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METHANOL AS A HIGH PURITY HYDROGEN SOURCE FOR FUEL CELLS: A BRIEF REVIEW OF CATALYSTS AND RATE EXPRESSIONS

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Hydrogen is the fuel of the future, therefore many hydrogen production methods are developed. At present, fuel cells are of great interest due to their energy efficiency and environmental benefits. A brief review of effective formation methods of hydrogen was conducted. It seems that hydrogen from steam reforming of methanol process is the best fuel source to be applied in fuel cells. In this process Cu-based complex catalysts proved to be the best. In presented work kinetic equations from available literature and catalysts are reported. However, hydrogen produced even in the presence of the most selective catalysts in this process is not pure enough for fuel cells and should be purified from CO. Currently, catalysts for hydrogen production are not sufficiently active in oxidation of carbon monoxide. A simple and effective method to lower CO level and obtain clean H_2 is the preferential oxidation of monoxide carbon (CO–PROX). Over new CO–PROX catalysts the level of carbon monoxide can be lowered to a sufficient level of 10 ppm.

Keywords: copper catalysts, noble metal catalysts, fuel cell, hydrogen production, CO-PROX

1. INTRODUCTION

The rising demand for energy in all developed countries causes the rising production of energy and a parallel increase of environmental pollution. Therefore, new energy sources should be effective and friendly for environment. New processes are being intensively developed. World Renewable Energy Network (WREN) formed in 1992 is one of the most effective organizations to support and enhance the utilization and implementation of renewable energy sources like solar-, wind-, hydro-, bio-, ocean and hydrogen energy and others. Some aspects of catalytic processes in search for alternative fuels are described in several works (Mastalir et al., 2007; Momirlan and Veziroglu, 2005; Spivey, 2005; Yong et al., 2013). Yong et al. (2013) described reaction mechanisms in their review and concluded that no consensus on the surface reaction mechanisms had been established. Hydrogen seems to be a commercially important element. Using hydrogen in polymer electrolyte proton-exchange membrane fuel cells (PEMFC) can be a promising technology of safe energy. These are galvanic cells fed by hydrogen. At present, they are the most interesting objective of research in many automobile research centers. Vehicles that use hydrogen as their onboard fuel for motive power have much better efficiency factors in fuel cells and a lower toxic content of exhaust gases compared with classical engines. Fuel cells are also used in stationary applications. They can be compacted in batteries with power values

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*Corresponding author, e-mail: m.lach@iich.gliwice.pl from a few kW to hundreds of megawatts (Squadrito et al., 2014). Buildings can also be heated by fuel cells (Dodds et al., 2014). Hydrogen is mainly produced from natural gas or in the reaction of electrolysis of water; these are expensive and dangerous processes. To avoid transport it is strongly recommended to produce hydrogen in the destination place. There are very strict restrictions concerning purity of hydrogen used in fuel cells, particularly the maximum content of carbon monoxide should be 10-20 ppm in low-temperature fuel cells; and below 2 vol.% in high-temperature fuel cells (Snytnikov et al., 2012). Special catalysts should be applied to reduce CO content.

The aim of our work was to present effective catalysts developed in new processes and available kinetic indications useful in reactor modeling.

2. PROCESSES OF HYDROGEN PRODUCTION FROM METHANOL

Important processes (Yong et al., 2013; Mastalir et al., 2007) are as follows:

- thermal decomposition of methanol (DM)
- partial oxidation of methanol (POM)
- steam reforming of methanol (SRM)
- oxidative steam reforming of methanol (OSRM)

2.1. DM – Decomposition of methanol

The reverse reaction to synthesis of methanol from carbon monoxide and hydrogen:

$$\mathrm{CH_3OH \rightarrow 2H_2 + CO} \qquad \Delta H^0 = +91\, kJ/mol \tag{1}$$

gives a product mixture containing up to 67 mol% of hydrogen. However, the reduction of such a high level of CO 33 mol% to about 10 ppm is technologically very difficult and therefore not profitable from the economic point of view. The decomposition of methanol is an endothermic catalytic reaction. DM catalysts are classified into two groups: Cu-based (in particular Cu/ZnO, Cu/Cr_2O_3, etc.) and those based on elements of 8th group (Ni, Ni-Pt, Pt, Pd, Rh) supported on SiO_2, $Al_2\,O_3$, ZrO_2 (Kapran et al., 2015). Depending on the catalyst used, the process temperature varied from 473 to about 1200 K (Laosiripojana at al., 2006).

2.2. POM - Partial oxidation of methanol

Also in this reaction:

$$\mathrm{CH_3OH + 0.5 \cdot O_2 \rightarrow 2H_2 + CO_2} \quad \Delta H^0 = -192\, kJ/mol \tag{2}$$

a mixture containing up to 67 mol% of hydrogen is formed, if pure (and expensive) oxygen is used. Practically, air is used, so hydrogen is produced with 41% yield. It is a very exothermic reaction, so heating is not supplied, but controlling such a process causes many operating problems. Though CO does not exist as a reaction product in Eq. (2), it has been detected in this reaction over Cu- and Pd-containing catalysts on oxide carriers (Alejo et al., 1997; Agrell et al., 2001, 2003; Cubeiro et al., 1998; Navarro et al., 2002) because of undesired reactions: DM, SRM, full oxidation of methanol towards carbon dioxide and water, water gas shift reaction (WGS) and reverse water gas shift reaction (RWGS). Undesired reactions result in lowering the yield of hydrogen and increase in the yield of CO, which goes up to dozen mol% or even more. The lowest selectivity with respect to CO (1.5 mol%) has been obtained over Au/TiO_2-MO_x (M= Fe, Co, Zn) catalysts (Chang et al., 2006).

