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Effect of methanol on the kinetics of methane-to-CO_2 exchange in gas hydrates

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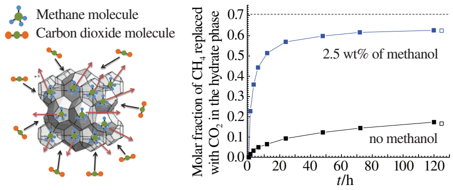
The effect of methanol on the kinetics of CH_4/CO_2 exchange in gas hydrate below the ice melting point was studied. It was shown that in the presence of 2.5 wt% of methanol at P = 2.25 MPa and T = 263 K the molar fraction of CH_4 replaced with CO_2 increased more than three times.



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Gas hydrates are currently being considered as a potential energy source due to the huge amount of fuel gas that is trapped in gas hydrate bearing sediments both underwater and in permafrost regions.[1–3] There are three feasible approaches for production of gas from gas hydrate deposits.[4–6] The first one involves altering the P–T conditions in hydrate-bearing sediments to decompose gas hydrate and produce fuel gas by heating, depressurizing, adding chemicals, *etc*.[4–12] The second method is crushing the hydrate-bearing sediment and mechanical transporting of the resulting slurry to the gas production facility.[5–7] The third method is methane to CO_2 exchange, when carbon dioxide injected into the hydrate-bearing sediments[13–17] replaces methane molecules in the crystal lattice of gas hydrates. The hydrate of carbon dioxide is more thermodynamically stable than methane hydrate,[13,17–22] hence the reaction of CH_4/CO_2 swapping occurs spontaneously. This method can potentially provide additional benefits by allowing long-term sequestering of carbon dioxide while producing fuel gas. The only field experiment on implementation of this technology showed that when carbon dioxide was pumped into the reservoir with gas hydrates, near wellbore area was overgrown with CO_2 hydrate so the further pumping of the CO_2 was not possible, and so the engineers stopped the field trial and switched to pumping of the N_2/CO_2 mixture.[23] It is known, that addition of nitrogen decreases the dissociation pressure of CO_2 hydrate,[24] however the nitrogen molecules can occupy the framework cages built with water molecules which limits the ability of hydrate as a storage medium for carbon dioxide. Slow reaction kinetics is another issue limiting the potential use of this method. According to some estimates, the complete conversion of methane hydrate into CO_2 hydrate may take many years.[25] It is currently considered that there are two stages of the heterogeneous reaction of CH_4/CO_2 exchange in the hydrates.[17,26,27] In the first (fast) stage, a layer of liquid water forms on the surface of a particle of methane hydrate. This water layer quickly converts into a film of CO_2 hydrate coating methane hydrate. The second (slow) stage occurs *via* the diffusion of carbon dioxide molecules inside the hydrate particles and methane molecules diffuse in the opposite direction. The kinetics of the methane-to-CO_2 exchange process has been studied earlier.[25–39] However, the surface area available for the reaction, which is one of the fundamental parameters affecting the reaction rate, has only been considered in a few works.[25–27] In many papers, the reaction kinetics was studied in a porous hydrate-bearing medium.[31–39] In this instance, pores may have an impact on the kinetics, and therefore pose a challenge to the conclusions that are particularly revelant to kinetics. Recently, the other aspects of the kinetics of formation of the gas hydrates with CH_4 and CO_2 from the bulk and dispersed water phase were studied.[40,41,42] The features of the methane-CO_2 exchange at temperatures below the ice melting point have been discussed.[25,30,37] Almost all data were obtained at the temperatures above the ice melting point.[39,45] The alcohol is considered to be a thermodynamic inhibitor for both methane hydrate and CO_2 hydrate, lowering their decomposition pressures, therefore the addition of even a small amount of methanol can cause the partial dissolution of gas hydrate. At that point the effect of methanol[43,44] on the replacement process was studied only for hydrate-containing porous media.[39,45]

In this work, we aimed to study the kinetics of methane-carbon dioxide exchange in gas hydrates at temperatures below the ice melting point with and without methanol additions using ‘pure’ hydrate powder and ensuring moderate stirring of the system to avoid probable impact of factors affecting permeability of the samples.

Here we used the methods of methane samples preparation and analysis of composition and specific surface areas of the methane hydrate powder samples described in our recent work.[25,†] The characteristics are shown in Table 1.

