Article

Raw Biogas as Feedstock for the OCM Process

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Abstract: The paper presents the research results obtained in the process of oxidative coupling of methane, in which unpurified biogas was used as the feedstock. Biogas obtained from two kinds of biomass materials, i.e., plant materials (potato and beet pulp, Corn-Cob-Mix—biogas 1) and animal waste (waste from fish filleting—biogas 2) was considered. The influence of temperature, the ratio of methane/oxygen and total flows of feedstock on the catalytic performance in oxidative coupling of methane process was investigated. Comparative tests were carried out using pure methane and a mixture of methane-carbon dioxide to simulate the composition of biogas 2. The process was carried out in the presence of an Mn-Na₂WO₄/SiO₂ catalyst. Fresh and used catalysts were characterised by means of powder X-ray diffraction, X-ray photoelectron spectroscopy, and low-temperature nitrogen adsorption techniques. In oxidative coupling of methane, the type of raw material used as the source of methane has a small effect on methane conversion (the differences in methane conversion are below 3%), but a significant effect on the selectivity to C₂. Depending on the type of raw material, the differences in selectivity to C₂ reach as high as 9%. However, the Mn-Na₂WO₄/SiO₂ catalyst operated steadily in the tested period of time at any feedstock composition. Moreover, it was found that CO₂, which is the second main component of biogas in addition to methane, has an effect on catalytic performance. Comparative results of catalytic tests indicate that the CO₂ effect varies with temperature. Below 1073 K, CO₂ exerts a small poisoning effect on methane conversion, while above this temperature the negative effect of CO₂ disappears. In the case of selectivity to C₂₊, the negative effect of CO₂ was observed only at 1023 K. At higher temperatures, CO₂ enhances selectivity to C₂₊. The effect of CO₂ was established by correlating the catalytic results with the temperature programmed desorption of CO₂ investigation. The poisoning effect of CO₂ was connected with the formation of surface Na₂CO₃, whose concentration depends on temperature.

Keywords: biogas; OCM; oxidative coupling of methane; Na₂WO₄/Mn/SiO₂ catalyst; methane; biomass

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1. Introduction

The oxidative coupling of methane has been extensively studied for over 30 years, but the feedstock was usually pure methane; meanwhile, one of the important sources of methane is biogas. Biogas is produced by microorganisms in anaerobic conditions from organic matter. To produce biogas, different organic feedstocks such as municipal, industrial, agricultural waste, waste from slaughterhouses, food waste products, and energy crops can be used [1–6]. It was recently demonstrated that industrial fish processing waste can be efficiently converted to methane in a mono-digestion process [7]. Biochemical potential methane of fish waste was 540.5 mL/g_{VS} (vs—volatile solids) [7], whereas the potential of methane production from waste activated sludge (WAS), depending on the

organic co-substrates (agricultural, industrial, municipal) used, were in the range of 90–1480 mLCH₄/gV_{Sadded} [6]. Optimization of methane fermentation process of food waste products made it possible to obtain the biogas in an amount 740.4 cm³ · g_{ODM}^{−1} (ODM—Organic Dry Matter) with 68.6% methane, at the substrates mixture containing 50% of meat, 40% dairy products, 10% fruit and vegetables [2]. Unfortunately, the use of biogas directly as a feedstock for synthesis is difficult due to its varied composition and the presence of impurities. The biogas yield and composition are influenced by the temperature, pH, type of feedstock, organic loading rate, hydraulic retention time, C/N (carbon/nitrogen) ratio, the presence of pollutants such as heavy metals compounds, digester type and pretreatment method [1–10]. Typically, in addition to methane, biogas contains 20–50% of CO₂ and other trace compounds such as H₂S, NH₃, siloxanes, chlorines, H₂ and O₂, various volatile organic compounds (VOCs) [8,9,11]. H₂S and other sulfur compounds are abundant in agricultural biogas, while silicon compounds are found in low or undetectable amounts [10]. The high amounts of halogenated and organic silicon compounds in landfill biogas is largely the result from industrial waste [8]. The concentrations of VOCs can be high in biogas, especially if they came from organic materials with compounds originating from the biological degradation process, like aromatics and terpenes [8].

Biogas, after cleaning and upgrading, is currently used primarily for the production of electricity/heat, steam; it can also be used as engine fuel, or injected into the gas network. However, recently there has been a growing interest in the possibility of using biogas as a raw material for syntheses. Previous research with the use of biogas included, among others: the process of methanation of carbon dioxide contained in biogas enriched with hydrogen [12–14], co-production of methane and urea (bio methane—urea co-production) [15], conversion of biogas to: syngas, “bio hydrogen” [16–30], or liquid fuels as a result of the contact of biogas with the fraction of liquid crude oil containing a catalyst [31]. The possibility of direct conversion of biogas to methanol is also investigated with the use of methanotrophs—aerobic bacteria capable of using both methane and carbon dioxide as a carbon source for methanol synthesis [32–34]. The attractiveness of this type of solution is related to, *inter alia*, the possibility of using purified or untreated biogas [32], while in the case of catalytic processes, deep cleaning is usually necessary to remove impurities causing deactivation of the catalyst. Although biogas can be purified and upgraded so that the purity of methane is >97%, it is an expensive process [35–37]. The cleaning and upgrading methods, as well as the methods of biogas utilisation, have been described in many reviews [38–46]. In recent years some attention has also been paid to techno-economic analyses of the OCM process in order to assess the suitability of biogas as a feedstock for the OCM process [47,48]. The conducted analyses show that biogas, as a cheap and easily available raw material, can be an important source of methane for the OCM process. One of the proposed solutions with the use of biogas is to increase its calorific value as a result of its conversion in the OCM process [49,50].