2.3. SRM - Steam reforming of methanol

The reaction formula is as follows:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \Delta H^0 = +50\, kJ/mol \tag{3}$$

The yield of hydrogen reaches (Mastalir et al., 2007; Yong et al., 2013) up to 75 mol%. The disadvantages are that this reaction is endothermic and that simultaneously the reversible reaction WGS/RWGS (5) occurs. Proper catalysts allow a decrease in CO level and decrease in the temperature of the process.

2.4. OSRM – Oxidative Steam Reforming of Methanol

In recent years, OSRM process has attracted a lot of attention.

$$CH_3OH + (1-2n)H_2O + nO_2 \rightarrow (3-2n)H_2 + CO_2 \tag{4}$$

The process represented by Eq. (4), is a combined reaction of POM and SRM with quick start-up, (Park and Kwon, 2015), conducted in the presence of a small amount of oxygen, n mols. Lower amounts of CO are observed in the exit gas, compared with SRM process, but there are additional products from oxidation of methanol: formaldehyde and dimethyl ether. Lopez et al. (2012) in investigation on Cu and Ni impregnated on ZrO_2 catalysts in oxidative steam reforming of methanol, obtained high methanol conversion and the biggest hydrogen yields for temperatures about 350 °C. Unfortunately, for the most active catalyst, these results correspond to hydrogen selectivity of about 70% and CO selectivity of 30%. For less active catalysts hydrogen yields were by about 25% lower, hydrogen selectivity equalled to about 90 - 95 % and that of CO from 5 to 10%.

Pojanavaraphan et al. (2012, 2014) when investigating Au/CeO_2 and $Au/Ce_{1-x}Zr_xO_2$ catalysts obtained the highest methanol conversion of 92% at 400°C, with H_2 and CO concentration of 15% and 2500 ppm, and a very good stability for Au deposits on CeO_2-ZrO_2 oxide catalyst with Zr/(Ce+Zr) ratio – 0.25, calcination temperature – 400 °C and Au loading 3 mass%.

The best results have been obtained for $Cu/Zn/Al_2O_3$ catalyst originating from hydrotalcite precursor (Liu et al., 2003). It was up to 500 ppm, but the value was still too high.

It seems that at present, hydrogen from steam reforming of methanol process is the best fuel source to be applied in fuel cells, because of the highest yield of hydrogen at a low amount of CO.

3. STEAM REFORMING OF METHANOL

The interest in steam reforming of methanol process arose in the 1980s. Up to 2005 an assumption was made, that decomposition of methanol (1) is connected with water gas shift (WGS) reaction (5) (Amphlett et al., 1985; Barton et al., 1980 ; Santacesaria et al. 1978):

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{5}$$

After detailed investigations such an assumption was later rejected. Now it is supposed that formation of methyl formate as an intermediate is most probable (Idem and Bakhshi, 1996; Jiang et al., 1993; Jiang et al., 1993; Papavasiliou et al., 2009; Takahashi et al., 1982; Takezawa and Iwasa, 1997; Yong et al., 2013).

According to Papavasiliou et al. (2009) the production of hydrogen and carbon dioxide by SRM over Cu-containing catalysts could proceed through the following paths:

- methanol decomposition and WGS

$$CH_3OH \rightarrow 2H_2 + CO \tag{1}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{5}$$

- via methyl formate intermediate
  - methanol dehydrogenation to formaldehyde and H_2

$$CH_3OH \rightarrow HCHO + H_2 \tag{6}$$

$$CH_3OH + HCHO \rightarrow HCOOCH_3 + H_2 \tag{7}$$

  - or direct dehydrogenation of methanol to methyl formate and H_2

$$CH_3OH + HCHO \rightarrow HCOOCH_3 + H_2 \tag{8}$$

  - hydrolysis of methyl formate

$$HCOOCH_3 + H_2O \leftrightarrow CH_3OH + HCOOH \tag{9}$$

  - formic acid decomposition

$$HCOOH \rightarrow H_2 + CO_2 \tag{10}$$

- via formaldehyde intermediate
  - methanol dehydrogenation to formaldehyde

$$CH_3OH \rightarrow HCHO + H_2 \tag{6}$$

  - formaldehyde hydrolysis

$$CH_3OH \rightarrow HCHO + H_2 \tag{11}$$

  - formic acid decomposition

$$HCOOH \rightarrow H_2 + CO_2 \tag{10}$$

SRM process is carried out at atmospheric pressure, usually at a temperature of about 520 K, the substrate mole ratio of CH_3OH/H_2O of about 1, in a stream of inert gas (N_2 or Ar) of GHSV = 3 300 – 8 000 h^{-1}. Before the process begins, catalysts are reduced in hydrogen diluted in nitrogen.

Since the 1980s there have been many attempts to work out more active, selective and stable catalysts (Ilinich, 2013; Rameshan et al., 2012; Urasaki et al., 2005; Yong et al., 2013). For every catalytic system the mechanism of the process could be different, so kinetic investigations are needed.

3.1. Catalysts for SRM process

Copper- based catalysts and catalysts based on group VIII-X metals are used for methanol steam reforming (Sá et al., 2010). According to many literature reports the catalysts composed of metals of VIII-X group present higher long-term stability compared to copper-based catalysts but much lower reaction activities (Takezawa and Iwasa, 1997). Their costs are a serious problem. Copper- based catalysts favor the production of H_2 with high selectivity towards CO_2 (therefore low selectivity towards CO) and for that reason many researchers have been focusing on Cu-based catalysts for the application of hydrogen in fuel cell system.

