Direct hydrogenation of CO₂ to dimethyl ether (DME) over hybrid catalysts containing CuO/ZrO₂ as a metallic function and heteropolyacids as an acidic function

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Abstract

Dimethyl ether (DME) is considered as a substitution of diesel oil. It can be used in diesel engines because of its high cetane number (> 55). The combustion process does not generate particle matter (PM) or sulphur oxides (SO_x) pollutions. One of the methods to obtain DME is direct synthesis from a CO₂ and H₂ mixture. On the other hand, CO₂ is an attractive reagent, which is a safe and economical source of carbon. The aim of this work was to obtain DME in the direct process from the mixture CO₂ and H₂ in the presence of hybrid catalyst. In these catalytic the CuO/ZrO₂ was selected as a metallic function. The montmorillonite K10 modified by heteropolyacids was selected as an acidic function. The catalysts were obtained by different preparation methods and contained various types of heteropolyacids. The catalysts were characterized by following methods: BET/BJH, XRD, SEM, DCS/TG, NH₃-TPD and FT-IR. The direct hydrogenation of CO₂ was performed in the high pressure fixed-bed flow reactor connected online with GC equipped with TCD and FID detectors. It was shown that both synthesis method of metallic function and the type of heteropolyacids have influence on the total catalytic activity of the hybrid catalyst. The acidity and thermal stability of HPAs are identified as the most important parameters having a decisive influence on the overall catalytic activity of the samples.

Keywords Dimethyl ether (DME) · CO₂ hydrogenation · Hybrid catalyst · CuO/ZrO₂ · Heteropolyacids

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Introduction

In recent years, the concentration of CO₂ in the atmosphere has been constantly increasing, having an impact on global climate change [1]. Therefore, a growing number of countries and researchers are interested in developing technologies to reduce CO₂ emissions and developing efficient carbon dioxide utilization systems. Synthesis of CO₂-derived chemicals includes synthesis of urea [2], CO [3], methane [4], methanol [5–7], dimethyl ether [8, 9], and other hydrocarbons [10]. Among them, dimethyl ether appears very promising because of its physicochemical properties and possibilities of applications.

Dimethyl ether (DME) is considered as a substitution of diesel oil in diesel engines due to its high cetane number (> 55). Undoubted advantage of using DME as a fuel would be a significant reduction of air pollution. During DME combustion, soot impurities are not generated, which is an important problem in engines running on traditional diesel oil. No toxic sulfur oxides are also emitted and the amount of nitrogen oxides is considerably decreased. Nowadays, dimethyl ether is produced from syngas (1), but also CO₂ and H₂ mixture can be used as a feedstock (2).

The DME synthesis proceeds in two steps: hydrogenation of CO/CO₂ into methanol (3, 4) and subsequent dehydration of methanol into DME (5). All reactions are exothermic, therefore, low temperature facilitates shifting the reaction balance towards the products. Moreover, in accordance to the Le Chatelier's principle an increase in pressure increases the amount of methanol produced.

Hybrid catalysts used in a direct dimethyl ether synthesis exhibit metallic and acidic functions. The metallic function is responsible for hydrogenation of carbon dioxide, whereas the acidic function contributes to dehydration of methanol. Mostly, CuO/ZnO catalysts with different additives [11–13] are used as the metallic functions. At the same time, zeolites [14, 15] or γ -Al₂O₃ [16] are commonly applied as the acidic function.

In commercial production of methanol from syngas, the catalytic system CuO/ZnO/Al₂O₃ is used. In this case, the elevated temperature (250–280 °C) and pressures up to 6–8 MPa are needed [17]. On the other hand, in industry production, the syngas is enriched with 5% of CO₂, which causes increased activity of copper-zinc catalyst. The commercial catalytic system has low activity in synthesis

of methanol from CO_2 and H_2 mixture under 250 °C [18] because of low reactivity of the CO_2 molecule. The increase of temperature makes the CO_2 activation much easier. At the same time, high reaction temperature facilitates the sintering of Cu crystals which leads to deactivation of the catalyst. Currently it is considered that copper plays a role of an active phase during catalytic synthesis of methanol. However, the type of the support must be very carefully considered, because metallic copper poorly interacts with CO_2 molecule [19]. The TiO_2 – SiO_2 modification of industrial catalyst improves CO_2 conversion from 15.8 to 40.7% and yield to methanol from 3.7 to 16.7% [20]. Similarly, Inui et al. [21] claims that Ga_2O_3 and Pd added to $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ improves catalytic activity in both CO and CO_2 hydrogenation.

