Research Article

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CO₂ hydrogenation to dimethyl ether over In₂O₃ catalysts supported on aluminosilicate halloysite nanotubes

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Abstract: This work presents results on CO₂ hydrogenation to dimethyl ether (DME) over bifunctional catalysts consisting of In₂O₃ supported on natural clay halloysite nanotubes (HNT), and HNT modified with Al-MCM-41 silica arrays. The catalysts were characterized by TEM, STEM, EDX-mapping, NH₃-TPD, XRD, low-temperature nitrogen adsorption, TPO, and H₂-TPR techniques. Catalytic properties of In₂O₃/HNT and In₂O₃/Al-MCM-41/HNT in the CO₂ hydrogenation to DME were investigated in a fixed-bed continuous flow stainless steel reactor at 10–40 atm, in the temperature range of 200–300°C, at GHSV = 12,000 h⁻¹ and molar ratio of H₂:CO₂ = 3:1. The best catalyst for CO₂ hydrogenation was In₂O₃/Al-MCM-41/HNT that provided DME production rate 0.15 gDME/(gcat·h)⁻¹ with DME selectivity 53% and at 40 bar, GHSV = 12,000 h⁻¹, and T = 250°C. It was shown that In₂O₃/Al-MCM-41/HNT exhibited stable operation for at least 40 h on stream.

Keywords: CO₂ hydrogenation, dimethyl ether, indium oxide catalysts, halloysite nanotubes, mesoporous aluminosilicates

1 Introduction

Currently, many efforts of various researchers around the world are being made to solve environmental problems. Air pollution is considered one of the main such problems. Various options are offered – the use of alternative energy sources, such as solar [1], wind [2], and biofuel [3]. However, it is also necessary to pay great attention to the utilization of CO₂. The ever-growing production capabilities of different countries lead to an increase in carbon dioxide emissions into the atmosphere. This is the reason for the increase in the so-called “greenhouse effect,” which leads to an increase in the global temperature of the planet and, accordingly, climate change. This, as well as the fact that CO₂ is an inexpensive, readily available compound, requires the search for new technologies, methods, and ways of processing carbon dioxide. Recently, more and more attention of researchers from all over the world has been attracting the study of the reaction of CO₂ hydrogenation into various compounds such as methane [4], methanol [5–8], dimethyl ether (DME) [9–11], or hydrocarbons [12]. Among these compounds, DME attracts attention as a multipurpose product – it is used in the synthesis of methyl acetate, dimethyl sulfate, various petrochemical compounds, as a feedstock for powering fuel cells [13–15]. Due to its properties – high cetane number (55–60), low autoignition temperature, and high oxygen content (~35%), DME is considered as an alternative to diesel fuel or LPG. In terms of its physicochemical properties, DME is close to LPG, which allows its simple storage and transportation.

Commonly, DME is synthesized according to a two-stage scheme through the synthesis of methanol (MeOH) from synthesis gas on Cu/ZnO/Al₂O₃ (CZA) catalyst and its subsequent conversion into DME on a solid acid catalyst. However, the direct synthesis of DME is thermodynamically more favorable than the synthesis of methanol [16], which attracts more attention to the study of this
process. Catalysts for the direct synthesis of DME by hydrogenation of CO$_2$ are divided into two types: first, a mechanical mixture of catalysts for the synthesis of methanol and a catalyst for its dehydration; second, a catalyst called “bifunctional” which contains both types of necessary catalytic sites on its surface. Typically, first type systems are prepared by mixing or grinding of methanol synthesis and acidic components. Such method has some disadvantages like disintegration of its components during the reaction, mass, and heat transfer limitations [17]. So, recently, bifunctional catalysts have attracted much attention of scientists [10]. Another challenge is to perform direct DME synthesis with high selectivity without formation of CO. Industrial Cu/ZnO/Al$_2$O$_3$ methanol synthesis catalyst is also known to be active in reverse water gas shift (RWGS) reaction causing hydrogen losses due to formation of CO.