Table 1. Cu/ZnO-based catalysts for SRM

Cat. No	Cu/ZnO additives	*t* [°C]	Methanol conversion [%]	Molar ratio S/M**	CO selectivity* [%]	References
1		240	78.8	1.3	0.221	Wang et al., (2007)
2		200	27	1.2	1.2	Shishido et al., (2011)
2		300	100	1.2	4.6	Shishido et al., (2011)
3		220	16.4	1	0.2	Liu et al., (2003)
3		260	66.8	1	0.9	Liu et al., (2003)
4	Al_2O_3	200	47.4	1.2	0	Shishido et al., (2011)
4	Al_2O_3	300	100	1.2	7.3	Shishido et al., (2011)
5	Al_2O_3	250	74	1.1	0.47	Huang et al., (2009)
5	Al_2O_3	270	89.2	1.1	0.92	Huang et al., (2009)
6	Al_2O_3	250	90	1	1	Purnama et al., (2004)
7	Al_2O_3	220	14.7	1	0.2	Liu et al., (2003)
7	Al_2O_3	260	58.4	1	0.8	Liu et al., (2003)
8	Al_2O_3	220	40	1.4	0.6	Patel and Pant (2006)
8	Al_2O_3	260	90	1.4	1.9	Patel and Pant (2006)
9	Al_2O_3	300	100	1.3	1.2	Lindström et al., (2002)
10	Al_2O_3/ CeO_2	250	60.2	1.1	0.31	Huang et al., (2009)
10	Al_2O_3/CeO_2	270	79.3	1.1	0.66	Huang et al., (2009)
11	Al_2O_3/ Y_2O_3/In_2O_3	400	100	1.3	1.3	Matsumura (2014)
11	Al_2O_3/ Y_2O_3/In_2O_3	500	75	1.9	1.9	Matsumura (2013)

*Definition of CO selectivity $S_{CO} = \dfrac{F_{CO}^{out}}{(F_{H_2}^{out} + F_{CO_2}^{out} + F_{CO_2}^{out})} \cdot 100\%$

**S/M – steam to methanol molar ratio

Table 2. $Cu/ZnO/ZrO_2$-based catalysts for SRM

Cat. No	$Cu/ZnO/ZrO_2$ additives	*t* [°C]	Methanol conversion [%]	Molar ratio *S/M*	CO selectivity [%]	
12		500	100	2.5	2.5	References
13		200	45	1.0	0	Lachowska (2004)
13		160	8	1.0	0	Lachowska (2004)
14	Al_2O_3	260	97	1.4	0.6	Patel and Pant (2006)
14	Al_2O_3	220	50	1.4	0.1	Patel and Pant (2006)
15	Al_2O_3	300	77	1.1	0.7	Chang et al. (2012)
16	Al_2O_3	250	76.7	1.1	0.44	Huang et al. (2009)
16	Al_2O_3	270	92.7	1.1	0.97	Huang et al. (2009)
17	Al_2O_3/CeO_2	250	77.6	1.1	0.32	Huang et al. (2009)
17	Al_2O_3/CeO_2	270	89.4	1.1	0.85	Huang et al. (2009)
18	CeO_2	200	100	1.0	1.6	Madej-Lachowska (2012)
18	CeO_2	160	73	1.0	0.79	Madej-Lachowska (2012)
19	CeO_2/Cr_2O_3	200	100	1.0	1.88	Madej-Lachowska (2012)
19	CeO_2/Cr_2O_3	160	53	1.0	0	Madej-Lachowska (2012)
20	Ga_2O_3	220	100	1.0	0.9	Lachowska (2006)
20	Ga_2O_3	160	16	1.0	0	Lachowska (2006)
21	La	200	100	1.0	0	Madej-Lachowska (2012)
21	La	160	50	1.0	0	Madej-Lachowska (2012)

The majority of these catalytic systems contain metallic copper dispersed on the surface of ZnO and ZrO_2 with Al_2O_3 or Cr_2O_3 and sometimes SiO_2 or CeO_2 addition. Similar catalysts were applied long time ago in methanol synthesis from CO + H_2 and CO_2 + H_2 mixtures. In these reactions metallic Cu is the active component acting in synergy with ZnO while Al_2O_3 and SiO_2 are the agents lowering the sintering of active components (Skrzypek et al., 1994; Hansen, 1997). High dispersion of copper and good cooperation of Cu with ZnO is the main objective in SRM catalyst production. Extension of specific surface of catalyst is also very beneficial. Various methods of its preparation have been used: co-precipitation (CP), hydrothermal synthesis (HT), wet impregnation (WT), gel co-precipitation (CGP), precursors of citrate decomposition (CDP) and polymer template sol-gel method (PTSG). CP and CGP are relatively simple methods. However, from our earlier experiments (Kulawska, 2008), they do not assure full repeatability of crystalline structure in all series of preparation. By using CDP or PTSG methods highly active and thermally stable nanostructure catalysts are prepared (Sá et al., 2010).

The characteristics of selected catalysts are listed in Table 1 (CuZnO - based catalysts), Table 2 ($CuZnOZrO_2$ - based catalysts), Table 3 and in Figs. 1 - 2. A detailed catalyst composition has not been given in many cases. The mole ratio of water to methanol varied in the range of 1.0 - 1.3**.** Differences in methanol conversion and CO selectivity for the same catalyst composition can result from various methods of preparation and various reaction parameters. The majority of researchers did not give data for CO selectivity. There is a great discrepancy in the formula of CO selectivity. Due to lack of full experimental data it is hard to reach proper view of results found in literature. So, we could make only a rough comparison of results obtained in many different laboratories.