[†] The powder of methane hydrate was synthesized as follows: finely crushed ice was loaded into the cell at liquid nitrogen temperature. The cell was flushed 3 times with 1 MPa of methane and pressurized with 15 MPa of this gas. Then it was put into the refrigerator at temperature of 277 K for at least 24 h. After that the cell was frozen to the temperature of liquid nitrogen, hydrate was extracted, ground again and put back to the cell cooled to 77 K. The cell was again placed into the refrigerator at 277 K for at least 24 h. Then the cell was cooled to 77 K, the hydrate

Table 1 Basic characteristics of the initial methane hydrate samples.

Experiment [methanol added (wt%)]	Composition (volume of emitted gas/ml g_{water}^{-1})	Mean particle diameter/μm	Specific surface area/ $m^2\ g^{-1}$
0	207	137.5	37.0
2.5	215	127.5	32.7

Two experiments were carried out at the same *P–T* conditions (2.25 MPa, 263 K) to determine the effect of added methanol on the kinetics of the CH_4–CO_2 exchange process: one without the addition of methanol and the other with addition of 2.5 wt% (relative to the mass of hydrate) alcohol. The changes in the composition of the gas phase during the experiments are shown in Figure 1. Figure 2 illustrates the calculated changes in the composition of the mixed CH_4/CO_2 hydrate *vs.* time. The results of the direct measurement of the mixed CH_4/CO_2 gas hydrate composition after completion of the kinetic experiment and its melting are also shown in Figure 2.

At the end of the experiments the hydrate compositions calculated on the basis of changes in concentration of the gases in the gas phase were close to those measured after melting, this indicated that the way of hydrate composition estimating was correct. The results presented in the figures show that methanol has dramatically accelerated the kinetics of the reaction of CH_4–CO_2 exchange in gas hydrates. To our best knowledge, these results are the first evidence of the catalytic effect of methanol on the CH_4–CO_2 exchange reaction in gas hydrate obtained with the samples of ‘pure’ hydrates (not in porous media). In both cases the fastest reaction rates are observed during the initial 24 h of the experiment. After that, the reaction rates sharply decrease and wherein in the presence of methanol the reaction rates become slower than without the addition of the alcohol.

The equilibrium compositions of the gas and hydrate phases at 2.25 MPa and 263 K were calculated using CSMGEM software.[20] The quantities of the components loaded into the autoclave were used for these calculations as input data. Figures 1 and 2 indicate that in the absence of methanol, the compositions of both gaseous and hydrate phases have been significantly different from their equilibrium values. These data are consistent with the model that implied that the reaction rate slows down with time because of the formation of a hydrate/ice crust on the surface of the hydrate particles, which limits the diffusion of CO_2 molecules inside the hydrate particles and CH_4 molecules in the opposite direction.[25]

In the case when methanol was added, the situation becomes more complicated. One can see from Figure 1 that the gas phase composition is close to the equilibrium composition. However, as shown in Figure 2, for the hydrate phase, the difference

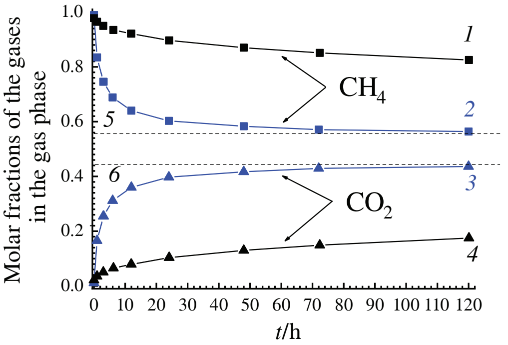

Figure 1 Changes in the composition of the gas phase *vs.* time during the CH_4–CO_2 swapping process at 2.25 MPa, 263 K. Black lines (without addition of methanol): *1* – methane concentration, *4* – carbon dioxide concentration. Blue lines (with addition of 2.5 wt% methanol): *2* – methane concentration, *3* – carbon dioxide concentration. Horizontal dashed lines: *5* and *6* – equilibrium concentrations of CH_4 and CO_2 in the gas phase, respectively (without methanol addition).