Up to now many studies concerning the application of pure methane and different mixtures of gases with simulated biogas are investigated in OCM process [49–55]. In the tests carried out with the use of pure methane and the mixture CH₄ + H₂S + O₂ + N₂ + CO₂ as a feed stream, under OCM process conditions, the Mn-Na₂WO₄/SiO₂ catalyst worked stably during 100 h of tests [49,51]. The presence of various pollutants present in biogas may have both a positive and negative impact on the OCM process and the stability of the catalyst operation. Trace amounts of chlorine derivatives (compounds potentially present in biogas) have a positive effect on the selectivity to C₂ and ethylene/ethane molar ratio [52]. The addition of steam to the stream of reactants, when the Mn-Na₂WO₄/SiO₂ catalyst was used, also had a beneficial effect on the OCM process [50,52–54], especially when H₂O was added at the beginning of the process [53,54]. On the other hand, the presence of H₂S in the stream of reactants reduces the methane conversion and selectivity to C₂, but the deactivation of the catalyst is significantly influenced by the concentration of H₂S, O₂ and the temperature at which the process is carried out. [27,49]. Carbon dioxide occupies a special place among the components of biogas, because its contribution to biogas

can be over 50% in volume. Research shows that the presence of carbon dioxide in the feed stream plays an important role in the OCM process, and the effect of its presence depends mainly on the process conditions (temperature and the methane/oxygen molar ratio), its concentration in the stream, and the type of catalyst [52,55]. However, the use of raw unpurified biogas as a feedstock without purification has not been a subject of research so far.

This paper presents the results of tests in which two types of crude unpurified biogas were used as the feedstock in the OCM process carried out in the presence of the $2\text{Mn}_5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst. Biogas was obtained from plant biomass (including the most popular substrate in the world for biogas plants, which is corn silage) and animal waste. Biomass from animal waste is difficult to manage but, as shown by recent studies, it has a high potential for methane production in the mono-digestion process [7]. These two types of biogas were selected in order to compare the properties of biogas obtained from plant biomass and animal waste in terms of their use as a source of methane for the OCM process. The obtained results were compared with those obtained for pure methane and for a mixture simulating the composition of biogas 2, i.e., containing methane and carbon dioxide in the same volume ratios as in biogas 2.

2. Results and Discussion

2.1. Physicochemical Characterization

The low temperature N_2 adsorption data for the multicomponent $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst before and after the catalytic reaction are summarized in Table 1. The data for individual SiO_2 , Mn/SiO_2 , and $\text{Na}_2\text{WO}_4/\text{SiO}_2$ components are provided as reference. The analysis of low temperature N_2 adsorption isotherms reveals that the deposition of manganese on silica support has only a small influence on the total pore volume (V_{total}) and specific surface area (S_{BET}), while the deposition of the Na_2WO_4 phase leads to the destruction of a porous structure of the support. These dramatic changes in S_{BET} and V_{total} are due to the phase transformation of amorphous silica into crystalline α -cristobalite occurring in the thermal treatment of the catalysts. It has been found that such phase transformation of amorphous silica to either α -cristobalite or quartz is facilitated by sodium cations [56,57] originating, in our case, from Na_2WO_4 . Amorphous silica transforms into α -cristobalite in the temperature range 1743–1973 K [56–58]. However, it was found that in the presence of sodium ions, the transformation of silica into α -cristobalite is possible already in the temperature range of 1023–1123 K [56,57,59,60]. Low-temperature SiO_2 transformation to cristobalite was also observed in the case of the Na/SiO_2 and $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts [57,61]. It was also found that the presence of sodium in the form of NaOH leads to crystallization only at 1173 K, and the α -cristobalite phase is accompanied by the α -tridimite phase (at 1023 K, only the amorphous phase is present) [57]. In the samples containing no sodium ions, but containing manganese or tungsten ions, the low-temperature transformation of silica to α -cristobalite did not occur. The presence of crystalline α -cristobalite in all the samples containing Na_2WO_4 is confirmed with XRD (Figure 1). For all of those samples, reflections characteristic of the crystal phases of quartz and Na_2WO_4 were present simultaneously. The intensity of reflections due to quartz increases after the OCM reaction, regardless of the presence of CO_2 , which suggests a further phase transformation during the process.

Table 1. Porosity and phase composition of fresh and used catalysts ^a.

Sample	S_{BET} (m^2g^{-1})	V_{Total} (cm^3g^{-1})
SiO ₂	474	0.83
Mn/SiO ₂	427	0.78
Na ₂ WO ₄ /SiO ₂	2.1	<0.01
Mn-Na ₂ WO ₄ /SiO ₂	1.9	<0.01
Mn-Na ₂ WO ₄ /SiO ₂ ^a	1.9	<0.01
Mn-Na ₂ WO ₄ /SiO ₂ ^b	2.0	<0.01
Mn-Na ₂ WO ₄ /SiO ₂ ^c	1.9	<0.01
Mn-Na ₂ WO ₄ /SiO ₂ ^d	1.9	<0.01

^a Used sample after process with mixture of CH₄ + O₂ + He (for all used catalysts the reaction conditions in caption to Figure 1). ^b Used sample after process with mixture of CH₄ + CO₂ + O₂ + He. ^c Used sample after process with mixture of biogas 1 + O₂ + He. ^d Used sample after process with mixture of biogas 2 + O₂ + He.