The $Cu/ZnO/ZrO_2$ catalyst is the “primary” one, and small amounts of various metal oxides with a suitable promoter improve catalytic activity and carbon monoxide selectivity at relatively low temperature. As in the methanol synthesis, Cu/ZnO synergy is crucial for the performance of a catalyst used in fuel cells. The disadvantages of copper catalysts are weak thermal stability and susceptibility to impurities like sulfur, chlorine and phosphorus. Also, carbon monoxide is formed in large amounts. It is connected with temperature, see investigations of Madej-Lachowska et al. (2012).

Table 3. Other Cu-based catalysts for SRM

Cat. No	Cu additives	t [°C]	Methanol conversion [%]	Molar ratio *S/ M*	CO selectivity* [%]	References
22	Cr_2O_3/Al_2O_3	300	63	1,3	1.1	Lindström et al, (2002)
23	Mn spinel	240	80	0	0.7	Liu et al, (2008)
23	Mn spinel	260	93	0	0.7	Liu et al, (2008)
24	$Y_2O_3/Pr_2O_3/$ Al_2O_3	240	80[a]	0		Yang and Chan (2011)
24	$Y_2O_3/Pr_2O_3/$ Al_2O_3	280	99[a]	0.09		Yang and Chan (2011)
25	ZrO_2		100	1,3	0.51	Yao et al, (2006)
26	ZrO_2	250	92	1	0,22	Purnama et al, (2004)
27	ZrO_2/Al_2O_3	300	44	1,3	0,75	Lindström et al, (2002)

[a] H_2 yield [%]

While considering thermodynamic relations of a system of chemical reactions (3 and 5), the constraint in this process is temperature. The relationship between equilibrium conversion and temperature is almost linear in reaction (3) but almost exponential in reaction (5) rising faster for substrate ratios ≤1. Although any increase in temperature above 480 K is beneficial for methanol conversion, it causes rapid increase in CO selectivity. So, investigation of Lindström et al. (2002) should be carefully considered because conducted at such a high reaction temperature and at surprisingly high gas hourly space velocity equal to 25 000 h^{-1}. Additionally, the obtained CO selectivity was relatively high and methanol conversion high only for classic Cu/Zn/Al catalyst supported on Zr. From a practical point of view, lower reaction temperatures in the reformer are desirable because of the lower temperature difference between the reactor and the fuel cell (Liu et al., 2008).