According to the recent density functional theory calculations [18], it is possible to obtain methanol with high selectivity via the hydrogenation of CO$_2$ on indium oxide. The reaction proceeds by the cyclic mechanism of the formation of oxygen vacancies and subsequent activation of CO$_2$ on them. Later, these calculations were experimentally confirmed. It was shown that methanol with $\sim$100% selectivity is achieved on bulk In$_2$O$_3$ at low CO$_2$ conversions [19]. These works gave an impetus to further extensive studying of catalysts on indium oxide in the hydrogenation of CO$_2$ – the effect of various supports, preparation methods, the structure of indium oxide, and various additives on the catalytic activity [20–24]. Thus, indium oxide as a catalyst for methanol synthesis looks promising. An acid component is required for the design of a bifunctional DME direct synthesis catalyst. Usually, γ-Al$_2$O$_3$ or various zeolites – H-ZSM-5, Y, MOR, FER – are used as an acid catalyst in a two-stage process [17,25–33].

In this work for the first time, halloysite aluminosilicate nanotubes (HNT) were used as an acid support for the direct synthesis of DME catalysts. Halloysite nanotubes (HNT) have a rolled tubular structure (length $\sim$1–2 μm, inner diameter 10–30 nm) [34–37]. In particular, halloysite was successfully applied as a support for catalysts of various applications, including aromatics hydrogenation [38–42], DME conversion to olefins [43], hydrogen production [44], Fischer–Tropsch synthesis [45], xylene isomerization [46,47], catalytic cracking [48], photocatalysis [49,50], etc. Its feature is that HNT contains two different types of active centers – functional groups of SiO$_2$ are present on the surface of nanotubes, while Al$_2$O$_3$ groups are located inside. This surface chemistry allows the metal component to be applied to both the external and internal surfaces, depending on the desired properties.

Nowadays, core-shell structure catalysts, such as Cu–ZnO–Al$_2$O$_3$@HZSM-5 [51] or CuO–ZnO–Al$_2$O$_3$@SiO$_2$–Al$_2$O$_3$ [52], are intensively studying in direct DME synthesis from CO$_2$. These systems prevent metal particles from sintering [53] and deactivation due coke formation by side reactions [54]. So, in the literature there are works on the modification of carbon surface with MCM-41 [36] to make core-shell structure. This core-shell halloysite – based aluminosilicate composite is promising for catalytic applications due to high specific surface area and enhanced thermal and mechanical properties [39]. However, pure MCM-41 doesn’t have the required acid sites on its surface. Therefore, before using it as a support, the surface was modified with aluminum in order to increase acid sites. The resulting Al-MCM-41 has a large amount of acid sites, which are necessary to produce DME by CO$_2$ hydrogenation.

In this work, we present novel bifunctional In$_2$O$_3$ catalysts supported on natural clay nanotubes (10 wt% In$_2$O$_3$/HNT) and composite with structured mesoporous silica (10 wt% In$_2$O$_3$/MCM-41/HNT) for CO$_2$ hydrogenation to DME.

2 Experimental section

2.1 Synthesis and characterization of catalysts

As a support for catalysts, HNT (≥98%, Sigma-Aldrich, St. Louis, MO, USA) and ordered mesoporous composite Al-MCM-41/HNT were used. This modified support was prepared by the template synthesis method as described in literature [43]. Cetyltrimethylammonium bromide (≥98%, Sigma-Aldrich, St. Louis, MO, USA) was used for the formation of MCM-41. Aluminum isopropoxide (≥98%, Sigma-Aldrich, St. Louis, MO, USA) was used as an aluminum source. The weight ratio between Al-MCM-41 and HNT in the synthesized support was 60/40%.

In$_2$O$_3$/HNT and In$_2$O$_3$/Al-MCM-41/HNT catalysts were synthesized by the incipient wetness impregnation method of HNT and Al-MCM-41/HNT with aqueous solutions of indium nitrate(III) (Reakhim, Moscow, Russia, purity 99.99%) taken at desired ratio, respectively. The samples were dried at 80°C in air for 4 h and after that calcined at 400°C (heating rate 1°C min$^{-1}$) for 3 h in air.

Actual In$_2$O$_3$ loadings in the catalysts were determined by inductively coupled plasma atomic emission spectrometry (Optima instrument; Perkin-Elmer).

Transmission electron microscope (TEM) JEOL JEM-2100 (UHR) operated at 200 kV (the lattice resolution of
0.19 nm) and equipped with LaB6 gun was employed to investigate structure, morphology, and chemical composition of the obtained samples. The samples for the TEM analysis were prepared by the dispersing in ethanol. The as-prepared dispersed solution was dropped onto carbon-coated formvar TEM Cu grid (300 mesh, Ted Pella, Inc.). The acquisition of TEM/HRTEM images was performed in TEM mode using Olympus Quemesa 11 megapixel CCD camera. The collection of each EDX map was performed in STEM mode with help of EX-2406JGT energy dispersive X-ray (EDX) analyser.