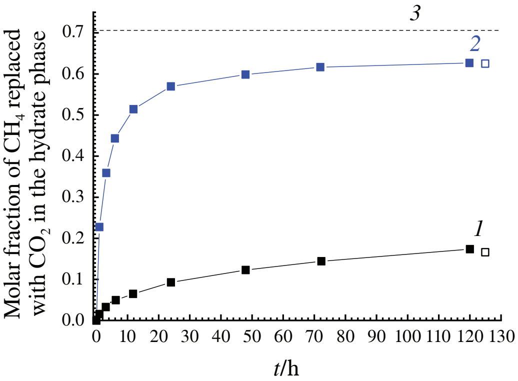

Figure 2 Changes of the fractions of CO_2 in gas hydrate *vs.* time during the CH_4–CO_2 swapping process at 2.25 MPa, 263 K: *1* – without addition of methanol, *2* – with addition of 2.5 wt% of methanol. The empty squares present the results of direct measurement of hydrate composition after its melting. The horizontal dashed line *3* corresponds to the equilibrium composition of the hydrate phase calculated for the experiment without methanol.

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was extracted and ground. Part of the obtained hydrate powder was used to characterize its properties (composition and specific surface area) the other part was used to study the kinetics of methane–CO_2 exchange in gas hydrates.

The experiments performed to investigate the kinetics of CH_4/CO_2 exchange in methane hydrates comprised of three distinct stages. In the first stage, 25 g of characterized methane hydrate powder were loaded into 252 ml autoclave cell cooled to 77 K. The cell was then closed and purged three times with 1 MPa of methane precooled to 255 K. The mixer was turned on at 100 rpm and the cell was left for 1.5–2 h to reach the intended *P–T* conditions. By the end of this stage, the pressure in the cell was 5.0 ± 0.5 MPa and the temperature reached the value of 263 K at which we planned to investigate the kinetics of CH_4/CO_2 exchange in gas hydrates. In the second stage a reservoir filled with CO_2, which had been precooled to the same temperature as the autoclave stirred cell, was connected to the autoclave, the stirring speed was set at 300 rpm, and carbon dioxide was blown through the cell for 10 min to replace methane from the gas phase. During the replacement of the gas phase, the pressure was not reduced below the dissociation pressure of pure methane hydrate to prevent its decomposition. After the completion of the CO_2 injection process, we immediately took samples of gas to analyze the composition of the gas phase in the autoclave. Then the stirring speed was reduced to 100 rpm. For the experiment with methanol, the alcohol was injected into the cell quickly after taking a sample of the gas for analysis. For its injection, a tube with valves on both sides was filled with the required amount of methanol. Then it was cooled to the temperature of an autoclave and connected to a valve on the top of the cell. On the opposite side, this capillary was connected to the reservoir with CO_2. The capillary was purged with CO_2 three times and pressurized. Then the valves between the tube and the autoclave were open to push methanol into the cell and the system was left for five days. Periodically (after 1, 3, 6, 12, 24, 48, 72 and 120 h), samples of the gas phase were taken for analysis to track its changes and to build the kinetic curves. In the third stage, the pressure was reduced, and the autoclave was purged three to four times with 1 MPa of nitrogen precooled to 255 K. The chiller temperature was then set to 293 K in order to dissociate the hydrate. The samples of gas after hydrate decomposition have also been analyzed to check the correctness of the obtained kinetic curves. Khromos GKh-1000 gas chromatograph equipped with a TCD detector and a Porapak column 3 m long and 4 mm in diameter QS 80/100 mesh was used to perform analysis of the gas phase composition. The molar volumes of the gas mixtures at experimental *P–T* conditions were calculated with CSMGEM software.[20] The obtained values were used for calculations of the hydrate compositions at different stages.

Table 2 Calculated equilibrium compositions and molar fractions of the phases for the used mixtures of components.

Methanol added (wt%)	Composition (mol%)											
	hydrate phase				gas phase				liquid aqueous phase			
	CH_4	CO_2	H_2O	CH_3OH	CH_4	CO_2	H_2O	CH_3OH	CH_4	CO_2	H_2O	CH_3OH
0	4.1	9.87	86.03	–	44.4	55.6	0.0	–	–	–	–	–
	PMF[a] = 0.821				PMF[a] = 0.179				PMF[a] = 0			
2.5	3.76	10.36	85.88	0	39.02	60.94	0.01	0.03	0.01	2.11	79.74	18.08
	PMF[a] = 0.739				PMF[a] = 0.204				PMF[a] = 0.057			

[a] PMF – phase molar fraction.

between its determined and equilibrium compositions is much greater. In general, there is no doubt that the addition of a small amount of methanol dramatically promotes the conversion of the CH_4–CO_2 exchange process in gas hydrates. It is important to note that in this case the estimation of errors for the calculated values of the gas hydrates composition is not possible, thus the assumptions about the origin of the observed difference between the compositions of the phases and the equilibrium values (random or random + systematic error) are challenging. The analysis of the experimental data with added methanol suggests that sharp decrease in the reaction rate can be caused either by achieving thermodynamic equilibrium between the outer layers of the mixed CH_4/CO_2 particles or by abrupt decrease in the thermodynamic driving force of the reaction due to approaching the phases compositions to the equilibrium values. Inasmuch as carbon dioxide concentration in the hydrate phase is 10–20% lower the one obtained with CSMGEM equilibrium values, it is safe to assume that the central part of the hydrate particles still contains the fragments of unreacted methane hydrate, but its quantity is significantly lower than in the experiment without addition of methanol.