Figure 1. XRD patterns of (a) fresh (A) SiO₂, (B) Mn/SiO₂, (C) Na₂WO₄/SiO₂ and (D) Mn-Na₂WO₄/SiO₂ samples and (b) Mn-Na₂WO₄/SiO₂ samples after OCM process using mixture of (A) biogas1 + O₂ + He and (B) biogas2 + O₂ + He (C) CH₄ + O₂ + He, (D) CH₄ + O₂ + CO₂ + He. Reaction conditions: T = 1053 K; GHSV = 11,550 cm³ · g^{−1}_{cat} · h^{−1}; m_{cat} = 400 mg; total flow rate = 77 cm³ · min^{−1}; molar ratio (in all cases); V_{CH₄}:V_{O₂}:V_{He + CO₂ + N₂} = 14.4:4.3:58.3; Reaction time = 220 min.

Moreover, in the fresh and used Mn-Na₂WO₄/SiO₂ samples, small reflections characteristic of crystalline Mn₂O₃ were detected. The Mn₂O₃ signals are not observed for the Mn/SiO₂ sample, which can be explained either by high dispersion of the manganese phase on amorphous SiO₂ in the absence of Na₂WO₄ or by a relatively low detection limit of the XRD technique. For the Mn/SiO₂ sample, only small reflections characteristic of the Mn₃O₄ spinel phase were found. In the fresh and used Mn-Na₂WO₄/SiO₂ catalyst, they overlap with much more intense peaks of α-cristobalite and Na₂WO₄. To conclude, the XRD results of the used catalysts indicated the absence of significantly abundant new structures, regardless of the type of feedstock.

The chemical composition of the Mn-Na₂WO₄/SiO₂ catalyst surface were determined using the XPS spectra. Figure 2 shows the XPS Mn 2p, W 4f and O 1s spectra for the fresh and used catalysts. The Mn 2p spectra of all catalysts (fresh and used) show a doublet of Mn 2p_{3/2}–Mn 2p_{1/2}, at approximately 642 eV and 653 eV.

Figure 2. XPS spectra of (a) Mn 2p, (b) W 4f and (c) O 1s level for fresh and used Mn-Na₂WO₄/SiO₂ catalysts. (A) fresh catalyst; (B) used catalyst—feedstock biogas 1 + O₂ + He, (C) used catalyst—feedstock biogas 2 + O₂ + He, (D) used catalyst—feedstock CH₄ + O₂ + He.

Additionally, a small satellite is visible at 647 eV, indicating the existence of Mn²⁺ in addition to Mn³⁺ [62]. However, the clearly outlined satellite peak, indicating a higher concentration of Mn²⁺ on the catalyst surface, is observed only when the CH₄ + O₂ + He mixture is used as feedstock. The intensity of the MnO satellite depends on the degree of reduction of the catalyst; during the reoxidation of the catalyst, its intensity decreases [62]. The W 4f XPS spectra of the fresh and used catalyst (Figure 1) have spin-orbit doublets ca. at 36 and 38 eV for W 4f_{7/2} and W 4f_{5/2}, respectively, which were assigned to W ions with 6+ oxidation state [62].

Table 2 shows binding energies and surface elemental compositions of the fresh catalyst Mn-Na₂WO₄/SiO₂ and the catalysts after the OCM process, when a mixture of unpurified biogas (biogas 1 or biogas 2) or pure CH₄ with oxygen and inert gas (He) was used as a feedstock.

Table 2. XPS results for fresh and used Mn-Na₂WO₄/SiO₂ catalysts ^a.

Feedstock	Na (1s)		W (4f)		Mn (2p)		O (1s) SiO ₂		O (1s) MO _x	
	BE (eV)	In (at %)	BE (eV)	In (at.%)	BE (eV)	In (at.%)	BE (eV)	In (at.%)	BE (eV)	In (at.%)
Fresh catalyst	1071.7	4.48	36.0	0.71	642.7	0.62	533.1	30.96	530.7	9.25
CH ₄ + O ₂ + He	1071.7	4.89	36.0	0.82	642.5	1.57	533.0	45.71	530.6	12.9
Biogas 1 + O ₂ + He	1071.9	2.24	35.9	0.61	641.6	0.96	533.0	55.22	530.7	6.37
Biogas 2 + O ₂ + He	1072.1	3.27	35.9	0.58	642.1	1.16	532.8	54.37	530.5	7.22

^a Used samples after OCM reaction carried out at T = 1053 K; GHSV = 11550 cm³ · g^{−1}_{cat} · h^{−1}; m_{cat} = 400 mg; total flow rate = 77 cm³ · min^{−1}; molar ratio (in all cases); V_{CH₄}:V_{O₂}:V_{He + CO₂ + N₂} = 14.4:4.3:58.3, reaction time = 220 min.