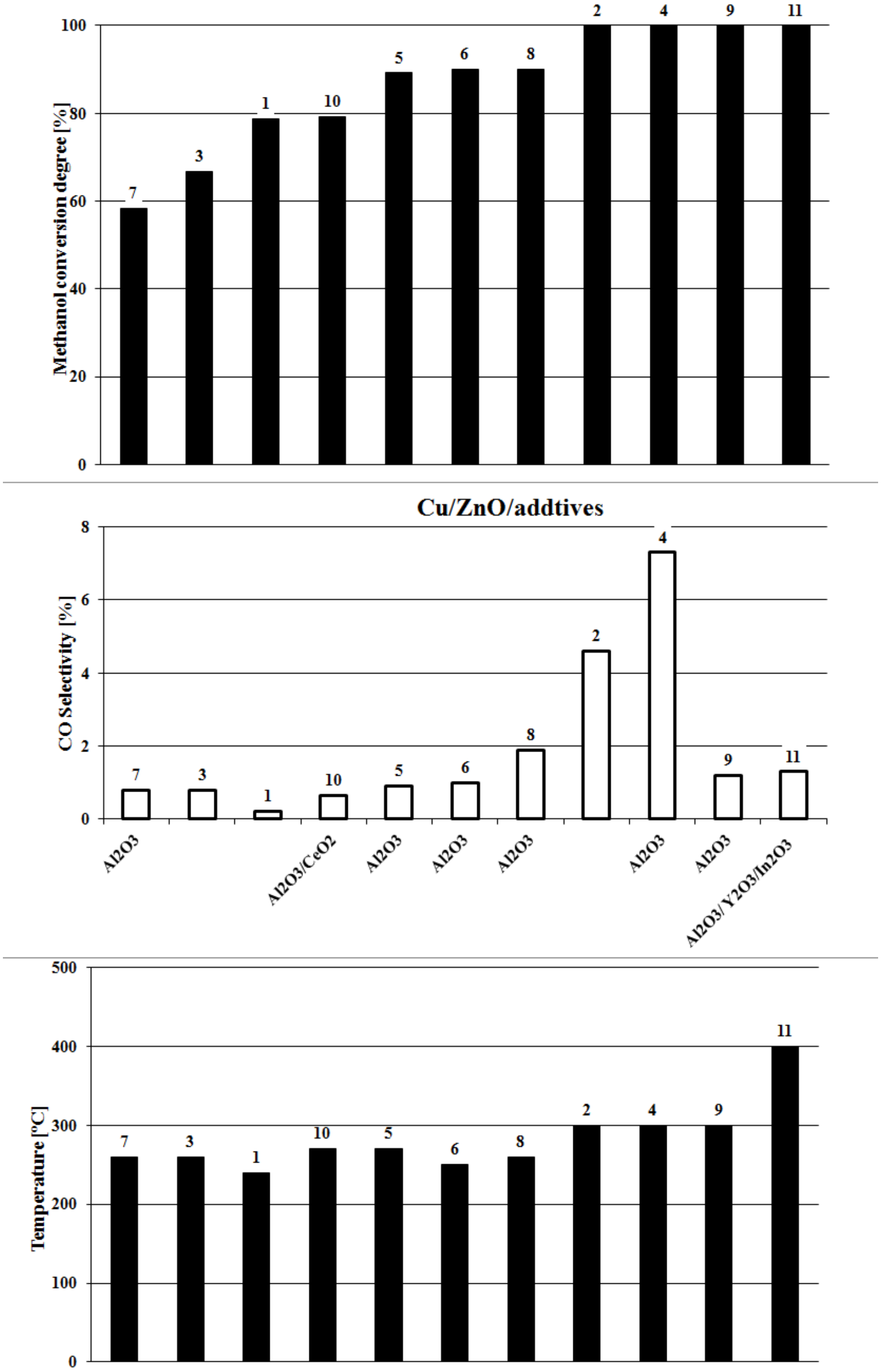

Fig. 1. Methanol conversion and CO selectivity for optimal temperature of Cu/ZnO/additive catalyts, where the numbers above the bars refer to the numbers in the first column of Table 1

It can be seen that many catalysts have high activity (near 100 % conversion of methanol), but the lowest level of CO is still at about 1000 ppm. Total elimination of CO is not possible because of the course of RWGS reaction.

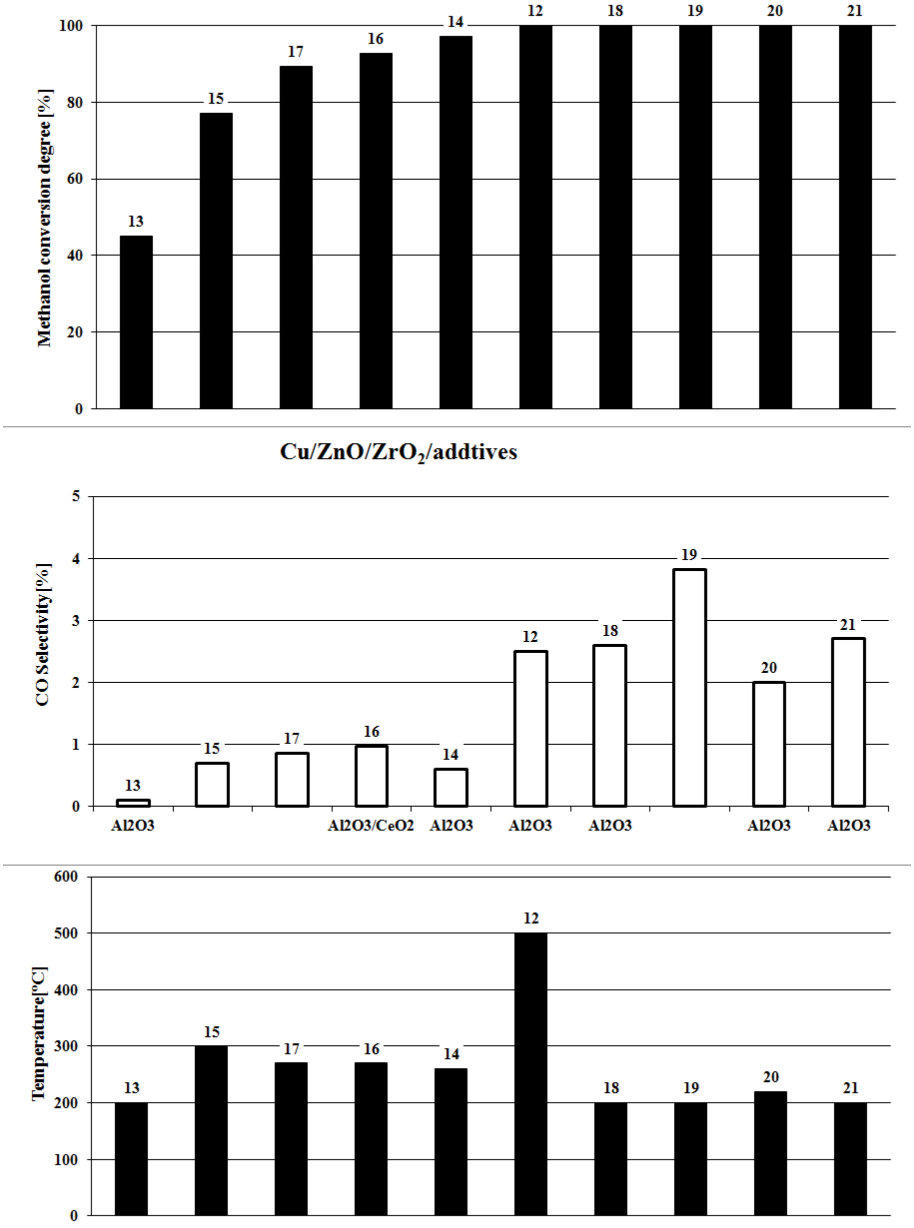

Fig. 2. Methanol conversion and CO selectivity for optimal temperature of Cu/ZnO/ZrO$_2$/additive catalyts where the numbers above the bars refer to the numbers in the first column of the Table 1

3.2. Kinetics of SRM process

SRM kinetic equations for the process conducted on copper catalysts are collected in Table 4. Some of them are Langmuir-Hinshelwood type, others, purely empirical, are in a power law form. There is no agreement regarding the effect of particular reagents on the reaction rate, do they have positive or inhibiting effect. Moreover, not all effects are considered; the effect of CO$_2$ and H$_2$O is often ignored. There are important differences in describing the effect of methanol concentration on the reaction rate; an exponent in power law equations differs from 0.04 (Idem and Bakhshi, 1996) to 0.7 (Papavasiliou et al., 2007). The effect of hydrogen concentration on the reaction rate is very often neglected or an inhibiting effect is described, with an exponent varying between 0 and -1.3 (Barton and Pour, 1980). Some of the listed kinetic equations have very complicated formulae, see Peppley et al. (1999) which contain concentrations of various types of active sites, equilibrium constants of intermediates and other constants. Their application is very narrow.