The specific BET surface areas ($S_{\text{BET}}$) and pore volume ($V_p$) of the support and the catalysts were determined using the low-temperature $N_2$-adsorption method using a TriStar3000 apparatus. Before experiment, all samples were outgassed in vacuum at 300°C, then nitrogen adsorption/desorption isotherms were recorded at −196°C. The specific surface area of the samples was calculated by the Brunauer–Emmett–Teller (BET) equation. The pore volume was evaluated in accordance with Barrett–Joyner–Halenda model.

NH$_3$ temperature-programmed desorption (NH$_3$-TPD) was used to evaluate the acid properties of the samples. The catalyst was saturated by mixture of NH$_3$ and $N_2$ at 100°C for 30 min. After that, the sample was purged with a stream of nitrogen to remove physisorbed ammonia at same conditions. Then NH$_3$-TPD curve was recorded up to 700°C with a rate of 10° per minute.

Temperature-programmed reduction (H$_2$-TPR) and temperature-programmed oxidation (TPO) experiments were carried out using a STA 409 PC Luxx derivatograph fitted with a QMS-200 mass spectrometer. For H$_2$-TPR, the samples (~50 mg) were heated from room temperature to 500°C (5°C min$^{-1}$) in a 10 vol% H$_2$–Ar mixture flowing at 100 mL min$^{-1}$. For TPO, samples were heated from 25°C to 800°C in a 10 vol% O$_2$–Ar mixture flowing at 100 mL min$^{-1}$.

X-ray structural analysis (XRD) of the samples was recorded on a Bruker D8 Advance (Bruker, Germany) diffractometer (CuKα) in the 2θ range of 8°–63° with a step 0.05° per 4 s. Analysis of the obtained diffraction data was carried out using the PowderCell 2.4 programme using the JCPDS international diffraction database as a reference.

### 2.2 Catalyst testing

Catalytic experiments on CO$_2$ hydrogenation were studied in a fixed-bed continuous-flow stainless steel reactor (inner diameter 8 mm) at a 10–40 atm pressure in the temperature interval 200–300°C, at GHSV = 12,000 h$^{-1}$ and molar ratio H$_2$:CO$_2$ = 3:1. Prior to the reaction, all the catalysts ($V_\text{cat} = 2$ cm$^3$, $m_\text{cat} = 1.4$ g for In$_2$O$_3$/HNT and 0.5 g for In$_2$O$_3$/Al-MCM-41/HNT, particle size of 0.5–1 mm) were pretreated at 300°C for 1 h in helium flow. The temperature was measured using a chromel-alumel thermocouple, which was placed in the middle of the catalytic bed. The results were obtained after multiple catalytic experiments. The catalysts were tested in several temperature increasing/decreasing cycles. At each temperature, the catalyst was kept for 1–2 h. Thus, total time onstream under CO$_2$ hydrogenation conditions was not less than 10 h. The catalytic performance during this period remained stable. The compositions of the inlet and outlet gas mixtures were analyzed by a gas chromograph (Chromos-1000) equipped with TCD and FID detectors and molecular sieve (5Å) and Carbowax columns. Argon was used as a carrier gas. The detection limits for CO, CO$_2$, CH$_4$, DME, and methanol were 5 × 10$^{-3}$ vol%. The carbon imbalance in all catalytic experiments was ±5%.

CO$_2$ conversion ($X_{\text{CO}_2}$), MeOH, and DME selectivity ($S_{\text{MeOH}}$, $S_{\text{DME}}$) were calculated as follows:

\[
X_{\text{CO}_2} (%) = \frac{C_{\text{CO}} + C_{\text{CH}_4} + C_{\text{MeOH}} + 2 \times C_{\text{DME}}}{C_{\text{CO}} + C_{\text{CH}_4} + C_{\text{MeOH}} + 2 \times C_{\text{DME}} + C_{\text{CO}_2}} \times 100
\]

\[
S_{\text{MeOH}} (%) = \frac{C_{\text{MeOH}}}{C_{\text{CO}} + C_{\text{CH}_4} + C_{\text{MeOH}} + 2 \times C_{\text{DME}}} \times 100
\]