The highest concentration of Na at the surface was found in the case of the fresh catalyst and the catalyst after the process, when a mixture CH₄ + O₂ + He was used as a feedstock. The use of raw biogas as a feedstock reduced the concentration of sodium ions at the catalyst surface, although in all cases the Na/W ratio on the surface was higher than 2, which indicates that some of the Na ions at the surface are not present in the form of the Na₂WO₄ compound, probably only in the form of Na₂O or Na₂O₂ [55].

The surface concentration of Na and W was higher on the catalyst used in the process, when the CH₄ + O₂ + He mixture was used as a feedstock, than on the surface of the fresh catalyst, indicating that some of the Na and W migrated from the mass to the surface. A

different situation was observed when raw biogas (1 and 2) was used as a feedstock. In this case, the concentration of Na and W on the surface was lower than on the fresh catalyst. Shi et al. [55] also observed a decrease of Na and W at the surface at high concentrations of CO₂ in the feedstock as well as when the inert gas contribution in the feed stream was increased. The surface concentration of Mn in the used catalysts (regardless of the type of feedstock) is higher than in the case of the fresh catalyst, wherein it is the highest in the case of the CH₄ + O₂ + He mixture. Shi et al. [55] observed that the concentration of Mn increases with increasing CO₂ concentration in the feed stream and decreases with dilution of inert gas reagents. As a result of the XPS O1 spectra deconvolution two peaks were obtained. The peak at about 533 eV corresponded to the O atoms bound in the SiO₂ form and the other peak at about 530 eV corresponded to the O atom in the metal oxides (MO_x). Oxygen present in the metal oxides has been recognized as surface active species of oxygen [55,58].

Table 2 shows the percentage contribution of oxygen atoms in MO_x and SiO₂ on the fresh and used catalysts. The amount of oxygen bound in the form of MO_x is much greater for the fresh catalyst and the catalyst after the process in which the CH₄ + O₂ + He mixture was used, than on the catalysts used in the process with biogas as a feedstock—then the amount of surface oxygen species (associated with the metal ions—MO_x) decreased significantly, i.e., by almost a half (in the case of both types of biogas).

Catalysts with lower Na and W ion concentrations on the surface also had lower MO_x-bound oxygen concentrations. The concentration of Na and W ions, as well as O in MO_x on the surface of the Mn-Na₂WO₄/SiO₂ catalyst, was significantly lower when raw biogas was used, compared to the fresh catalyst and treated with the pure methane + oxygen mixture. At the same time, regardless of the type of biogas used (biogas1 or biogas2), the concentrations of Na, W, O in MO_x were similar. This correlation, i.e., an increase in the concentration of O in MO_x with an increase in the concentration of Na and W ions, was observed also by Shi et al. [55]. The changes in the surface concentration of Na, W and O in MO_x on the catalyst are also influenced by the dilution of the feedstock with the CO₂ and inert gas [55]. It can be concluded that the migration of Na and W to the catalyst surface increases the storage capacity of surface active oxygen species [55].

XPS experiments confirm the absence of sulphur- or nitrogen-containing compounds on the surface of used catalysts. Indeed Gu et al. [49] found the presence of Na₂SO₄, based on the XPS studies, but the contribution of H₂S used in the research was very high, i.e., the share of H₂S in the stream was 0.33% mol, while the share of H₂S in biogas was 0–2000 ppm [11].

To determine the effect of surface carbonates on the catalytic behaviour of Mn-Na₂WO₄/SiO₂, temperature-programmed desorption (TPD) of CO₂ was carried out (Figure 3). In this experiment, a fresh Mn-Na₂WO₄/SiO₂ sample was treated in a pure CO₂ stream at various increasing temperatures (298, 923, 973, 1023, 1073, and 1123 K), and after cooling down, TPD profiles were recorded. All profiles in Figure 3 exhibit a small desorption maximum c.a. of 1100–1120 K, which confirms that the surface Na₂CO₃ is present at any investigated temperature. Semi-quantitative CO₂-TPD results (inset to Figure 3) indicate that the concentration of surface carbonates decreases rapidly above 1073 K. This correlates with the poisoning effect of CO₂ depicted in Figure S1A (Supplementary Materials) suggesting slight suppression of the OCM activity by high concentration of Na₂CO₃ on the surface of Mn-Na₂WO₄/SiO₂. The poisoning effect of CO₂ on CH₄ conversion is cancelled out above 1073 K, when the concentration of the surface Na₂CO₃ decreases rapidly. The effect of CO₂ on selectivity to C₂₊ is more complicated. Two inverse effects need to be considered. The first one, connected with the formation of less active and selective carbonates, is OCM retardation by surface poisoning. The second effect is positive probably due to the suppression of side reactions of methyl radicals with oxidized species. Such a promoting role of CO₂ on selectivity was reported over the Li/MgO catalyst [63,64]. It was found that in the presence of CO₂ the selectivity increases because the probability of methyl radicals coupling is enhanced with respect to the probability of their oxidation to CO₂ via

methoxide ions [63]. Our study indicates that the first poisoning effect predominates at low temperatures while the second positive effect dominates at high temperatures when the concentration of the surface Na_2CO_3 is relatively low.