Table 4. Kinetic equations of steam reforming of methanol

<table>
<tr><th>Catalyst</th><th colspan="4">Kinetic equation</th><th>E kJ mol^{-1}</th><th>References</th></tr>
<tr><td>Cu/ZrO$_2$/CeO$_2$
Cu content
4.4–31mass%</td><td colspan="4">$-r_M = kp_M^{0.6} p_W^{0.4} - k^{-1} p_C p_H^3$</td><td>109–61</td><td>Mastalir et al. (2005)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$
(BASF K3-110)</td><td colspan="4">$-r_M = kp_M^{0.63} p_W^{0.39} p_H^{-0.23} p_C^{-0.07}$</td><td>74</td><td>Samms et al. (2002)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$</td><td colspan="4">$-r_M = kp_M^{0.564}(11.6 + p_H)^{-0.647}$</td><td>103</td><td>Lee et al. (2004)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$</td><td colspan="4">$-r_M = kK_1 p_M p_H^{-0.5}((1 + kK_1 p_M p_H^{-0.5})(1 + (K_2 p_H)^{0.5})^{-1}$</td><td>111</td><td>Lee et al. (2004)</td></tr>
<tr><td>Cu/MnO/Al$_2$O$_3$</td><td colspan="4">$-r_M = kP_M^{0.04}$ at temperatures <190° C</td><td>80</td><td>Idem and Bakhshi (1996)</td></tr>
<tr><td>Cu/MnO/Al$_2$O$_3$</td><td colspan="4">$-r_M = k(p_M - p_C p_H^3 (K_p p_W)^{-1})(1 + Kp_M)^{-1}$</td><td>77</td><td>Idem and Bakhshi (1996)</td></tr>
<tr><td>Cu/MnO/Al$_2$O$_3$</td><td colspan="4">$-r_M = kp_M^{0.28} p_C^{0.99}$</td><td>78</td><td>Idem and Bakhshi (1996)</td></tr>
<tr><td>Cu/MnO/Al$_2$O$_3$</td><td colspan="4">$-r_M = k(p_M p_W p_H^{-1} - p_C p_H^2 K_p^{-1})/(1 + Kp_M)^{-4}$</td><td>117</td><td>Idem and Bakhshi (1996)</td></tr>
<tr><td>Cu$_{0.30}$Mn$_{0.70}$</td><td colspan="4">$-r_M = kp_M^{0.7} p_W^{0.5}$</td><td>71</td><td>Papavasiliou et al. (2007)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$
(BASF S3-85)</td><td colspan="4">$-r_M = k(K_1 p_M (K_3 \cdot p_H)^{-0.5}(1 + K_1 p_M (K_3 p_H)^{0.5} +$
$(K_3 p_H)^{-0.5})^{-2})$</td><td>110</td><td>Jiang et al. (1993b)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$
(BASF S3-85)</td><td colspan="4">$-r_M = kp_M^{0.26} p_W^{0.03} p_H^{-0.2}$</td><td>105</td><td>Jiang et al. (1993a)</td></tr>
<tr><td>Cu/ZnO
Girdler G66B)</td><td colspan="4">$-r_M = (kK_M p_M - k' p_{CO} p_M^2)/(1 + Kp_{CO})$</td><td>96</td><td>Amphlett et al. (1985)</td></tr>
<tr><td>Cu/ZnO/Cr$_2$O$_3$/
Al$_2$O$_3$</td><td colspan="4">$-r_M = k(p_M p_W)^{0.5} p_H^{-1.3}$</td><td>116</td><td>Barton and Pour (1980)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$
(BASF K3-110)</td><td colspan="4">$-r_M = kK_{CH_3O(1)} p_M p_H^{-0.5}(1 - p_H^3 p_C (kp_M p_W)^{-1} C_{S1}^T C_{S1a}^T / DEN^*$</td><td>103</td><td>Peppley et al. (1999)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$
(BASF)</td><td colspan="4">$-r_M = (kK_M p_M)/(1 + K_M p_M + K_W p_W)$</td><td>103</td><td>Santacesaria and Carrà, (1983)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$</td><td colspan="4">$-r_M = kp_M^{0.4}(1 - p_C P_H^3 / K_E p_M p_W)$</td><td>83</td><td>Geissler et al. (2001)</td></tr>
<tr><td>Cu/ZnO/Al$_2$O$_3$
(Süd-Chemie)</td><td colspan="4">$-r_M = kP_M^{0.6} P_W^{0.4}$</td><td>76</td><td>Purnama et al. (2004)</td></tr>
<tr><td>Cu/ZnO/ZrO$_2$/
Ga$_2$O$_3$</td><td colspan="4">$r = kp_M^{0,29} p_W^{-0.193}(0.5 + p_H)^{-1}$</td><td>57</td><td>Madej-Lachowska (2012)</td></tr>
<tr><td>Cu-Zn-Al</td><td colspan="4">$r = \frac{\eta \cdot k_M \cdot b_M \cdot p_M}{1 + b_M \cdot p_M + b_W \cdot p_W}$ inhibiting effect of water is included</td><td>119</td><td>Tesser (2009)</td></tr>
<tr><td>Cu-Zn-Al</td><td colspan="4">$-r_M = (\eta \cdot k_M \cdot b_M \cdot p_M)/(1 + b_M \cdot p_M + b_W \cdot p_W + b_H \cdot p_H)$
inhibiting effect of water and hydrogen is included</td><td>102</td><td>Tesser (2009)</td></tr>
<tr><td>Cu-Zn-Al</td><td colspan="4">$-r_M = k \cdot p_M^a \cdot p_W^b \cdot p_C^c \cdot p_H^d$</td><td></td><td rowspan="7">Tesser (2009)</td></tr>
<tr><td rowspan="6"></td><td>a</td><td>b</td><td>c</td><td>d</td><td></td></tr>
<tr><td>0.351</td><td>0</td><td>0.134</td><td>0</td><td>91</td></tr>
<tr><td>0.310</td><td>-0.151</td><td>0</td><td>0</td><td>101</td></tr>
<tr><td>0.389</td><td>0</td><td>0</td><td>0.195</td><td>85</td></tr>
<tr><td>0.235</td><td>0.216</td><td>0</td><td>0.436</td><td>80</td></tr>
<tr><td>0.402</td><td>-0.468</td><td>0.578</td><td>-0.793</td><td>117</td></tr>
</table>