Let us discuss the possible mechanism of the CH_4–CO_2 exchange in gas hydrates in the presence of methanol. When methanol is injected into the autoclave, part of it evaporates into the gas phase (Table 1). The remaining portion of the methanol comes into contact with the hydrate powder, bringing partial dissolution of the hydrate. One can consider that due to the stirring, the methanol quickly and evenly distributes in the hydrate sample. The data presented in Table 2 indicate that addition of 2.5 wt% of methanol results in the formation of about 10% of liquid phase (relative to the quantity of solid phase) that mainly consists of water and methanol. During the process of methane hydrate dissolution, methane molecules are being emitted into the gaseous phase. At the same time, the dissolved water molecules capture CO_2 molecules from both gas and liquid phases forming the CO_2 hydrate that at these P–T conditions is more stable than the methane hydrate. It is safe to assume that the amount of the liquid phase is sufficient to cover the entire surface of the solid particles with a thin film and to fill the cracks and pores between and inside these particles. We believe that in such a system, the process of methane–CO_2 exchange occurs not *via* a solid-phase process, but rather through multiple processes of dissolving–recrystallization of hydrate particles. Presumably, during the reaction the locations of these simultaneous processes differ, which results in a deeper conversion of the methane hydrate owing to the larger surface area of the hydrate exposed to the gas/liquid phase. Thefore, the presence of the unreacted methane hydrate at the end of the experiment can be explained by the inhomogeneous distribution of the hydrate sample in the cell after flushing it with CO_2. Part of the hydrate powder may remain on the walls of the cell and the injected methanol may not get into contact with it, so the necessary liquid water/methanol layer is not formed.

Thus, the obtained data prove the effectiveness of methanol as the catalyst in the process of CH_4/CO_2 exchange in gas hydrates. We assume that the findings reported here can be useful for further development of the approach and methods of gas production from gas hydrates deposits.

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References

1 Y. F. Makogon, *J. Nat. Gas Sci. Eng.*, 2010, **2**, 49; https://doi.org/10.1016/j.jngse.2009.12.004.

2 G. D. Ginsburg, *Geological Society*, *London*, *Special Publications*, 1998, **137**, 51; https://doi.org/10.1144/GSL.SP.1998.137.01.04.

3 K. A. Kvenvolden, *Rev. Geophys.*, 1993, **31**, 173; https://doi.org/10.1029/93RG00268.

4 G. J. Moridis, T. S. Collett, R. Boswell, S. Hancock, J. Rutqvist, C. Santamarina, T. Kneafsey, M. T. Reagan, M. Pooladi-Darvish, M. Kovalsky, E. D. Sloan and C. Coh, in *Advanced Biofuels and Bioproducts*, ed. J. W. Lee, Springer, New York, 2013, pp. 977–1033; https://link.springer.com/chapter/10.1007/978-1-4614-3348-4_37.

5 L. Liu, Z. Sun, L. Zhang, N. Wu, Q. Yichao, Z. Jiang, W. Geng, H. Cao, X. Zhang, B. Zhai, C. Xu, Z. Shen and Y. Jia, *Acta Geol. Sin.*, 2019, **93**, 731; https://doi.org/10.1111/1755-6724.13876.

6 L. Chen and S. Merey, *Oceanic Methane Hydrates*, Elsevier, Cambridge, MA, Gulf Professional, 2021; https://www.sciencedirect.com/book/9780128185650/oceanic-methane-hydrates.

7 D. Xiaoxu, W. Jiwei, H. Yuan, L. Haitao, Z. Shouwei, Z. Junlong, N. Shaohua, W. Guorong, M. Liang and W. Hualin, *Appl. Energy*, 2023, **351**, 121673; https://doi.org/10.1016/j.apenergy.2023.121673.

8 Y. F. Makogon, S. A. Holditch and T. Y. Makogon, *Oil & Gas Journal*, 2005, **103**, 43; https://www.ogj.com/drilling-production/production-operations/ior-eor/article/17236287/russian-field-illustrates-gas-hydrate-production.