\[
S_{\text{DME}} (%) = \frac{2 \times C_{\text{DME}}}{C_{\text{CO}} + C_{\text{CH}_4} + C_{\text{MeOH}} + 2 \times C_{\text{DME}}} \times 100
\]

\[
W_{\text{DME}} (\text{g DME} \cdot (\text{g cat} \cdot \text{h})^{-1}) = \frac{F_{\text{DME}} \times M_{\text{DME}}}{m_{\text{cat}}}
\]

where $C_t$ – outlet concentrations (vol%), $F_t$ – flow rate (mol h$^{-1}$), $n_t$ – mole amount (mol), $m_t$ – catalyst weight (g), $M_t$ – molecular weight (g mol$^{-1}$).

### 3 Results and discussion

#### 3.1 Characterization of catalysts

The catalysts were characterized by TEM, STEM, EDX-mapping, NH$_3$-TPD, XRD, low-temperature nitrogen adsorption, TPO, and H$_2$-TPR techniques. The In$_2$O$_3$ loading, textural parameters, and structural data obtained from XRD patterns of fresh and used In$_2$O$_3$, In$_2$O$_3$/HNT, and In$_2$O$_3$/Al-MCM-41/HNT are presented in Table 1. We can see
Table 1: In$_2$O$_3$ loading, $S_{\text{BET}}$, pore volume, and coherent scattering region

| Catalyst          | Textural characteristics | In$_2$O$_3$ |
|-------------------|--------------------------|-------------|
|                   | $S_{\text{BET}}$ (m$^2$·g$^{-1}$) | $V_p$ (cm$^3$·g$^{-1}$) | wt% | CSR (nm) |
| HNT               | 71                       | 0.16        | —   | —        |
| MCM-41/HNT        | 514                      | 0.42        | —   | —        |
| In$_2$O$_3$       | Fresh                    | 68          | 0.41| 100      | 13 |
| 10%               | Fresh                    | 62          | 0.13| 9.12     | 16.5 |
| In$_2$O$_3$/HNT   | Used                     | 61          | 0.13| 9.12     | 16.4 |
| 10% In$_2$O$_3$/   | Fresh                    | 412         | 0.31| 8.71     | 10.1 |
| Al-MCM-41/HNT     | Used                     | 410         | 0.3 | 8.71     | 10.1 |

*CSR – coherent scattering region.

Table 2: Acidity properties of catalysts and supports

| Sample                  | Weak and medium acid sites ($\mu$mol·g$^{-1}$) | Strong acid sites ($\mu$mol·g$^{-1}$) | Total acidity ($\mu$mol·g$^{-1}$) |
|-------------------------|-----------------------------------------------|--------------------------------------|----------------------------------|
| HNT                     | 22                                            | 122                                  | 144                              |
| Al-MCM-41/HNT           | 35                                            | 495                                  | 530                              |
| 10% In$_2$O$_3$/HNT      | 17                                            | 98                                   | 115                              |
| 10% In$_2$O$_3$/Al-MCM-41/HNT | 31                                             | 451                                   | 482                              |

As shown in Table 2, the acidity of unmodified halloysite is seriously lower than that of HNT/Al-MCM-41 due to the fact that modified with aluminum MCM-41 has strong acid sites on the surface [43]. The total amount of acid sites on the surface of In$_2$O$_3$ supported catalysts is reduced in comparison with supports. This fact can be explained by partial blocking of the pores by the indium oxide particles. For the catalysts after the experiment, we can say that total amount of acid sites remained the same.

Figure 1 shows the XRD patterns for fresh and used catalysts. According to XRD data, we can say that indium oxide on the surface 10% In$_2$O$_3$/HNT has cubic crystal phase structure [21] with crystallite size of 13 nm. In case of 10% In$_2$O$_3$/Al-MCM-41/HNT, the crystallite size of the indium oxide is slightly smaller – 10 nm. We assumed that this is due to the higher dispersion of indium oxide particles. As we can see from the diffraction patterns of the used catalysts (curve 3 and 5 on Figure 1), there are no significant changes in the number and composition of the peaks. We only note that for the used catalysts, the
peaks related to indium oxide are slightly smaller compared to fresh catalysts. Both used catalysts don’t have any considerable changes in the crystal structure – pore volume and CSR remained almost the same. This tells us that indium oxide particles are stable on the catalysts surface.