Figure 3. Temperature-programmed desorption of CO_2 for the $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ sample. Experiment conditions: heating rate 10 K/min; CO_2 adsorption temperatures: (A) 298, (B) 923, (C) 973, (D) 1023, (E) 1073 and (F) 1123 K.

2.2. Catalytic Performance

Figure 4 displays the temperature effect on the catalytic performance of $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ in the presence of raw biogas (biogas 1) as a source of methane. The tests were carried out in the temperature range of 1013–1113 K. In the temperature range of 1013 K–1053 K, the conversion of methane, selectivity to C_2 and the molar ratio ethylene/ethane increase with an increase in temperature. Above 1053 K, the selectivity to C_2 decreases, and the conversion of methane in the temperature range of 1073 K–1113 K does not change. At a molar ratio of CH_4/O_2 equal 3.3 and a volumetric flow rate of $V = 77 \text{ cm}^3/\text{min}$, when “biogas 1” was used as a feed, the optimal temperature range for the OCM process was 1053 K–1073 K. These observations are consistent with the literature, which show that obtaining high ethylene yields in the OCM process carried out in the presence of the $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst requires the use of high temperatures of 1053 K–1123 K [65,66]. The process of OCM is also significantly influenced by the methane/oxygen molar ratio in the feed stream. Tests are usually conducted at a methane/oxygen molar ratio of 2–7 [65–67], although it has been shown that in the presence of the $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst the highest C_2 yield can be achieved with a methane/oxygen ratio in the range of 2–4 [66,68]. A high concentration of oxygen in the feed stream favours the conversion of methane, as well as ethane, to ethylene dehydrogenation processes, hence the higher the ethylene/ethane ratio, the lower the methane/oxygen molar ratio. Unfortunately, a high concentration of oxygen in the feed stream also favours over oxidation reactions in which carbon oxides CO_x are formed, therefore, with an increase of the methane/oxygen molar ratio, the selectivity to C_2 decreases [68]. This trend was also observed when biogas was used as a source of methane (Figure 5).

The addition of CO_2 to the reaction stream exerts a small poisoning effect on methane conversion, but at the same time it promotes selectivity to C_{2+} (Figure S1). This effect rises with an increase in the partial pressure of CO_2 , however only for the low-pressure range (below 26 kPa). At a higher partial pressure of CO_2 , both the conversion of CH_4 and selectivity to C_{2+} remain almost constant. As was mentioned above, the presence of CO_2 in the stream inhibits the oxidation of CH_4 and C_{2+} hydrocarbons to CO_x , probably by poisoning sites responsible for a deep oxidation that leading to an increase in C_2

selectivity [69,70]. Contrary to this, the negative effect of CO₂ is associated with the poisoning of the active sites for the coupling reaction. By competitive chemisorption of carbon dioxide and oxygen on the same active sites the amount of converted methane and the amount of C₂₊ products are reduced.

Figure 4. The influence of temperature on the OCM process. Source of methane—"biogas 1". Reaction conditions: GHSV = 11550 cm³ · g^{−1}cat · h^{−1}; m_{cat} = 400 mg; molar ratio of CH₄:O₂:CO₂:He + N₂ = 3.3:1:1.2:12.4; total flow rate = 77 cm³ · min^{−1}.

Figure 5. Influence of the methane/oxygen molar ratio on the OCM process. Source of methane—"biogas 1". Reaction conditions: T = 1053 K; GHSV = 11550 cm³ · g^{−1}cat · h^{−1}; m_{cat} = 400 mg; total flow rate = 77 cm³ · min^{−1}, molar ratio of CH₄:O₂:CO₂:He + N₂ = 1.4:1:0.5:4.6; CH₄:O₂:CO₂:He + N₂ = 2.3:1:0.8:8.1; CH₄:O₂:CO₂:He + N₂ = 3.3:1:1.2:12.4; CH₄:O₂:CO₂:He + N₂ = 6.3:1:2.2:24.25.

Often, the poisoning effect of CO₂ is explained by blocking the active sites by surface carbonates generated in situ during the OCM process [71,72]. In the case of the mixed Mn-Na₂WO₄ catalysts, two carbonates, i.e., MnCO₃ and Na₂CO₃, may be produced. However, under the OCM conditions, Na₂CO₃ is the only stable carbonate. Wang et al. [73] have reported that Na₂CO₃ decomposes between 773–1173 K. Moreover, based on the XPS data, they have estimated that in Mn-Na₂WO₄ containing catalysts, 20–40% of surface sodium cations are in the form of Na₂CO₃ after the process carried out at 1073 K [71]. In a classical OCM process, the carbonates originate from the CO₂ produced in a total oxidation reaction, whereas the CO₂ introduced intentionally into the stream of reagents

can be an additional factor enhancing the concentration of surface Na_2CO_3 species leading to the observed changes in catalytic behaviour. Moreover, CO_2 may have impact on the $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst structure by changing the interaction between Na^+ and WO_4^{2-} as well as the structure of W species, that is, WO_4 or WO_6 [55]. Shi et al. [55] found that low concentrations of CO_2 favour the formation selective in OCM Na_2WO_4 sites with tetrahedral WO_4 sites, while increasing the CO_2 concentration in the feed stream weakens Na^+ and WO_4^{2-} interaction and leads to generation less active and selective MnWO_4 .