9 L. Chen, Y. Feng, J. Okajima, A. Komiya and S. Maruyama, *J. Nat. Gas Sci. Eng.*, 2018, **53**, 55; https://doi.org/10.1016/j.jngse.2018.02.029.

10 Y. Konno, T. Fujii, A. Sato, K. Akamine, M. Naiki, Y. Masuda, K. Yamamoto and J. Nagao, *Energy Fuels*, 2017, **31**, 2607; https://doi.org/10.1021/acs.energyfuels.6b03143.

11 S. R. Dallimore and T. S. Collett, *Bull. - Geol. Surv. Can.*, 2005, **585**, 28; https://doi.org/10.4095/220714.

12 X. S. Li, C.-G. Xu, Y. Zhang, X.-K. Ruan, G. Li and Y. Wang, *Appl. Energy*, 2016, **172**, 286; https://doi.org/10.1016/j.apenergy.2016.03.101.

13 K. Ohgaki, K. Takano, H. Sangawa, T. Matsubara and S. Nakano, *J. Chem. Eng. Jpn.*, 1996, **29**, 478; https://doi.org/10.1252/jcej.29.478.

14 B. Anderson, R. Boswell, T. S. Collett, H. Farrell, S. Ohtsuki, M. White and M. Zyrianova, in *Proceedings of 8th International Conference on Gas Hydrates (ICGH8-2014)*, July 28–August 1, 2014; https://netl.doe.gov/sites/default/files/netl-file/nt0006553-field-trial-review.pdf.

15 X. Zhou, S. Fan, D. Liang and J. Du, *Energy Convers. Manage.*, 2008, **49**, 2124; https://doi.org/10.1016/j.enconman.2008.02.006.

16 M. Aminnaji, M. F. Qureshi, H. Dashti, A. Hase, A. Mosalanejad, A. Jahanbakhsh, M. Babaei, A. Amiri and M. Maroto-Valer, *Energy*, 2024, **300**, 131579; https://doi.org/10.1016/j.energy.2024.131579.

17 M. Aminnaji, M. F. Qureshi, H. Dashti, A. Hase, A. Mosalanejad, A. Jahanbakhsh, M. Babaei, A. Amiri and M. Maroto-Valer, *Energy*, 2024, **300**, 131580; https://doi.org/10.1016/j.energy.2024.131580.

18 M. F. Qureshi, J. Zheng, H. Khandelwal, P. Venkataraman, A. Usadi, T. A. Barckholtz, A. B. Mhadeshwar and P. Linga, *Chem. Eng. J.*, 2022, **432**, 134290; https://doi.org/10.1016/j.cej.2021.134290.

19 M. F. Qureshi, H. Khandelwal, A. Usadi, T. A. Barckholtz, A. B. Mhadeshwar and P. Linga, *Energy*, 2022, **256**, 124625; https://doi.org/10.1016/j.energy.2022.124625.

20 E. D. Sloan and C. A. Koh, *Clathrate Hydrates of Natural Gases,* 3rd edn., CRC Press, Boca Raton, 2008; https://doi.org/10.1201/9781420008494.

21 J.-M. Herri, A. Bouchemoua, M. Kwaterski, A. Fezoua, Y. Ouabbas and A. Cameirao, *Fluid Phase Equilib.*, 2011, **301**, 171; https://doi.org/10.1016/j.fluid.2010.09.041.

22 S. M. Everett, C. J. Rawn, B. C. Chakoumakos, D. J. Keffer, A. Huq and T. J. Phelps, *Am. Mineral.*, 2015, **100**, 1203; https://doi.org/10.2138/am-2015-4929.

23 D. Schoderbek, H. Farrell, K. Hester, J. Howard, K. Raterman, S. Silpngarmlert, K. L. Martin, B. Smith and P. Klein, *ConocoPhillips gas hydrate production test final technical report*, 2013; https://netl.doe.gov/sites/default/files/netl-file/nt0006553-final-report-hydrates.pdf.

24 V. R. Belosludov, Y. Yu. Bozhko, O. S. Subbotin, R. V. Belosludov, R. K. Zhdanov, K. V. Gets and Y. Kawazoe, *Molecules*, 2018, **23**, 3336; https://doi.org/10.3390/molecules23123336.

25 D. A. Strukov, S. A. Kartopol'cev, A. K. Sagidullin, V. G. Smirnov, A. Y. Manakov and S. S. Skiba, *Thermochim. Acta*, 2024, **736**, 179737; https://doi.org/10.1016/j.tca.2024.179737.