The In$_2$O$_3$/HNT and In$_2$O$_3$/Al-MCM-41/HNT catalysts were studied by TEM, STEM, and EDX techniques. Figure 2 shows the TEM images of the fresh and used catalyst In$_2$O$_3$/Al-MCM-41/HNT, which are obviously similar.

HNT were observed in both samples, and the images show that the nanotubes remained stable under reaction conditions. The same results were obtained for the In$_2$O$_3$/HNT catalyst. Also, in Figure 2b and d, we can see the structure of the mesoporous MCM-41 type silica deposited on the outer surface of HNTs. Some agglomerates of fresh and used In$_2$O$_3$/Al-MCM-41/HNT catalysts were studied by STEM and EDX-mapping. Results are shown in Figure 3. It is seen that the STEM images (Figure 3c and d) of both catalysts are similar. It can be noted that the indium particles are located mainly in the same place as the silicon particles in the case of both catalysts. Thus, it can be concluded that In$_2$O$_3$/Al-MCM-41/HNT catalyst contains two types of active sites on the surface – indium oxide particles, supported on silica, and alumina oxide particles.

Catalysts were examined by H$_2$-TPR (Figure 4) to study reducibility of catalysts. We can see that pure indium oxide isn’t reduced in the investigated temperature range. For the In$_2$O$_3$/Al-MCM-41/HNT, hydrogen consumption occurs only at ~170°C, indicating that the indium oxide nanoparticles are mainly localized on mesoporous silica of Al-MCM-41 type. This peak can be correlated to reduction of In$_2$O$_3$ surface and can also be attributed as indirect evidence of the formation of oxygen vacancies on the surface of indium oxide [57,58]. For the In$_2$O$_3$/HNT, there is also a peak at ~170, which could be assigned to reduction of In$_2$O$_3$ surface particles on the outer (SiO$_2$) tubes surface as for the In$_2$O$_3$/Al-MCM-41/HNT. Calculation of H$_2$-consumption over In$_2$O$_3$/Al-MCM-41/HNT shows us that 20% of In$_2$O$_3$ loading was reduced. In the case of In$_2$O$_3$/HNT, there are 16% In$_2$O$_3$ on 170°C peak. So, in In$_2$O$_3$/Al-MCM-41/HNT, a higher amount of surface active indium oxide is observed.

Based on the data obtained, it can be concluded that the 10% In$_2$O$_3$/HNT and 10% In$_2$O$_3$/Al-MCM-41/HNT catalysts contain two types of sites on their surface – In$_2$O$_3$ particles as a metal component for the synthesis of methanol and acidic sites of HNT or Al-MCM-41/HNT for its further dehydration to DME.

Figure 2: TEM images of fresh (a and b) and used (c and d) In$_2$O$_3$/Al-MCM-41/HNT catalyst.
Figure 3: TEM images (a,c), STEM images (b,d) and the corresponding Al, Si and In mapping of fresh (a,c) and used (b,d) In$_2$O$_3$/Al-MCM-41/HNT catalyst.
3.2 Catalytic results

The catalytic properties of the In$_2$O$_3$, 10% In$_2$O$_3$/HNT, and 10% In$_2$O$_3$/Al-MCM-41/HNT in CO$_2$ hydrogenation samples were measured at $T = 200$–300°C, $P = 10$–40 atm, and GHSV = 12,000 h$^{-1}$, respectively. Figure 5 shows temperature dependencies of CO$_2$ conversion and selectivity to MeOH (Figure 5a) and DME (Figure 5b) for In$_2$O$_3$, In$_2$O$_3$/HNT, and In$_2$O$_3$/Al-MCM-41/HNT catalysts. Only CO, H$_2$O, CH$_3$OH, and DME were detected as products; no hydrocarbons were identified.

Among the tested catalysts, In$_2$O$_3$ catalyst exhibited the lowest CO$_2$ conversion, but the highest methanol selectivity over the entire temperature range. This can be explained by the fact that no DME was observed in reaction products. It seems to be quite obvious, since this catalyst does not have required acid sites on its surface. We can see that CO$_2$ conversion increases with increasing temperature from 1% at 200°C up to 4% at 300°C. The selectivity for methanol, on the contrary, decreases with increasing temperature from 99% at 200°C to 65% at 300°C due to the CO formation by RWGS reaction.