The OCM process, which was carried out alternately using a gas stream with and without CO_2 (Figure S2), showed that each time CO_2 was added to reagents the stream selectivity to C_{2+} increased, while at the same time the conversion of methane decreased slightly. The effect of CO_2 disappears after its removal from the reagents stream (replacing CO_2 with an inert gas). This indicates clearly that under the experiment conditions CO_2 does not modify the surface of $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ permanently.

The effect of CO_2 on the process also depends on temperature and oxygen concentration (Figure S3). Up to 1073 K, CO_2 exerts a poisoning effect on the conversion of CH_4 , while above this temperature (at 1123 K) the conversion is similar for a process with and without CO_2 . The addition of CO_2 has a similar poisoning effect on selectivity to C_{2+} . In this case, however, starting from 1073 K, the CO_2 addition promotes selectivity to C_{2+} . This result indicates clearly that the negative effect of CO_2 on OCM can be cancelled out by a temperature increase above 1073 K.

A significant influence of CO_2 on the OCM process was also visible in the case of using raw biogas. Figure 6 shows the influence of the feed composition on selectivity to C_2 , the methane conversion and the ethylene/ethane molar ratio. A higher C_2 selectivity was observed when CO_2 was present in the stream, while the methane conversion and ethylene/ethane molar ratio were slightly lower than in the absence of carbon dioxide.

Figure 6. Influence of feedstock composition on methane conversion, selectivity to C_2 and ethylene/ethane molar ratio. Reaction conditions: $T = 1053 \text{ K}$; $\text{GHSV} = 11,550 \text{ cm}^3 \cdot \text{g}^{-1}\text{cat} \cdot \text{h}^{-1}$; $m_{\text{cat}} = 400 \text{ mg}$; total flow rate = $77 \text{ cm}^3 \cdot \text{min}^{-1}$; molar ratio of $\text{CH}_4:\text{O}_2 = 3.3$ (in all cases); $V_{\text{CH}_4}:V_{\text{O}_2}:V_{\text{He}} + \text{CO}_2 + \text{N}_2 = 14.4:4.3:58.3$. Symbols: (■) biogas 1 (as source of methane), (▲) biogas 2 (as source of methane), (●) mixture of $\text{CH}_4 + \text{CO}_2 + \text{O}_2 + \text{He}$, (★) mixture of $\text{CH}_4 + \text{O}_2 + \text{He}$.

The highest selectivity to C_2 was obtained by using “biogas 2”. Similar results were obtained when a mixture composed of pure components (i.e., methane, oxygen, carbon dioxide and helium), simulating the composition of biogas 2, was used. The use of a mixture devoid of carbon dioxide (CO_2 was replaced with helium) resulted in decreasing the selectivity to C_2 and increasing the conversion rate of methane. Similar results as in the case of the $CH_4 + O_2 + He$ mixture were obtained with the use of raw “biogas 1”, i.e., a mixture poor in CO_2 . The methane conversion, regardless of the composition of feedstock used, differed slightly, i.e., by about 3%. In the tested period of time, regardless of the type of feedstock used, the $Mn-Na_2WO_4/SiO_2$ catalyst worked stably (Figure 6).

The presence of an inert gas influences the catalytic performance in the OCM process as well. The results presented in Figure 7 were obtained using the feedstock diluted with helium and/or carbon dioxide and nitrogen (the presence of carbon dioxide and nitrogen results from its presence in biogas). The total contribution of these gases (helium, carbon dioxide and nitrogen) to the reaction mixture was 43% (vol.). Reducing the contribution of helium in the feed stream to less than 30% (vol.) while maintaining the volumetric flow rate (Figure 7) causes an increase in the methane conversion and the ethylene/ethane molar ratio, and decreases selectivity to C_2 . This effect is independent of the type of raw material used. Diluting the feed stream with helium, keeping the biogas/methane and oxygen flow rate constant, but increasing the total volumetric flow rate of the feed stream lowers the methane conversion and the ethylene/ethane molar ratio. Selectivity to C_2 , in the range up to $80\text{ cm}^3 \cdot \text{min}^{-1}$, increases with an increasing proportion of inert gas in the reaction mixture, and then decreases (Figure 6). Dilution of the reactants stream with inert gas had a negative effect on the methane conversion and the ethylene/ethane molar ratio, but a positive one on selectivity to C_2 . However, the positive effect on the selectivity to C_2 was observed only when the contribution of helium to the feed stream was about 70%.

Figure 7. Influence of diluting feedstock with inert gas (helium) on the OCM process. Reaction conditions: $T = 1053\text{ K}$; $m_{\text{cat}} = 400\text{ mg}$; molar ratio of $CH_4:O_2 = 3.3$ (in all cases); total flow rate = $77\text{ cm}^3 \cdot \text{min}^{-1}$; $V_{CH_4}:V_{O_2} = 14.4:4.3$ (solid line); $V_{CH_4}:V_{O_2} = 37.8:11.3$ (dotted line). Symbols: (■) biogas 1 (as source of methane), (▲) biogas 2 (as source of methane), (●) mixture of $CH_4 + CO_2 + O_2 + He$, (★) mixture of $CH_4 + O_2 + He$.