Currently, it is considered that ZrO_2 addition facilitates CuO dispersion on the support surface. As a consequence, conversion of CO_2 increases [22]. Fisher and Bell in their study state that ZrO_2 improves copper's catalytic activity during methanol synthesis both from CO/H_2 and CO_2/H_2 mixtures [23]. What is more, during hydrogenation of CO_2 a considerable amount of water is formed, leading to a decreased catalytic activity of $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst [24]. This effect is associated with oxidation of active copper to copper oxide.

The dehydration of methanol into DME requires acidic centers on the catalyst's surface. The methanol molecule can be adsorbed on both Brønsted and Lewis acid centers [25]. The total concentration of acidic centers on the surface and their strength have an important influence on the catalytic activity. It is known that mainly weak and medium acid centers are responsible for dehydration of methanol, while the presence of strong acid centers favors receiving of olefins [26]. Commercial catalyst, with Al_2O_3 as the acidic function, rapidly loses its catalytic activity because of the hydrophilic character. Aluminum oxide adsorbs water which is formed during the reaction. This leads to blocking of the active centers on the catalyst surface, a problem that has to be overcome by high temperature [27].

Zeolites constitute yet another class of the catalysts of acidic character. The strength and the type of the acid centers on the catalyst's surface is related to the structure of zeolite and its Si/Al ratio. Commonly, H-ZSM-5 is used because of its better hydrophobic character than Al_2O_3 . However, due to the high reaction temperature (above 270 °C) hydrocarbons can be observed among created products. It is related to the high acidity of this zeolite. To improve its selectivity to DME and preserve high methanol conversion simultaneously, it is needed to decrease the amount of strong acid centers maintaining the total acidity at high level [28].

Heteropolyacids (HPAs) might be an interesting alternative to using Al_2O_3 or zeolites as the acidic function. Heteropolyacids are strong solid acids containing the Brønsted type of acid centres [29]. Two types of HPA structures are known: Keggin ($\text{XM}_{12}\text{O}_{40}^{n-}$) and Wells–Dawson ($\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$), where X-heteroatom e.g. P, Si, etc.; M-atom addenda e.g. W, Mo, etc. In catalytic reactions, HPAs with the Keggin structure are usually used because of higher total acidity and thermal stability [30]. The acidity of Keggin HPAs is connected with the type of addenda atom: $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) is more acid than $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPMo). At the same time HPAs have small specific surface area, therefore their immobilization on a high-surface support is necessary.

The aim of the studies was to obtain DME in direct route from CO_2 and H_2 mixture in the presence of hybrid catalyst. Promising results on the addition of ZrO_2 to the commercial catalyst ($\text{CuO}/\text{ZnO}_2/\text{Al}_2\text{O}_3$) were an inspiration of investigating a CuO/ZrO_2 as the metallic function. The montmorillonite K10 modified by heteropolyacids was selected as the acidic component. HPAs are well known in catalysis but—to the best of our knowledge—have not been used in the direct hydrogenation of CO_2 to DME yet. Therefore, our main focus was to examine the effect of the composition of the acid function of the hybrid catalyst (consisting of HPMo and HPW heteropolyacids deposited on montmorillonite K10) on the conversion and selectivity in the CO_2 to DME process. In our studies HPW and HPMo were impregnated on montmorillonite K10 which is thermally resistant and has a high surface area [31].

Experimental

Preparation of hybrid catalysts

The metallic component was prepared by co-precipitation method using NaOH or citric acid as a precipitant agent in accordance with the procedure presented in our previous article [32]. On the basis of the earlier results, Cu/ZrO_2 synthesized with **NaOH** (CZ_{NaOH}) and **citric acid** ($\text{CZ}_{\text{citric}}$) calcinated at $350\text{ }^\circ\text{C}$ was chosen as the metallic functions.

