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*In memory of Professor Jerzy Skrzypek*

# COPPER/ZINC CATALYSTS IN HYDROGENATION OF CARBON OXIDES

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A review concerning main processes of hydrogenation of carbon oxides towards synthesis of methanol, mixture of methanol and higher aliphatic alcohols and one-step synthesis of dimethyl ether as well as methanol steam reforming is given. Low-temperature methanol catalysts and low-temperature modified methanol catalysts containing copper as primary component and zinc as secondary one are described.

**Keywords:** Cu-based catalysts, methanol synthesis, steam reforming of methanol, higher aliphatic alcohol synthesis, dimethyl ether

## 1. INTRODUCTION

Synthesis gas is an important chemical very widely used in chemical industry. It is produced either from coal or from petroleum. It is a mixture of carbon monoxide and hydrogen in a very wide range of concentrations. It usually also contains carbon dioxide and nitrogen. Processing of synthesis gas using either homogeneous or heterogeneous catalysis gives various chemicals: methanol, higher aliphatic alcohols, saturated and unsaturated aliphatic hydrocarbons, acetic acid, formic acid, substitute natural gas, ethylene glycol.

Kinetics of heterogeneous catalytic reactions is a major part of the chemical reactor engineering area. The use of catalysts in chemical processes can reduce the activation energy of a chemical reaction thereby increasing the rate and, in some cases, the selectivity of the process. It is the reason for which the majority of chemical processes carried out on an industrial scale are catalytic processes. The most commonly used catalysts are heterogeneous ones. An important role of these processes is the hydrogenation of carbon oxides, such as methanol synthesis, and those associated with methanol: synthesis of higher aliphatic alcohols, ether synthesis, decomposition and reforming of methanol.

Copper mixed oxides in a partially reduced state are well known as excellent catalysts for many reactions, such as hydrogenation of organic compounds, alcohol decomposition or dehydrogenation of alcohols and ester hydrogenolysis. Some metal oxides may be incorporated into the catalyst and act as promoters or stabilising agents.

The scope of the article was to present the investigations of Jerzy Skrzypek and his team in the area of catalytic hydrogenation of carbon oxides.

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## 2. METHANOL SYNTHESIS (MS)

Methanol is one of the key industrial chemicals produced by heterogeneous catalysis. It can be used to produce a wide range of chemicals or to convert them into more complex hydrocarbons. Nowadays, its significance is increasing since it is applied as chemical energy carrier i.e. the fuel for fuel cells and as a potential substitute for gasoline (Centi and Perathoner, 2009). Methanol produced from carbon dioxide and hydrogen may be considered as an agent for hydrogen storage and distribution. Methanol, ethanol, gasoline and diesel have been discussed for on board reforming, of which methanol is considered the most favourable alternative (Agrell et al., 2003; Mastalir et al., 2005). The effective utilisation of $CO_2$ is of great significance from the point of view of global environmental protection. $CO_2$ is considered as a major source of global warming caused by the so-called greenhouse effect (Ma et al., 2009). Before the 1970s, methanol was produced from $CO/H_2$ mixture at 673 K and 20 MPa over ZnO catalyst promoted by $Cr_2O_3$ or $Al_2O_3$ (Waugh, 2012) – the so-called "high pressure" method. This method had been replaced by the "low pressure" method, which used $CuOZnOAl_2O_3$ – "copper" catalyst. The addition of CuO to the methanol synthesis catalyst allowed the reduction of both pressure to 5 – 10 MPa and temperature to 453 – 523 K, thus significantly reducing energy consumption during the production. Additionally, from that moment, the removal of $CO_2$ from the reaction mixture was not necessary, as methanol was produced from a mixture of hydrogen, carbon monoxide, and small amounts of carbon dioxide. The copper catalyst was characterized by the excellent activity and selectivity, but its sensitivity to overheating and poisoning (by sulphur, chlorine and phosphorus) caused its short time life. Catalysts for the synthesis of methanol are obtained in several steps (Fig. 1).

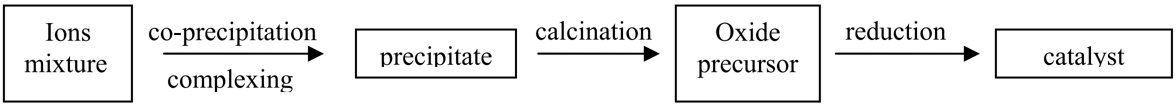


Fig. 1. Diagram of catalyst preparation

Most of the methanol synthesis catalysts were obtained by the carbonate method (co-precipitation) – from aqueous solutions containing nitrates of the appropriate metals and sodium carbonate at constant pH = 7 – 8, and subsequent calcination of the obtained precipitate at 623 K. The complexing of the solution components by using citric acid was followed by drying and calcination at 623 K (Courty et al., 1973). Cu-based catalysts achieved their active form after reduction of CuO to metallic Cu or to $Cu^0/Cu^{+1}$ (Oguchi et al., 2005; Skrzypek, 1994).