As shown in Figure 7, GHSV has an effect on the conversion of methane and selectivity to C_2 . Increasing the GHSV causes a decrease in the conversion of methane and the ethylene/ethane molar ratio, while increasing selectivity to C_2 . At low GHSV, the conversion of methane is low and the main product is C_2H_6 [74]. With the extension of the residence time, the conversion of methane and the selectivity to ethylene increase, but the selectivity to ethane lowers [74,75], because most of the C_2H_4 is formed via C_2H_6 [74].

A similar direction of changes in catalytic properties was also observed in the case of the OCM process carried out on other catalysts previously [74–77]. It was found that gas hourly space velocity (GHSV), flow rate and contact time have an impact on both conversion and product distribution.

3. Materials and Methods

3.1. Feedstock

Two types of raw, unpurified biogas were used for the research. Biogas obtained from plant materials, labelled “biogas 1” and biogas derived from waste of animal origin, labelled “biogas 2”, were used as feedstock. “Biogas 1” was made from potato pulp, beet pulp and Corn-Cob-Mix. Each of the raw materials was anaerobically digested in a separate glass reactors. The biogas obtained from the vegetable raw materials was mixed and labelled “biogas 1”. To produce “biogas 2”, waste from carp processing was used.

The collected waste was homogenized, and its moisture content and dry organic matter content were determined. The biomass was hydrated to 90% humidity, which is the optimal humidity for wet methane fermentation, and then placed in 2 dm³ fermenters, along with the inoculum. The support material was digestate from an agricultural biogas plant. Each batch was divided into four such fermenters plus a fermenter containing only the inoculum. The fermenter with inoculum was a reference object against which yields from each fermenter were compared. Thus, prepared fermenters were placed in a chamber with temperature control. Next, the samples were subjected to static methane fermentation, according to the methodology of DIM DIN 38414. It consisted of a single introduction of substrates into the fermentation chambers and the carrying out of the process until its completion. The pH in the fermenters was maintained at 6.5–6.9 due to the alkalinity of the fats present in the fermented biomass. The appropriate pH was maintained due to the inoculation additive. The methane fermentation process lasted 30 days. The gas resulting from methane fermentation was collected in variable volume tanks for each fermenter. The NANO SENS 60 m was used to measure the moisture content of the produced biogas and to determine its chemical composition. The results of the parameters of the process carried out were read daily at the same time and automatically saved to the computer disk using measuring software. Details on the process of obtaining biogas1 and biogas 2 have been described in the literature [78,79].

Biogas 1 and biogas2 composition were analysed using a gas chromatograph, the Agilent 6890N (Agilent Technology, Santa Clara, CA, USA) equipped with two columns (molecular sieve 5A for the analysis of N_2 , CO and O_2 and Hayesep Q for the analysis of H_2 , CO_2 , and hydrocarbons) and TCD. Based on chromatographic analyses, the content of the main biogas components (ie CH_4 , CO_2 , N_2 and O_2) was determined. In “biogas1”, the volume ratio of $CH_4:CO_2:O_2:N_2 = 1:0.34:0.014:0.052$, and in “biogas2” it was $CH_4:CO_2:O_2:N_2 = 1:0.57:0.016:0.06$. Moreover, the following mixture was used for the tests: CH_4 (99.95% Linde Gaz Polska) + O_2 (99.96% Linde Gaz Polska) + CO_2 (99.96% BOC-Gaz) + He (99.999%—BOC-Gaz), in which the contents of methane and carbon dioxide corresponded to those of biogas 2. Comparative tests were also carried out also using the mixture $CH_4 + O_2$ (99.95%)—Linde Gaz Polska + He (99.999%—BOC-Gaz).

3.2. Catalysts Preparation

The catalysts were prepared by the impregnation technique. Dry-silica gel pore size 60 Å, 35–60 mesh particle size (Sigma-Aldrich) was impregnated at room temperature by the incipient wetness method with an aqueous solution of $Mn(NO_3)_2 \times 4H_2O$ (97%,

CHEMPUR) or/and Na_2WO_4 (99%, Aldrich). In a typical procedure, 1 g of silica was impregnated with 1 cm³ of a solution containing desirable content of each salt needed for obtaining 2 and 5 wt% of Mn and Na_2WO_4 , respectively. After impregnation the materials were dried for 15 h at 393 K and calcined at 1173 K for 8 h. The Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst was obtained by impregnation of SiO_2 in two steps with an aqueous solution of $\text{Mn}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ and Na_2WO_4 (Aldrich), respectively. After each impregnation, the materials were dried for 15 h at 393 K. The dried materials (after the second impregnation step) were calcined at 1173 K for 8 h. Obtained in this manner, catalysts were pelleted and crushed to obtain a fraction with a grain size of 0.2–0.3 mm.

3.3. Catalysts Characterization

Powder X-ray diffraction (XRD) patterns were collected on an X'Pert Pro instrument (Panalytical, Almelo, Netherlands) operated at 40 kV and 30 mA, equipped with a Cu K α ($\lambda = 0.154$ nm) X-ray radiation source. The diffractograms were recorded in the 2θ range between 10° and 70° with a 2θ step size of 0.0167° .

Nitrogen adsorption-desorption isotherms were measured at 77K using a ASAP 2020 instrument (Micrometrics, Norcross, GA, USA). The samples were degassed at 523 K before measurements for 12 h in a degas port of the sorption analyser. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of $P/P_0 = 0.05$ – 0.15 . Total pore volumes were obtained from the amount of nitrogen adsorbed at $P/P_0 = 0.95$ or near that value.

