# Direct conversion of methane to methanol

| 7% of total | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Question | 6.1 | 6.2 | 6.3 | 6.4 | 6.5 | 6.6 | 6.7 | 6.8 | 6.9 | 6.10 | **Total** |
| Points | 2 | 4 | 1 | 2 | 4 | 3 | 3 | 3 | 4 | 6 | **32** |
| Score | | | | | | | | | | | |

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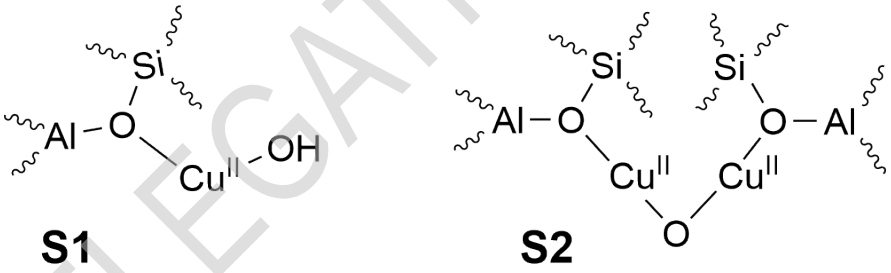
Methane is widely available as natural gas making it an attractive feedstock for the chemical industry, such as for the production of methanol. However, control of this process is challenging as methanol is more easily oxidized than methane.

Overoxidation is avoided in a chemical looping process, where active sites of copper-exchanged zeolite catalysts provide only the single oxygen atom required for oxidation to methanol and are consumed. In a second step, the catalyst is regenerated with oxygen in the absence of methane. The scheme below shows two potential catalytic copper sites.




**S1** **S2**

During the reaction, $\mathrm{Cu^{II}}$ is reduced to $\mathrm{Cu^{I}}$.

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| **6.1** | **Give** the number of **S1** sites and the number of **S2** sites required to oxidize one methane molecule to methanol. | 2pt |

In the absence of oxygen, the formed methanol does not desorb from zeolite. If the reaction is performed in a container with constant volume and temperature (an autoclave), a pressure drop results only from the consumption of methane, which can be considered as an ideal gas. In a $1\ \mathrm{L}$ autoclave containing $200\ \mathrm{mg}$ of zeolite loaded with $4.3\ \mathrm{wt.\%}$ copper, the initial methane pressure $p_0 = 933\ \mathrm{Pa}$ dropped to $p_\infty = 925\ \mathrm{Pa}$ after completion of the reaction at $528\ \mathrm{K}$.

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| **6.2** | **Compute** the percentage of copper that reacted. | 4pt |