C - carbon dioxide, H - hydrogen, M - methanol, W - water; C_S^T - concentration of active sites

Tesser et al. (2009) conducted very detailed investigations on industrial $CuO/ZnO/Al_2O_3$ catalyst – BASF K-3-10. They found water to be an inhibiting agent at a constant partial pressure of methanol and to be responsible for low methanol conversion, the reaction rate is a linear function of the initial mole substrate ratio of CH_3OH /H_2O. They proposed 3 types of kinetic equations based on their experiments and literature data. Two of them are of Langmuir-Hinshelwood type; in the first the inhibiting effect of water is included, while in the second – the inhibiting effect of water and hydrogen. In both equations an effectiveness factor is introduced concerning the effect of internal diffusion in catalyst tablets.

The third kinetic equation is an expression in a power law form with various values of exponents for different mechanisms. In authors' opinion, all these equations satisfactorily describe kinetic data. However, applicability ranges for these equations are not precisely stated. Therefore, they can only be considered an estimation. The most reliable are papers by Jiang et al. (1993a) and Samms et al. (2002). Jiang et al. (1993a) proposed power law equations of SRM process in the presence of an industrial $CuO/ZnO/Al_2O_3$ catalyst, BASF S3-85. They conducted kinetic experiments in the temperature range of 445-535 K at methanol conversion below 20%. The reaction rate has been determined as a function of concentrations of products and initial concentrations of substrates. The effect of partial pressure of methanol on the reaction rate (exponent equal to 0.26) and the inhibiting effect of partial pressure of H_2 (exponent equal to -0.2), neither the effect of partial pressure of H_2O (exponent equal to 0.03), nor the effect of partial pressure of CO_2 on the reaction rate was found.

Samms et al. (2002) carried out their kinetic investigations over a $CuO/ZnO/Al_2O_3/MgO$ catalyst [Synetix 33-5] in the temperature range of 435-535 K, for values of the initial mole substrate ratio of CH_3OH /H_2O equal to 1, 2/3, and 1/2. Similarly to Jiang et al. (1993a) they found an effect of partial pressure of methanol and partial pressure of H_2, and no effects of partial pressures of H_2O and CO_2.

Kinetic propositions of Idem and Bakhshi (1996) should be treated very cautiously. The authors presented four various kinetic equations, the two of them in a power law form, based on the same experiments, over the same catalyst. The values of activation energy were very close for the three equations, but the practically constant value of the reaction rate (the exponent of partial pressure of methanol close to zero) makes these estimations somewhat uncertain. In the last equation, in a more complicated form, the exponent of fourth power in the denominator could excessively change the results.

Such attempts at estimation of the reaction rate of SRM reveal complexity of the process. It is also concerned with a very complex structure of catalysts used; an effect of any metal acting is not apparent in coupling with other components. The authors of these kinetic investigations cannot describe one experimental set with one kinetic equation. So, it is impossible for the reader to select proper relationships for their own experiments.

4. CATALYSTS FOR PREFERENTIAL OXIDATION OF CARBON MONOXIDE (CO-PROX)

Regardless of the method used, the hydrogen feed gas for energy production produced by converting a conventional fuel such as a natural gas, gasoline or methanol usually consist of: 45-74 vol. % H_2, 15-25 vol. % CO_2, 0.5-2 vol. % CO and a few vol. % H_2O and N_2 (Di Benedetto et al., 2013). This concentration of CO is too high for polymer electrolyte membrane fuel cells and the gas mixture requires reduction of CO concentration. Hydrogen produced even over the best selective catalysts should be purified from CO. Catalysts for hydrogen production are not sufficiently active in oxidizing of carbon monoxide. An additive process, in which carbon monoxide will be very selectively oxidized to carbon dioxide in the presence of significant excess of hydrogen is then needed. Catalytic preferential oxidation of carbon monoxide (CO-PROX) is a method to avoid poisoning of Pt-based anode in a proton exchange membrane fuel cell (PEMFC). CO–PROX catalysts should be very active in the oxidation of carbon monoxide to decrease its concentration to 10 ppm, following the reaction formula:

$$CO + 0.5O_2 \rightarrow CO_2 \tag{12}$$

Additionally, these catalysts cannot be active in the reaction of oxidation of hydrogen, it is in excess in the gas mixture, so in the presence of less selective catalysts the prevailing reaction could be as follows:

$$H_2 + 0.5O_2 \rightarrow H_2O \tag{13}$$

For assessment of the effectiveness of CO-PROX catalysts the selectivity towards CO is defined as a part of oxygen that oxidizes CO while the rest of oxygen oxidizes hydrogen:

$$S_{CO} = \frac{[CO]_1 - [CO]_2}{2([O_2]_1 - [O_2]_2)} \tag{14}$$

where: [CO], [O_2] – concentration of CO and O_2; Subscripts: 1,2 – initial, output