In contrast to bulk In$_2$O$_3$ for the supported In$_2$O$_3$/HNT and In$_2$O$_3$/Al-MCM-41/HNT catalysts, DME appears in reaction products, due to the presence of acid sites. Temperature dependence for DME selectivity is similar to methanol in case of bulk In$_2$O$_3$ – the curve decreases with increasing temperature. There are some reasons for that. First, methanol dehydration is exothermic reaction, so increasing temperature leads to decrease of DME/MeOH equilibrium ratio. Second, at high temperatures, RWGS reaction (which is endothermic) contributes more to product distribution. So, it should be an optimal temperature, where the combination of formation rate of DME and CO$_2$ conversion will be maximum. Over the temperature range, we can see that on In$_2$O$_3$/Al-MCM-41/HNT there are higher values of CO$_2$ conversion and DME selectivity than on In$_2$O$_3$/HNT. Most likely, it is connected with higher surface area and more acid sites on In$_2$O$_3$/Al-MCM-41/HNT catalyst. Figure 6 shows temperature dependencies of DME production rate on In$_2$O$_3$, In$_2$O$_3$/HNT, and In$_2$O$_3$/Al-MCM-41/HNT catalysts.

The highest DME formation rate of 0.15 g$_{\text{DME}}$ (g$_{\text{cat}}$·h$^{-1}$) was observed at 250°C on In$_2$O$_3$/Al-MCM-41/HNT. Further,
the performance of the most active and selective catalyst In$_2$O$_3$/Al-MCM-41/HNT was studied in more detail.

It is well-known that with increasing pressure, the equilibrium of the CO$_2$ hydrogenation reaction shifts towards the products according to the Le Chatelier principle. So, we studied the pressure influence on catalytic activity in DME direct synthesis from CO$_2$ and H$_2$. The results are shown in the Figure 7. The experiments were carried out at $T = 250^\circ$C, GHSV = 12,000 h$^{-1}$.

As expected, with increasing pressure, CO$_2$ conversion and DME selectivity also increase, while MeOH passes through the maximum at 20 atm and then decreases. This is in accordance with thermodynamic equations for this system [9]. The highest value of the DME formation rate is observed at 4 MPa. Note that at temperatures higher than 250$^\circ$C, $W_{\text{DME}}$ decreased, despite an increase in the CO$_2$ conversion due to a significant drop of DME selectivity.

One of the key properties of the catalyst, in addition to activity, is the stability under reaction conditions. A series of experiments were carried out to investigate this aspect. Figure 8 shows the effect of time-on-stream on the outlet product concentrations and CO$_2$ conversion. The In$_2$O$_3$/Al-MCM-41/HNT catalyst was tested at 250$^\circ$C, the inlet mixture H$_2$:CO$_2$ = 3:1, and GHSV = 12,000 h$^{-1}$. Under these conditions, only CO, MeOH, and DME were detected as reaction products; methane appeared only in trace amounts. During 10 h on stream, no significant changes were observed either in the conversion of CO$_2$ or in the MeOH and DME selectivity. No significant changes in the selectivity of DME were observed after 8 h of the experiment. After that, catalyst remained in operation conditions for 24 h, and after that catalyst activity was recorded. All the parameters, such as methanol, DME selectivity, and CO$_2$ conversion, remained the same. In our view, these results mean that indium oxide particles remained stable as well as acid sites of modified HNT. In addition, the spent catalyst was tested by TPO. No carbon deposition was observed. This means that acidic properties of HNT (strength and number of acidic sites) are optimal for DME synthesis reaction and do not induce condensation reactions.