The analysis of the temperature programmed desorption of carbon dioxide (CO_2 -TPD) was conducted in the quartz micro-reactor using TCD. Before measurement each sample (1.00 g) of catalyst was outgassed at a temperature of 1223 K under a dry helium stream (1 h, $V_{\text{He}} = 30$ cm³/min.). After cooling to set temperature (298 K, 923 K, 973 K, 1023 K, 1073 K or 1123 K) an adsorption of pure CO_2 was carried out at for 0.5 h. The excess of non-adsorbed CO_2 was removed at the set temperature by flushing the sample with dry helium for 0.3 h. After that the temperature was lowered to 773 K and desorption of CO_2 was carried out using a linear temperature rise with a ramp of 10 K/min.

A photoelectron spectrometer (ESCA/XPS) with an EA15 semispherical analyser (PREVAC, Rogów, Poland) was used for the XPS analysis. The source of Al K α radiation (1486.6 eV) was the RS 40B1 lamp (PREVAC) with the power of 180 W. The spectra were processed with the program CasaXPS 2.3.15. The electron binding energy (BE) scale has been calibrated using the maximum of Si 2p_{3/2} signal with BE = 103.5 eV.

3.4. Catalytic Performance

Catalytic tests were carried out in a continuous flow quartz reactor with the following dimensions: (external diameter) $\times$ (length) $\times$ (wall thickness) = $10 \times 270 \times 1$ mm. The weight of the catalyst was 400 mg (grain size 0.2–0.3 mm) and the temperature of the process was in the range between 1013 K and 1113 K (usually 1053 K). The methane/oxygen volumetric ratio was from 1.4 to 6.3 (typically $\text{CH}_4/\text{O}_2 = 3.3$), and the total volumetric flow rate was 77 cm³/min unless stated otherwise. The products of the reaction and the unreacted substrates were analysed using the Agilent 6890N gas chromatograph (Agilent Technology, Santa Clara, CA, USA) equipped with two columns (molecular sieve 5A for the analysis of N_2 , CO and O_2 and Hayesep Q for the analysis of H_2 , CO_2 , and hydrocarbons) and TCD.

The conversion of methane (X_{CH_4}) and selectivity to C_{2+} ($S_{\text{C}_{2+}}$) were calculated according to the following formulas:

$$X_{\text{CH}_4} = \frac{n_{(\text{inlet})\text{CH}_4} - n_{(\text{outlet})\text{CH}_4}}{n_{(\text{inlet})\text{CH}_4}} \cdot 100\% \quad (1)$$

$$S_{\text{C}_{2+}} = \frac{\sum a_i \cdot n_i}{n_{(\text{inlet})\text{CH}_4} - n_{(\text{outlet})\text{CH}_4}} \cdot 100\% \quad (2)$$

where: $n_{(inlet)CH_4}$ and $n_{(outlet)CH_4}$ are numbers of methane moles in the inlet and outlet of the reactor, respectively; n_i is a number of moles of the i -th product in the outlet and a_i is a number of carbon atoms in the “ i ” product (ethane, ethene, propane and propene).

Carbon balance in the catalytic tests was above 95%.

4. Conclusions

Unpurified biogas originating from two different raw materials was used as a feedstock in the oxidative coupling of methane. For comparison, a pure methane-based feedstock was investigated as well. The physicochemical analysis reveals small differences in the phase and chemical composition of $Mn-Na_2WO_4/SiO_2$ after the OCM process in which unpurified biogas and pure methane were applied. The surface concentration of Na, W and O in (MO_x) on the $Mn-Na_2WO_4/SiO_2$ catalyst was lower when biogas 1 or biogas 2 were used as a feedstock. Moreover, XPS study revealed the absence of sulphur on the surface of used catalysts in the OCM process with both biogases. This indicates that under OCM conditions, sulphur-containing compounds from both studied unpurified biogas did not poisoning catalyst.

The catalytic investigation has revealed that the type of feedstock used as the source of methane has a relatively small influence on the conversion of methane. The differences in methane conversion between all tested feedstock was below 3%. On the other hand, a more significant difference was observed in selectivity to C_2 . Depending on the feedstock, the differences in selectivity to C_2 reaches 9%. Moreover, it was found that the CO_2 that is one of the main components of biogas has influence on catalytic performance in the OCM process. The appropriate selection of process conditions, particularly the temperature (above 1073 K) and the CH_4/O_2 molar ratio (above 3.8) in feedstock, allows for the directing of the process in such a way that the presence of CO_2 has a beneficial effect on the C_2 selectivity and, at the same time, does not reduce the methane conversion.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12010054/s1>, Figure S1: (a) Variation of methane conversion and selectivity to C_{2+} with partial pressure of CO_2 over $Mn-Na_2WO_4/SiO_2$ catalyst. Figure S2: Variation of conversion of CH_4 and selectivity to C_{2+} with time-on-stream during repeatable switching on CO_2 during OCM process over the $Mn-Na_2WO_4/SiO_2$ catalyst. Figure S3: Variation of methane conversion and selectivity to C_{2+} with temperature in the OCM process carried out with and without CO_2 over $Mn-Na_2WO_4/SiO_2$ catalyst.

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