Prior to synthesis, the commercial montmorillonite K10 (**K10**) was at $120\text{ }^\circ\text{C}$ for 12 h. The amount of HPMo and HPW used for the synthesis was calculated to obtain theoretically one monolayer coverage of K10. The calculation was done considering the BET surface area of K10 and assumption that one Keggin unit occupies an area of $144\text{ }\text{\AA}^2$. Both heteropolyacids were introduced via wetness impregnation method resulting in **HPMo-K10** and **HPW-K10** systems. After the impregnation the solid was separated, washed, and dried at $90\text{ }^\circ\text{C}$ for 10 h.

The final hybrid catalysts was obtained by mechanical mixing of metallic and acidic components (grain size 0.64–1 mm) in a volume ratio 2:1.

Catalysts characterization

Specific area and porosity determination

The BET surface area, for both metallic and acidic functions were measured with nitrogen adsorption at $-196\text{ }^\circ\text{C}$ on Quantachrome Autosorb-1. Prior to measurements, samples were degassed for 18 h at $100\text{ }^\circ\text{C}$ under vacuum to remove adsorbed water and other surface impurities.

Crystal structure determination

Powder X-ray diffractions patterns (XRD) were collected using X'Pert PRO MDP diffractometer with Cu K α radiation, working in Bragg–Brentano geometry. The analysis was performed between 5° and 90° in 2 θ range with a measuring step 0.02°.

Morphology and surface composition

The morphology and surface composition of the synthesized samples were carried out using a high-resolution scanning electron microscope (JEOL JSM-7500F) with EDS-INCA PentaFETx3 system. Prior to the measurements, the samples were sprayed (K575X Turbo Sputter Coater) with 20 nm of chromium to increase a conductivity of the samples.

Thermal stability determination

Thermogravimetry/differential scanning calorimetry (TG-DSC) experiments were performed with a NETZSCH STA 409 thermobalance. Samples of about 20 mg were heated in air, at the rate of 10 °C/min, with endpoint at 700 °C.

Acidity measurements

The NH₃ temperature-programmed desorption (NH₃-TPD) measurements were carried out in quartz fixed-bed flow reactor connected online to the mass spectrometer (QMG 220 PRISMA PLUS). The signal of $m/z = 16$ (NH₃) was monitored during TPD. Prior to TPD run, the samples (50 mg) were activated in the He flow (40 mL/min) at 350 °C for 0.5 h. Next, the reactor was cooled down to 60 °C and a 3%NH₃/N₂ mixture was introduced for 0.5 h. Then, the sample were flashed in the He flow (40 mL/min) to remove physisorbed NH₃ and to obtain stable NH₃ line. TPD was performed from 60 to 680 °C with $\Delta T = 10$ °C/min under He flow (40 mL/min).

FT-IR spectroscopy

The FT-IR spectroscopy measurements were carried out using Excalibur series Digilab with a measure step 2 cm⁻¹ at room temperature. Number of scans taken during a single measurement was 100. For measurement purposes, the sample was ground in a mortar and applied to the silicon plate.

Catalytic activity tests

The hybrid catalysts were tested in the direct hydrogenation of CO₂ to DME. The reaction was performed in the high pressure fixed-bed flow reactor connected online with gas chromatograph (HP 5890 Series II) equipped with TCD and FID detectors. 1 cm³ of the hybrid catalyst, with the volume ratio of metallic and acidic component

equal to 2:1, was placed into the stainless reactor. Before the reaction, both the metallic and acidic function have been weighted separately and the mass of each catalyst was used to calculate STY_{DME} (Table 3). Prior to each reaction, the pre-treatment step of catalyst included reduction under atmospheric pressure in the flow of reduction mixture (5% H_2/N_2) equal to 60 mL/min at 200 °C for 3 h. Then, the reaction mixture (25% $CO_2 + 75\% H_2$) was passed over the catalyst bed at the flow rate equal to 10 mL/min in a temperature range 200–350 °C for 12 h. Next, the temperature was decreased to 220 °C. The catalytic reaction was carried out in the flow of reaction mixture (60 mL/min) and in the temperature range from 220 to 300 °C under the pressure of 4 MPa. Gas hourly space velocity was $3600 h^{-1}$.