Up to now, almost no works of using indium oxide for direct synthesis of DME can be found in literature; only...
Comparison of catalyst activities in CO₂ hydrogenation to dimethyl ether

| Catalyst                  | T (°C) | Pressure (atm) | GHSV (mL·(g<sub>cat</sub>·h)<sup>-1</sup>) | W (DME) (g<sub>DME</sub>·(g<sub>cat</sub>·h)<sup>-1</sup>) | Reference |
|---------------------------|--------|----------------|---------------------------------------------|-------------------------------------------------|-----------|
| In₂O₃/Al-MCM-41/HNT       | 250    | 40             | 12,000                                      | 0.15                                            | This work |
| CIZO/SAPO-34              | 250    | 30             | 6,000                                       | 0.08                                            | [59]      |
| CZA/HZSM-5                | 260    | 30             | 1,500                                       | 0.12                                            | [28]      |
| CZZ/Fe/ferrierite         | 260    | 50             | 8,800                                       | 0.435                                           | [29]      |
| CZA/HZSM-5                | 260    | 50             | 3,000                                       | 0.29                                            | [30]      |
| CZZ/MI                    | 240    | 50             | 10,000                                      | 0.325                                           | [17]      |
| CZZ/BEA                   | 260    | 30             | 8,800                                       | 0.3                                              | [31]      |
| CZZ/WO₃/ZrO₂              | 260    | 30             | 4,333                                       | 0.27                                            | [32]      |
| PdZn/TiO₂-H-ZSM-5         | 270    | 20             | 3,500                                       | 0.025                                           | [33]      |

<sup>1</sup>CuO-In₂O₃-ZrO₂<sub>2</sub>; <sup>2</sup>CuO-ZnO-Al₂O₃; <sup>3</sup>CuO-ZnO-ZrO₂.

one work devoted to the study Cu–In–Zr–O catalyst mixed with SAPO-34 zeolite for direct DME synthesis is available [59]. Basically, all works on the direct synthesis of DME from CO₂ and H₂ are devoted to the study of copper catalysts mixed with zeolites. So, we compared the best In₂O₃/Al-MCM-41/HNT catalyst with literature data. Table 3 shows comparative data, in particular, experimental conditions (temperature, pressure, flow), CO₂ conversion, and DME selectivity. Since a fairly large number of works devoted to the hydrogenation of CO₂ to DME are currently presented in the literature, the table shows those with similar experimental conditions with this work, in particular – pressure of 10–50 atm, temperature of 200–300°C, and inlet composition H₂:CO₂ = 3:1.

Catalytic activity of In₂O₃/Al-MCM-41/HNT is lower than literature data, but study of these systems is at the very beginning. Such systems look very promising due to the following factors: the possibility of a significant increase in CO₂ conversion and selectivity for DME after optimization of the catalyst composition, its dispersion, the method of preparation, and adding of promoters. According to the literature data [60], catalysts based on indium oxide make it possible to obtain methanol with a selectivity of about 100%, and with the appropriate selection of the acid component, high DME yields can be achieved. It is also important that In₂O₃/MCM-41/HNT catalyst shows good stability, due to the fact that indium oxide particles do not sinter during the reaction, and acid sites remain stable in presence of water. There is a wide field for further catalyst improvement, including optimization of In₂O₃ morphology and interaction with the support, tuning acidic properties, doping by metals active in CO hydrogenation, such as Cu, Pd, Ga, and even Ni and Co. These points will be the subject of our further studies.

4 Conclusion

Indium oxide catalysts, bulk and supported on aluminosilicate HNTs and modified HNTs with ordered Al-MCM-41 silica arrays, were studied in CO₂ hydrogenation to DME. Based on data from physicochemical methods, such as XRD, S<sub>BET</sub>, FTIR, and H₂-TPR, we can suggest that these catalysts have two types of active sites – indium oxide particles, which are responsible for methanol formation, and acid sites of HNT, which are responsible for methanol dehydration to DME. The influence of temperature and pressure was studied. The best catalyst for CO₂ hydrogenation was In₂O₃/Al-MCM-41/HNT that provides 4% CO₂ conversion with DME selectivity 53% and DME production rate 0.15 g<sub>DME</sub>·(g<sub>cat</sub>·h)<sup>-1</sup> at 40 bar, GHSV = 12,000 h<sup>-1</sup>, and T = 250°C. It was shown that this catalyst didn’t lose activity after 40 h of experiment. So, it is very promising systems, based on new material for direct hydrogenation of CO₂ to DME.

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Appendix

Figure A1: Low-temperature nitrogen adsorption isotherms for the HNT, Al-MCM-41/HNT, In$_2$O$_3$/HNT, and In$_2$O$_3$/Al–MCM-41/HNT samples.

Figure A2: NH$_3$-TPD curves for HNT, In$_2$O$_3$/HNT, Al-MCM-41/HNT, and In$_2$O$_3$/Al–MCM-41/HNT catalysts.