PROX Process is conducted at atmospheric pressure in the temperature range of 80-150^{0}C with oxygen excess, compared to the stoichiometric value. Active CO–PROX catalysts are mainly noble metals supported on oxide carriers promoted by base metal oxides. The most active are:

- catalysts containing copper: Cu/CeO_2 (Di Benedetto et al., 2013; Gu et al. 2014; Liu et al., 2004; Monte et al. 2014; Tang et al. 2014),
- catalysts containing dispersed gold: Au/SiO_2, Au/TiO_2, Au/Al_2O_3, Au/ Fe_2O_3 (Kung et al., 2003); Au/MgO promoted with Mn and Fe (Margitfalvi et al., 2004); Au/CeO_2–CoO_4 (Wang et al., 2008; Au/α-Fe_2O_3 (Avgouropoulos et al., 2002); Au(Pt-Au)/CeO_2 (Liu et al., 2013),
- catalysts containing platinum, rhodium or ruthenium: Pt/ γ-Al_2O_3 (Avgouropoulos et al., 2002); Pt(Pt-Au)/CeO_2 (Liu et al., 2013); K promoted Rh on zeolit USY (SiO_2/ Al_2O_3 (Tanaka et al., 2003); base metal promoted 5% Pt on monolithic cordierite impregnated with γ-Al_2O_3 Korotkikh and Farrauto, 2000) monolithic Pt/Fe on mordenit (Maeda et al., 2008); Pt (Ru, Rh)/ γ-Al_2O_3 (Kim et al., 2009).

Only in the presence of the catalysts containing platinum, rhodium or ruthenium, the level of carbon monoxide can be lowered to 10 ppm.

For this type of catalysts further investigations to optimize process parameters and composition of the catalysts are continued. The inhibition of oxidation of carbon monoxide by steam and carbon dioxide and the rate of deactivation of catalysts used are still the important problems to be investigated.

Dudfield et al. (2001) reported the construction of a CO-PROX reactor integrated with reforming of a methanol reactor. The set has been designed for automotive transport, 2.5 mass% Pt/Ru supported on hopcalite CO-PROX catalyst enables a decrease in CO concentration to 10 ppm thus enabling its application in 20 kW power fuel cells. The work has been granted as Mercatox Project coordinated by Wellman CJB Ltd. UK.

5. CONCLUSIONS

The production of hydrogen from methanol can be performed in 4 different ways: thermal decomposition of methanol (MD), partial oxidation of methanol (POM), steam reforming of methanol (SRM), oxidative steam reforming of methanol (OSRM). OSRM system integrates the advantages of POM and SRM, but also shares their disadvantages.

The development of Cu-based catalysts has been focused on steam reforming of methanol. An effort has been put in to improve the low surface area of the catalyst. Recently, Cu-based spinel-latticed catalysts have been extensively studied due to their high thermal stability, thus avoiding Cu sintering. Different mechanisms have been proposed concerning reactions occurring on copper surface and reactions at the boundary between Cu and metal oxide. Full explanation of these phenomena will allow to design an optimal catalyst and thus optimum process. Despite many attempts, the required purity of hydrogen production in SRM process over a Cu based catalyst was not obtained. Ensuring high purity of hydrogen is a priority, so preferential oxidation of carbon monoxide (CO-PROX) over the best catalysts should be applied. Agrell et al. (2002) proposed the addition of steam to the substrate mixture, decrease temperature and contact time to increase hydrogen purity, at the cost of conversion of methanol.

While that area of research is of great importance, it is also quite difficult, both in experimental and theoretical parts. The available body of literature concerning these topics is too small to describe it in certain terms. The most important tendencies in the production of high purity hydrogen for fuel cells have been described in the presented paper.

SYMBOLS

DEN	$= (1 + K_{\mathrm{CH_3O(1)}} p_M\, p_{\mathrm{H}}^{-0.5} + K_{\mathrm{OH(2)}} p_W\, p_{\mathrm{H}}^{-0.5})(1 + K_{\mathrm{H}(2a)}^{0.5} p_{\mathrm{H}}^{0.5})$
E	energy of activation, $\mathrm{kJ \cdot mol^{-1}}$
$GHSV$	gas hourly space velocity, $\mathrm{h^{-1}}$
k	rate constant for methanol stem reforming reaction; units are specific to the form of the rate expression
k^{-1}	rate constant for reverse methanol stem reforming reaction; units are specific to the form of the rate expression
K_i	equilibrium constant of reaction i or adsorption coefficient for surface species i
p	partial pressure of component, MPa
r	reaction rate, $\mathrm{mol \cdot s^{-1} \cdot g_{cat}^{-1}}$
t	temperature, °C
T	temperature, K

Greek symbols

η	effectiveness factor taking into account internal diffusion

Superscripts

a, b, c, e	exponents in power law equation

Subscripts

C	carbon dioxide
H	hydrogen
M	methanol
W	water

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