The CO_2 conversion and the selectivity to DME, methanol (MeOH), CO and CH_4 were calculated as follows:

$$CO_2 \text{ conversion} = \frac{\text{moles } CO_2, \text{input} - \text{moles } CO_2, \text{output}}{\text{moles } CO_2, \text{input}} \cdot 100; (\%)$$

$$\text{selectivity}_i = \frac{n_i \cdot \text{moles product}_i}{n_i \cdot \text{moles}_{DME} + n_i \cdot \text{moles}_{MeOH} + n_i \cdot \text{moles}_{CO} + n_i \cdot \text{moles}_{CH_4}} \cdot 100; (\%)$$

The space–time–yield to DME (STY_{DME}) was defined as follows:

$$STY_{DME} = \frac{\text{moles}_{DME} \cdot V_{CO_2} \cdot M_{DME}}{\text{moles}_{CO_2, \text{output}} \cdot w_{kat} \cdot 22,4} \cdot 60; \left(\frac{g_{DME}}{g_{kat} \cdot h} \right)$$

where n_i is the number of carbon atoms in product, V_{CO_2} (cm^3/min) is the volumetric rate of CO_2 , M_{DME} is the molar mass of dimethyl ether and w_{kat} is the mass of catalyst.

Results and discussion

Physicochemical characterization of the prepared catalysts

As mentioned earlier, the results presented in this publication are a continuation of the previous studies. Consequently, the physicochemical characterization of metallic components has been presented earlier [33]. It was shown that surface properties and catalytic activity strongly depend on the precipitation agent and the temperature of calcination. The metallic function prepared with NaOH shows the highest specific surface area and the highest active copper surface. At the same time the increase of the calcination temperature leads to decrease of the specific surface area and sintering of Cu crystals.

The BET surface area, total pore volume, and pore size results for acidic functions are presented in Table 1. Among them, montmorillonite K10 ($252 m^2/g$) shows the highest specific surface area. The impregnation of K10 with HPAs leads to a decrease of the specific surface area of K10. The deposition of HPMo and HPW

Table 1 Characterization of acidic functions: K10, HPW-K10, HPMo-K10

Acidic function	S_{SA} (m ² /g)	Pores size BJH _{des} (Å)	Pores volume BJH _{des} (cm ³ /g)	t-Method micropore surface area (m ² /g)	t-Method micropore volume (cm ³ /g)
K10	252	38.6	0.3	0	0
HPMo-K10	135	38.2	0.2	35	0.01
HPW-K10	91	38.2	0.1	49	0.02

S_{SA} specific surface area

on K10 causes the reduction of the specific surface area to 135 m²/g and 91 m²/g, respectively.

At the same time, application of heteropolyacids on the surface of K10 causes a significant decrease of pore volume from 0.33 cm³/g (K10) to 0.08 cm³/g and 0.15 cm³/g for HPW-K10 and HPMo-K10, respectively. Moreover, the micropores appeared when HPAs were impregnated on K10.

XRD patterns of the pure montmorillonite K10, HPW-K10, and HPMo-K10 are shown in Fig. 1. Impregnation of K10 with heteropolyacids (HPW-K10 and HPMo-K10) causes a slight decrease in intensity (for $2\theta = 20.8; 26.6; 42.4; 50.1^\circ$) or disappearance of some reflexes characteristic for K10 (for $2\theta = 19.1; 36.5; 39.4; 45.7^\circ$). This is due to a partial reduction in crystallinity of montmorillonite K10 after application of HPW and HPMo. At the same time, low intensity reflexes appear from the

Fig. 1 XRD patterns obtained for montmorillonite K10, HPW-K10 and HPMo-K10. (circle)— $H_3Mo_{12}O_{40}P$, (filled circle)— $H_3PW_{12}O_{40}$

heteropolyacid present in the system: $2\theta = 17.8; 20.6; 34.5; 59.9; 61.9^\circ$ (for HPW-K10) and $2\theta = 7.9; 9.2; 17.8; 20.0; 28.3; 35.0; 36.4^\circ$ (for HPMo-K10).