26 A. Falenty, J. Qin, A. N. Salamatin, L. Yang and W. F. Kuhs, *J. Phys. Chem. C*, 2016, **120**, 27159; https://doi.org/10.1021/acs.jpcc.6b09460.

27 B. R. Lee, C. A. Koh and A. K. Sum, *Phys. Chem. Chem. Phys.*, 2014, **16**, 14922; https://doi.org/10.1039/C4CP01780C.

28 M. Ota, Y. Abe, M. Watanabe, R. L. Smith Jr. and H. Inomata, *Fluid Phase Equilib.*, 2005, **228–229**, 553; https://doi.org/10.1016/j.fluid.2004.10.002.

29 M. Ota, K. Morohashi, Y. Abe, M. Watanabe, R. L. Smith, Jr. and H. Inomata, *Energy Convers. Manage.*, 2005, **46**, 1680; https://doi.org/10.1016/j.enconman.2004.10.002;

30 X. Zhang, Y. Li, Z. Yao, J. Li, Q. Wu and Y. Wang, *Energy Fuels*, 2018, **32**, 646; https://doi.org/10.1021/acs.energyfuels.7b02655.

31 L. Mu and N. von Solms, *Energy Fuels*, 2017, **31**, 3338; https://doi.org/10.1021/acs.energyfuels.6b01638.

32 X. Zhou, F. Lin and D. Liang, *J. Phys. Chem. C*, 2016, **120**, 25668; https://doi.org/10.1021/acs.jpcc.6b07444.

33 M. Li, A. R. Zuniga, P. L. Stanwix, Z. M. Aman, E. F. May and M. L. Johns, *Fuel*, 2022, **312**, 122830; https://doi.org/10.1016/j.fuel.2021.122830.

34 Q. Yuan, C.-Y. Sun, X. Yang, P.-C. Ma, Z.-W. Ma, B. Liu, Q.-L. Ma, L.-Y. Yang and G.-J. Chen, *Energy*, 2012, **40**, 47; https://doi.org/10.1016/j.energy.2012.02.043.

35 Y. Chen, Y. Gao, Y. Zhao, L. Chen, C. Dong and B. Sun, *Appl. Energy*, 2018, **228**, 309; https://doi.org/10.1016/j.apenergy.2018.05.126.

36 L.-L. Ren, M. Jiang, L.-B. Wang, Y.-J. Zhu, Z. Li, C.-Y. Sun and G.-J. Chen, *Energy*, 2020, **194**, 116869; https://doi.org/10.1016/j.energy.2019.116869.

37 Y. Xie, Y.-J. Zhu, T. Zheng, Q. Yuan, C.-Y. Sun, L.-Y. Yang and G.-J. Chen, *Chem. Eng. J.*, 2021, **403**, 126283; https://doi.org/10.1016/j.cej.2020.126283.

38 J. W. Jung, D. N. Espinoza and J. C. Santamarina, *J. Geophys. Res.*, 2010, **115**, 10102; https://doi.org/10.1029/2009JB000812.

39 J. S. Pandey, C. Karantonidis, A. P. Karcz and N. von Solms, *Energies*, 2020, **13**, 5238; https://doi.org/10.3390/en13205238.

40 A. S. Stoporev and A.Yu. Manakov, *Mendeleev Commun.*, 2022, **32**, 414; https://doi.org/10.1016/j.mencom.2022.05.042.

41 T. P. Adamova, D. A. Strukov, A. Yu. Manakov and A. N. Nesterov, *Mendeleev Commun.*, 2022, **32**, 823; https://doi.org/10.1016/j.mencom.2022.11.038.

42 D. A. Strukov and A. Yu. Manakov, *Mendeleev Commun.*, 2023, **33**, 614; https://doi.org/10.1016/j.mencom.2023.09.007.

43 M. E. Sarvestani, O. Norouzi, F. Di Maria and A. Dutta, *Energy Convers. Manage.*, 2024, **302**, 118070; https://doi.org/10.1016/j.enconman.2024.118070.

44 A. L. Maximov and I. P. Beletskaya, *Russ. Chem. Rev.*, 2024, **93**, RCR5101; https://doi.org/10.59761/RCR5101.45.

45 J. S. Pandey, S. Khan, A. P. Karcz and N. von Solms, *Fuel*, 2021, **299**, 120711; https://doi.org/10.1016/j.fuel.2021.120711.

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