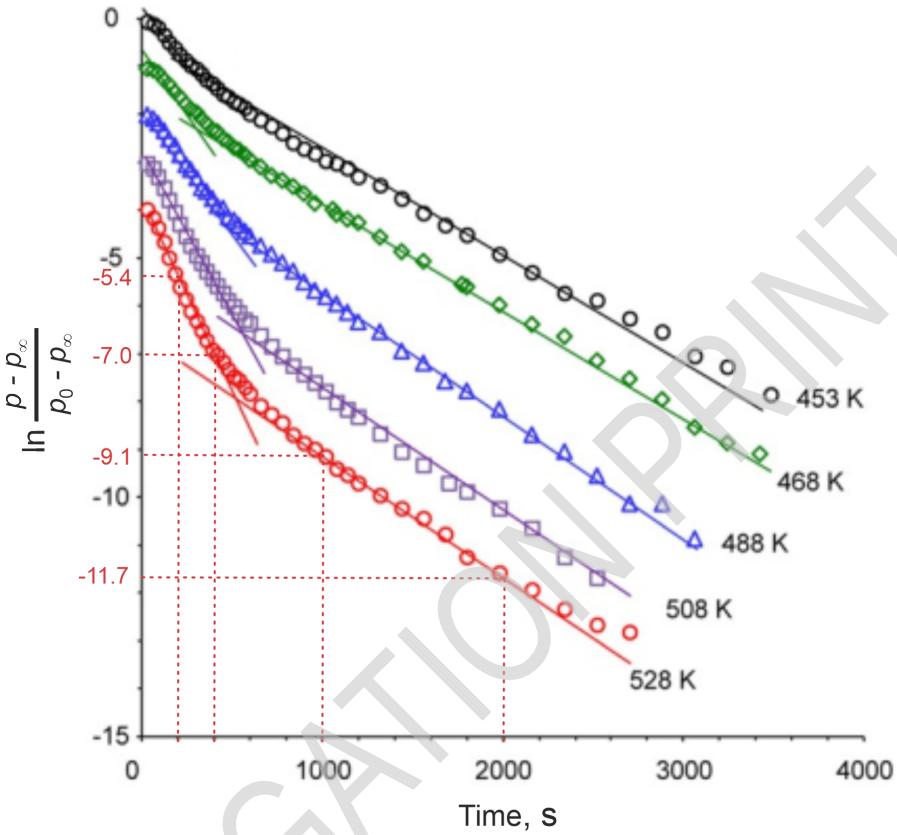


**Figure 1**: Semi-logarithmic graph of normalized methane pressure $p$ versus time for the reaction with copper-loaded zeolite containing sites **S1** and **S2** in an autoclave at various temperatures. The symbols denote experimental data points. The solid lines are linear fits to appropriate time ranges. The dotted lines are guides to the eyes.

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| **6.3** | Experimental data is plotted in **Figure 1**. Based on this, **decide** on the (pseudo) order of the oxidation of $CH_4$. **Tick** the box with the correct statement **on the answer sheet**. | 1pt |

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| **6.4** | **Write** down the (pseudo) rate law for the oxidation of $CH_4$ that is consistent with the experimental data under the given conditions. Note that it may depend on the concentrations of $CH_4$ as well as of sites **S1** and **S2** and on the rate constants. | 2pt |

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| **6.5** | **Tick** the boxes with correct statements **on the answer sheet**. | 4pt |

Paramagnetic sites **S1** can be observed by electron paramagnetic resonance (EPR) spectroscopy, whereas diamagnetic sites **S2** do not give an EPR signal. EPR spectroscopy measures the number of electron spins. Thus, the number of **S1** sites is proportional to the double integral $I_2$ of the EPR spectrum, i.e. **[S1]** $\propto I_2$. Spectra were measured at different temperatures $T$ and at each temperature at different times $t$ after initiating the reaction.

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| **6.6** | **Derive** the equation linear in time that relates $I_2(t)$ to the rate constant for the loss of **S1** sites. | 3pt |

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| **6.7** | **Tick** the boxes **on the answer sheet** for each measurement that needs to be calibrated with a known Cu(II) standard. | 3pt |

From EPR measurements, it is known that the rate constant for the reaction with **S1** sites at 528 K is $2.604 \times 10^{-3}$ $s^{-1}$.

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| **6.8** | Considering **Figure 1** and **based on a calculation**, **decide on the answer sheet** if methane reacts faster or slower with **S2** sites than with **S1** sites. | 3pt |

Methanol can be further converted into valuable olefins with different zeolite catalysts. In this process, one observes an intermediate product with molar mass 86.09 g $mol^{-1}$, elemental analysis ($55.8$ wt.% C, $7.0$ wt.% H) and an $^1$H NMR spectrum consisting of signals at four different chemical shifts (**a**: $12.2$ ppm $(1H, s)$, broad, disappears when $D_2O$ is added; **b**: $6.3$ ppm $(1H, d)$; **c**: $5.7$ ppm $(1H, d)$; **d**: $2.0$ ppm $(3H, s)$).

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| **6.9** | **Draw** the structure of the intermediate product and **assign** protons **a** and **d**. | 4pt |

The United States Department of Energy assigned 12 chemical compounds only containing C, H and O as platform chemicals. These are the most promising candidates, easy to prepare from renewable resources and with multiple target derivatives to be prepared from them.

One of them is compound **A**, that can either be further derivatized or used for example in medicinal applications or in detergents.

- $^1$H NMR in DMSO: $7.81$ ppm (**a**, s), $13.0$ ppm (**b**, s, broad, disappears when $D_2O$ is added), both signals have the same integral.
- $^{13}$C NMR: $165.1$ ppm (**1**), $150.6$ ppm (**2**) and $120.6$ ppm (**3**).
- MW: $156.03$ g $mol^{-1}$. Elemental analysis (EA): $46.15$ wt.% C, $2.56$ wt.% H.

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| **6.10** | **Give** a possible structure of **A** and **assign** all protons and carbon **1**. | 6pt |

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