In order to determine the thermal stability of the acid components of the hybrid catalysts, the differential scanning calorimetry with thermogravimetry measurements were carried out. The obtained thermographs are shown in Fig. 2.

The DSC thermogram of montmorillonite K10 exhibits one explicit endothermic peak at 106°C , which corresponds to the removal of physisorbed water. Montmorillonite K10 (black line) is thermally stable within the entire measured temperature range. The thermogram of pure HPW (gray line) shows two endothermic peaks and one exothermic peak; the endothermal peaks have maxima at 68 and 212°C . The former one corresponds to the removal of physisorbed water and the latter one is due to the desorption of two protons and the structural oxygen with the production of water molecule according to the equation below (6) [34]:

The high temperature exothermic peak appearing at 607°C corresponds to the collapse of the Keggin structure due to the loss of structural water [35]. The deposition of HPW on K10 results in the shift of the high-temperature exothermic peak to 565°C (light grey line). The collapse of the Keggin structure proceeds at a lower temperature in comparison with the pure HPW. At the same time, only one endothermic peak at 106°C is present. On the thermogram of the pure HPMo (dash dot line) two endothermic peaks with maxima at 87°C and 128°C are visible, which are assigned to the removal of physisorbed and structural water, respectively. At

Fig. 2 DSC thermograms obtained for montmorillonite K10 (black line), HPW (gray line), HPW-K10 (light grey line), HPMo (dash line) and HPMo-K10 (dash dot line)

the temperature of 442 °C, an exothermic peak is present. Then, the decomposition of the Keggin structure, preceded by the removal of another water molecule, takes place. The impregnation of HPMo on K10 results in shifting the maximum of exothermic peak to 402 °C, then the thermal stability of acidic function decreases. Furthermore, also endothermic peak at 105 °C is present. The above studies clearly indicate that the acid component modified by HPW is more thermally stable than that modified by HPMo.

The results obtained by the TPD-NH₃ method are presented in Fig. 3 and Table 2.

The NH₃-TPD desorption curves registered for acidic components of the hybrid catalysts are presented in Fig. 3. The obtained curves (red lines) were separated in the deconvolution process into components (green lines) with peak maxima corresponding to acid centers of a given strength. The acid sites were classified into the very weak (<150 °C) connected with physisorption of ammonia, weak (150–250 °C), medium (250–350 °C) and strong (350–500 °C).

Fig. 3 TPD-NH₃ curves of acidic functions

Table 2 Number of acidic sites and distribution of acid strengths

Acidic function	Concentration of acidic centers (mmol/g)				Total concentration of acidic centers (mmol/g)
	Very weak 60–150 °C	Weak 150–250 °C	Medium 250–350 °C	STRONG 350–500 °C	
K10	0.17	0.07	0.13	0.08	0.45
HPMo-K10	0.29	0.26	0.41	0.08	1.05
HPW-K10	0.38	0.38	0.52	0.48	1.76

Due to the HPW and HPMo decomposition at 565 and 402 °C, respectively (Fig. 2) the peaks which appear above these temperatures were not included in the acidity calculation.

The unmodified montmorillonite K10 contains very weak, weak, medium and strong acidic centers within which very weak and medium acid centers dominate. Before the modification, the total concentration of acidic centers for K10 is 0.45 mmol/g, while after HPAs deposition its acidity significantly increased to 1.05 mmol/g and 1.76 mmol/g for HPMo-K10 and HPW-K10, respectively. After addition of heteropolyacids, the participation of weak acid centers enhanced.

It is worth noticing that in this case the concentration of strong acid centers significantly increased (0.483 mmol/g). At the same time, when HPMo is introduced, the medium acid centers exhibit the largest concentration (0.414 mmol/g).

In order to determine surfaces morphology, SEM analysis was done (Fig. 4).

