cu-, Zn-, Cu/Zn- and Zn/Cu-ilerites are presented in Figs. 5-6. Fig. 5 shows the CO conversion and DME selectivity for metal-pillared ilerites (M: Cu, Zn) catalysts. The products are methanol, DME, H_2O and trace amount of CO_2. With increase in pressure from 10 to 30 bar, CO conversion increases (from about 21% to about 52%) for Cu-ilerite catalyst, which may indicate that the methanol synthesis reaction is the rate-limiting step in the direct DME synthesis reaction [9]. This implies that the DME synthesis reaction may be carried out under a similar pressure as in the conventional methanol synthesis. A sharp increase in CO conversion is observed when pressure is increased from 10 to 20 bar (from about 21% to about 50%). Fig. 5 shows that when pressure is increased in the range from 10 to 20 bar the DME selectivity increases (from about 16% to about 46%) for Cu-ilerite catalyst, while above 20 bar DME selectivity is slightly decreased. It can be explained by the Le Chatelier's principle, that is, the methanol synthesis reaction (Eq. (1)) is favorable with increasing pressure, while DME synthesis reaction (Eq. (2)) is not affected by pressure. This explanation can also be verified by the DME and methanol selectivities listed in Table 2. Zn-ilerite catalyst shows a similar trend with the Cu-ilerite catalyst, CO conversion was in the range of 18-44% and DME selectivity was in the range of 14-36%. These results are summarized in Table 2. It was possible to produce DME directly from synthesis gas over the Cu-ilerite catalyst. From these results, it was found that the optimum pressure is 20 bar for this reaction.

Because Cu and Zn are constituents of the methanol synthesis catalyst, Cu and Zn impregnated M-ilerite (Cu/Zn-ilerite and Zn/Cu-ilerite; M/M-ilerite) catalysts were synthesized as bifunctional catalysts and used in the reaction of direct DME synthesis from synthesis gas. Fig. 6 shows the catalytic activities at different pressures

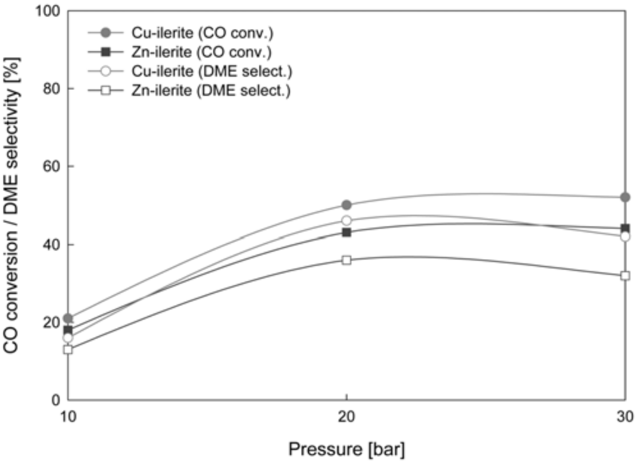

Fig. 5. Effect of pressure on CO conversion and DME selectivity for direct DME synthesis from syngas over M-ilerite (M: Cu, Zn) catalysts at 250 °C, $H_2/CO=2$.

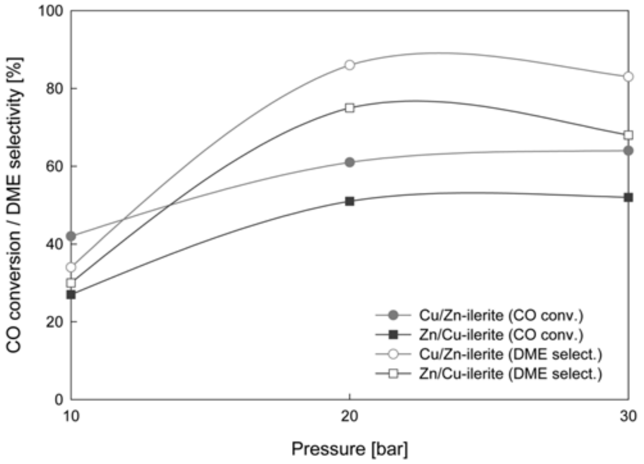

Fig. 6. Effect of pressure on CO conversion and DME selectivity for direct DME synthesis from syngas over M/M-ilerite (M: Cu, Zn) catalysts at 250 °C, $H_2/CO=2$.

Table 2. Effect of pressure on CO conversion, DME selectivity and CH_3OH selectivity of Cu-ilerite and Zn-ilerite catalysts at 250 °C, $H_2/CO=2$

Catalyst	CO conversion			DME selectivity			CH_3OH selectivity		
	10 bar	20 bar	30 bar	10 bar	20 bar	30 bar	10 bar	20 bar	30 bar
Cu-ilerite	21	50	52	16	46	42	81	50	53
Zn-ilerite	18	43	44	14	36	32	84	62	67

Table 3. Effect of pressure on CO conversion, DME selectivity and CH_3OH selectivity of Cu/Zn-ilerite and Zn/Cu-ilerite catalysts at 250 °C, $H_2/CO=2$

Catalyst	CO conversion			DME selectivity			CH_3OH selectivity		
	10 bar	20 bar	30 bar	10 bar	20 bar	30 bar	10 bar	20 bar	30 bar
Cu/Zn-ilerite	42	62	64	34	89	83	63	13	15
Zn/Cu-ilerite	27	51	52	30	75	68	65	21	30

(10-30 bar) for the direct DME synthesis reaction over metal/metal-pillared ilerite catalysts (M/M-ilerite). Cu/Zn-ilerite shows better catalytic activity than the Zn/Cu-ilerite at 250 °C, 20 bar, H_2/CO ratio of 2. Table 3 summarizes these results.

The CO conversions of the Cu/Zn- and Zn/Cu-ilerties were about 62% and about 51%, respectively, and the DME selectivities were about 89% and about 75%, respectively. Cu/Zn-ilerite shows higher CO conversion and DME selectivity than the Zn/Cu-ilerite. Cu/Zn-ilerite catalyst shows lower methanol selectivity than Zn/Cu-ilerite during the reaction, indicating that the Cu/Zn-ilerite catalyst has more potential to convert methanol (produced from syngas) to DME. It shows that the impregnated Cu enhances DME formation for the direct DME synthesis from syngas.

CONCLUSIONS

DME was directly synthesized from syngas over various metal-pillared ilerites. Metal-impregnated metal-pillared ilerite catalysts showed higher catalytic activity than the metal-pillared ilerites. It was proven that the bifunctional catalyst made up of Cu/Zn-ilerite was a proper catalyst for the direct DME synthesis from syngas in a single reaction step. Cu/Zn-ilerite catalyst showed the highest catalytic activity among the investigated catalysts in this study. In the case of Cu/Zn-ilerite, CO conversion reached up to about 62% with about 89% of DME selectivity. From the direct DME synthesis results, it was proven that the metal/metal-pillared ilerite catalysts (Cu/Zn-, Zn/Cu-ilerite) showed a bifunctional catalytic activity, and the prepared metal/metal-pillared ilerite catalysts are suitable catalyst for the direct DME synthesis. The optimum pressure for this reaction was 20 bar in this study.

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