The montmorillonite K10 (Fig. 4a) is characterized by the expanded, spongy surface. After HPW impregnation (Fig. 4b) block structures are observed. On the other hand, HPMo immobilization on K10 (Fig. 4c) leads to the appearance of fine-grained layered structures.

In order to check the interaction between metallic and acidic functions, the FTIR measurements were done. The results obtained for $\text{CZ}_{\text{NaOH}} + \text{HPMo-K10}$ and $\text{CZ}_{\text{NaOH}} + \text{HPW-K10}$ are shown in Fig. 5a, b, respectively. The displacement of the characteristic peaks coming from the Keggin anion toward lower frequency is present after mechanical mixing of metallic and acidic functions. For $\text{CZ}_{\text{NaOH}} + \text{HPMo-K10}$ (Fig. 5a) the following vibrations are shifted: P-O_a (from 1064 to 1045 cm^{-1}) and Mo=O_d (from 962 to 951 cm^{-1}). Moreover, the

Fig. 4 SEM micrographs of acidic functions: **a** montmorillonite K10; **b** HPW-K10; **c** HPMo-K10

Fig. 5 FTIR results for: (1) K10, (2) CZ_{NaOH}, (3) HPMo-K10, (4) CZ_{NaOH}+HPMo-K10 before reaction, (5) CZ_{NaOH}+HPMo-K10 after reaction, (6) HPW-K10, (7) CZ_{NaOH}+HPW-K10 before reaction, (8) CZ_{NaOH}+HPW-K10 after reaction

Mo=O_d vibrations (870 cm⁻¹) disappear. For CZ_{NaOH}+HPW-K10 (Fig. 5b) the part of characteristic peaks is also shifted: vibrations related to P-O_a (from 1080 to 1060 cm⁻¹), W=O_d (from 982 to 962 cm⁻¹) and W-O_b-W (from 889 to 893 cm⁻¹). Also, at 1100 cm⁻¹ a shoulder appears. This effect informs about the asymmetry of the P-O_a vibrations induced by the HPA non-conductive interactions with oxides. At the same time the peaks corresponding to the selected vibrations shift as a result of changing proton-anion interaction within HPA. This effect can result from the decrease of hydration rate or strong interaction between the Keggin anion with the active centers of the support.

The FTIR results obtained for CZ_{NaOH}+HPMo-K10 after reaction (Fig. 5a) demonstrate the absence of the characteristic peaks derived from HPMo Keggin structure. Along with the DSC thermograms (Fig. 3) this result indicates the collapse of the HPMo Keggin structure during the catalytic reaction. By contrast, the FTIR spectrum of CZ_{NaOH}+HPW-K10 (Fig. 5b) after reaction contains peaks derived from the HPW Keggin structure. However, most of them are even more shifted toward lower frequencies. This indicates changes in the HPW Keggin structure during the catalytic reaction. Therefore, HPMo is less stable than HPW under the reaction conditions. Damyanova et al. observed similar effect when heteropolyacids were impregnated on ZrO₂ [35]. They observed that the temperature of HPMo decomposition decreased with the increasing amount of ZrO₂ because of the strong HPMo—ZrO₂ interactions. At the same time, an interplay between HPW and ZrO₂ is weaker (HPW decomposition higher than 500 °C).

Results of catalytic activity measurements

The obtained samples were tested in the direct CO₂ hydrogenation to DME. The focus was to examine the effect of the heteropolyacids deposition on montmorillonite K10 on the conversion and selectivity in the studied process. Apart from DME, other products of the reaction, namely methanol, methane, and CO were also detected.

The obtained catalytic results are presented in Table 3 and Fig. 5.

Table 3 CO₂ conversion and selectivity to different products for all catalytic systems

Hybrid catalyst w _{kat} (g)	Temperature (°C)	Conversion CO ₂ (%)	Selectivity (%)				STY _{DME} (g _{DME} /g _{kat} h)
			DME	MeOH	CO	CH ₄	
CZ _{NaOH} +K10 1.140	220	4.2	9.1	54.9	35.8	0.1	1.8
	240	4.4	11.3	31.4	57.1	0.2	4.8
	260	7.5	8.6	16.4	74.7	0.2	8.0
	280	13.8	6.3	10.1	83.3	0.3	11.1
	300	18.1	5.9	8.6	84.8	0.7	15.1
CZ _{NaOH} +HPW-K10 1.239	220	2.8	43.1	12.8	43.8	0.2	9.1
	240	4.6	24.6	8.9	66.2	0.3	11.7
	260	10.3	14.1	6.0	79.4	0.5	14.6
	280	16.0	11.1	5.4	82.7	0.8	18.9
	300	18.6	11.1	5.9	81.8	1.2	23.8
CZ _{NaOH} +HPMo-K10 1.112	220	5.2	23.7	34.6	41.0	0.6	4.7
	240	5.4	15.8	18.5	64.7	1.0	7.5
	260	9.9	10.7	11.7	75.9	1.8	9.4
	280	15.6	5.9	7.3	84.5	2.4	10.7
	300	18.4	4.3	6.9	82.5	6.3	9.6
CZ _{citric} +K10 1.250	220	5.1	16.8	62.4	19.4	1.4	1.5
	240	3.4	19.2	43.1	37.1	0.6	4.8
	260	4.3	25.4	24.4	49.2	1.0	13.7
	280	7.5	15.6	16.5	66.5	1.5	14.4
	300	8.8	14.3	10.3	73.3	2.1	23.2
CZ _{citric} +HPW-K10 1.066	220	4.3	60.3	17.1	20.1	2.5	9.1
	240	2.7	46.5	14.5	36.9	2.1	13.6
	260	4.9	32.0	11.6	54.4	2.1	18.2
	280	8.9	26.9	11.0	59.1	3.1	23.2
	300	14.1	14.1	6.9	75.9	3.1	24.8
CZ _{citric} +HPMo-K10 1.029	220	1.8	16.7	55.9	22.4	5.0	2.4
	240	2.6	19.6	34.2	39.2	7.1	5.8
	260	4.7	15.8	22.6	53.7	7.9	9.7
	280	8.6	11.2	13.3	65.9	9.7	12.6
	300	13.3	6.6	7.6	73.4	12.4	12.4

The CO₂ conversion increases with increasing temperature for all catalytic systems. This parameter practically does not depend on the type of acidic function. The highest CO₂ conversions were obtained for the hybrid catalysts with metallic function synthesized by co-precipitation method with NaOH. As described in our previous paper [32], for the CZ_{NaOH} metallic function the active copper phase is better dispersed on the catalyst surface. This suggests that CuO in the CZ_{NaOH} component is better exposed to substrates than in the CZ_{citric} component what results in higher CO₂ conversion.

At the same time, the catalytic selectivity strongly depends on the types of both components of the hybrid system (acidic and metallic functions) as well as the temperature of the reaction.

The catalysts with unmodified acid function (CZ_{NaOH}+K10 and CZ_{citric}+K10) lead the reaction towards methanol (at lower temperatures) and CO (at higher temperatures) as the main products. It implies that unmodified acid function (K10) does not work efficiently. The K10 surface has too low total concentration of acid sites (0.45 mmol/g) to entirely dehydrate methanol into DME. Instead of that, at higher temperatures, the endothermic RWGS reaction is favored in accordance with the reaction (7):

When the acidic component is composed of montmorillonite K10 modified with HPW, the selectivity to DME is improved, regardless of the type of metallic function.

The addition of HPW on K10 causes also a significant decrease of selectivity to methanol. The HPW impregnation on K10 surface improves dehydration of methanol. The HPW-K10 surface has the highest total acid sites concentration (1.76 mmol/g). At the same time, mainly weak and medium acid centers (0.896 mmol/g) with a lower number of strong acid centers (0.483 mmol/g) are present, what favors production of DME. However, a lot of CO is formed as a by-product.

When the acidic component is composed of montmorillonite K10 modified with HPMo, the selectivity to DME is not improved when CZ_{citric} is used as the metallic function. When CZ_{NaOH} is used, the selectivity to DME is enhanced in the temperature range from 220 to 260 °C. The highest selectivity to DME (60.3% at 220 °C) is obtained for CZ_{citric}+HPW-K10.

At the same time, impregnation of K10 by HPMo leads to the improved selectivity to CO and CH₄. The surface of HPMo-K10 has a lot of weak and medium acid centers (0.673 mmol/g) and a little of strong acid centers (0.083 mmol/g), but total acidity is lower (1.05 mmol/g) than for HPW-K10. Furthermore, using CZ_{citric} as metallic function favors CH₄ appearance. For all catalytic systems, the amount of methanol decreases with the increase of temperature. Meantime, the quantity of CO definitely increases. This observation suggests that when the reaction temperature increases, the contribution of RWGS reaction also increases.

The most efficient catalyst in the whole temperature range is CZ_{citric}+HPW-K10 system (Table 3). The modification of acid function with HPW always improves

STY_{DME} , regardless of the type of metallic function, in comparison with the catalysts containing unmodified acid function (K10). On the other hand, the influence of HPMo addition depends on the type of metallic function used in the catalytic system and on the temperature of the process. The STY_{DME} increases (in comparison with catalyst containing the unmodified acid function) in the temperature range from 220 to 240 °C, but in the temperature range from 260 to 300 °C the STY_{DME} decreases when CZ_{NaOH} is used as the metallic function. While hybrid catalyst contains CZ_{citric} as a metallic function, the STY_{DME} rises in the temperature range 220–260 °C. At higher temperatures, STY_{DME} decreases progressively. That indicates a strong interaction between the metallic and acidic components of the hybrid catalyst.

The direct comparison of the catalytic results reported in the present manuscript with data available in the literature is not straightforward. This is mostly due to significant differences between the conditions of the conducted catalytic reaction such as pressure, contact time or composition of the reaction mixture. Recently, Naik et al. reported the catalytic activity of $CuO-ZnO-Al_2O_3$ and $CuO-ZnO-ZSM-5$ (Si/Al=60) catalysts (200 °C, 5 MPa, GHSV=3000 mL/g_{kat}h) [36]. The conversion of CO_2 was 15% and 29%, respectively. At the same time the selectivity to DME for catalyst containing alumina was 5% and 75% for catalyst with ZSM-5. Frusteri et al. [37] described the catalytic results for $CuZnZr$ -MFI hybrid catalyst (240 °C, 3 MPa, GHSV=2500 mL/g_{kat}h). In these conditions, the reported conversion of CO_2 reached 19% and selectivity to DME 8.6%. Change of the acid component to FER (Si/Al=8) (240 °C, 3 MPa, GHSV=8800 NL/g_{kat}h) leads to slightly decreasing conversion of CO_2 (17%) and increasing selectivity to DME (42%) [38]. The most efficient catalyst (CZ_{citric} +HPW-K10) shows 47% selectivity to DME and 5% CO_2 conversion. This result fits well into the activities reported above; DME is produced with relatively high selectivity, but lower conversions of CO_2 are observed.

Conclusions

The direct CO_2 hydrogenation to dimethyl ether (DME) was studied over hybrid catalysts. In these catalytic systems, the mixture of copper and zirconium oxides—obtained via different preparation methods—was selected the metallic component. The montmorillonite K10 modified by heteropolyacids was selected as the acidic component. Two types of heteropolyacids were chosen: phosphorus-molybdenum and phosphorus-tungsten ones.

It was shown that catalytic activity of the hybrid catalysts is a result of metallic and acid components activity. Both synthesis method of metallic function and the type of HPA have influence on the total catalytic activity of hybrid catalysts. It is due to the evolving surface properties such as specific surface area, crystallinity, and acidity. The addition of HPAs clearly influences the activity of the hybrid catalyst. The acidity and thermal stability of HPAs are identified as the most important parameters having a decisive influence on the overall catalytic activity of the samples. The results show that the phosphorous-tungsten heteropolyacid (HPW) has high surface acidity and is more stable in the reaction conditions than phosphorous-molybdenum one, therefore its presence most often had a positive effect on the catalytic performance of the studied

systems. However, the final effect depends on the type of metallic function and the type of heteropolyacids.

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