The investigations over the new methanol synthesis catalyst, started in Poland by Błasiak, resulted in a patent (Patent 34000, 1950). It was one of the first patents on copper–based catalysts in the world. The catalyst patented by Błasiak was prepared by co–precipitation method and contained 62.5 wt.% CuO, 25 wt.% ZnO and 7.5 wt.% $Al_2O_3$. It was successfully used in the 1950s at Chemical Works Oświęcim in methanol synthesis (Kotowski, 1963). Since the early 50's a significant number of patents appeared relating to the composition and preparation methods of the methanol synthesis catalysts. A feature common to all copper catalysts was the presence, in addition to copper oxide, zinc oxide as well as the carrier (initially $Al_2O_3$ or $Cr_2O_3$) and eventually promoters – of transition elements introduced separately or in combination. Most researchers do not think it is copper but rather Cu/ZnO system that is responsible for the activity of copper catalysts (Behrens et al., 2012; Hadden et al., 1995; Nakamura et al., 2003; Okamoto et al., 1984; Peter et al., 2012; Santiago et al., 2012; Waugh, 2012). Okamoto (Okamoto, 1984) found that strong interaction between Cu and ZnO results in an electron transfer from ZnO to Cu metal and the formation of two types of Cu metal species as well as stabilised $Cu^{1+}$ species. According to Behrens (Behrens et al., 2012) ZnO functions as a physical spacer between copper particles and helps disperse the Cu phase in the course of catalyst preparation and thus is responsible for the Cu surface area; its presence increases the intrinsic activity of Cu-based methanol synthesis catalysts, an effect known as the Cu-ZnO synergy. The active site on Cu/ZnO based catalysts has not been, as yet, comprehensively understood. Fujiwara (Fujiwara et al., 1994) underlined the importance of preparation method and suggested the ratio of copper to zinc – 3:7, but in a number of patents this value varies from 1 to 3. On the other hand it is well known that the activity of Cu-based catalyst depends on the area of metallic copper (Peter et al., 2012; Wang et al., 2010) and copper dispersion, that are function of copper concentration and calcination temperature. H. Oguchi (Oguchi et al., 2005) investigating $CuO/CeO_2/ZrO_2$ catalyst in methanol steam reforming process reported that catalyst activity increases with the copper content up to 80 wt.% CuO, and a further increase of Cu content results in its rapid decrease (Lee and Lee, 1995). Okamoto reported that maximum activity of Cu/ZnO catalysts was obtained for CuO content equal to about 70%.

Apart from catalytic investigations, research was also conducted on the mechanism and kinetics of the process, although the exact mechanism is not clearly discussed. Methanol can be produced in direct reaction of carbon monoxide and hydrogen:

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

and carbon dioxide hydrogenation:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{2}$$

Until the mid 70's, it was believed that methanol is formed in reaction (1). However, Rozowski's works (Rozowski and Kagan, 1976) clearly showed that over Cu based catalysts, methanol is produced via hydrogenation of carbon dioxide (2) accompanied by the reverse water gas shift reaction (RWGSR):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{3}$$

This theory has been widely accepted and confirmed by numerous researchers including Skrzypek and Lee (Lee et al., 1993; Skrzypek et al., 1991). As methanol formation is an exothermal reaction with a reduction in the number of moles, a decrease of temperature and rise in pressure should favour the reaction thermodynamically, but chemically inert $CO_2$ needs high temperature to activate and then to form methanol (Skrzypek et al., 1990, Skrzypek et al., 1995). However, a new possibility for the use of excess carbon dioxide for methanol production appeared. Despite the Cu/ZnO catalyst being used so successfully for conventional methanol synthesis from syngas, a mixture of $H_2$, CO and small amounts of $CO_2$, exhibits a tendency to be deactivated prematurely at high $CO_2$ partial pressures. Therefore, it became necessary to develop a novel catalyst for methanol synthesis from $CO_2$ and $H_2$ or from $CO_2$–rich syngas (Goehna and Koenig, 1994). It is important to develop a highly selective catalyst in order to avoid the formation of by-products that may be formed in the process, such as water, hydrocarbons and higher alcohols.

Investigations were performed over Au, Ag and Cu based catalysts (Słoczyński et al., 2004; Strunk et al., 2009) in methanol synthesis process. Słoczyński et al. (Grabowski et al., 2011; Słoczyński et al., 2004), while investigating $M/(3ZnO\cdot ZrO_2)$ system (M=Cu, Ag, Au) obtained the best results for Cu catalysts. Strunk found that Au/ZnO catalysts were more active in methanol synthesis than pure ZnO, but they exhibited higher activity in the absence of $CO_2$. But, well known Pd-based catalyst requires higher temperature than Cu-based catalyst.

Literature reports concerning the advantageous influence of zirconium have been appearing for several years (Arena et al., 2008; Ihm et al., 1997; Lee et al., 1993; Lee et al., 1995; Ortelli et al., 2001; Słoczyński et al., 2001; Wambach et al.,1999). The authors investigated various modifiers of $Cu/ZnO/Al_2O_3$ catalyst and realised that Zr improved its activity in methanol synthesis from $H_2 + CO_2$. Bonura (Bonura et al., 2011) examining influence of Zr, Ce and Cr on binary Cu/ZnO-based catalyst activity found that Zr is the best. According to Wambach (Wambach et al., 1999) $ZrO_2$ by itself is a catalyst for the synthesis of methanol in contrast to commonly used support – $Al_2O_3$. Zirconia provides adsorption sites for the surface reaction intermediates and, moreover, metal/$ZrO_2$ systems exhibit excellent mechanical and thermal stability, a moderately high specific surface and good semiconducting properties.

Numerous papers concerning influence of oxide additives on the activity of Cu-based catalysts were presented over past decades (Huang et al., 2004; Ihm et al., 1997; Jun et al., 1997; Kilo et al., 1997; Lee et al., 1995; Maniecki et al., 2009). Ihm in the investigations of Cu/$ZrO_2$ precursor promoted by Ce, Cr, Cs, Zn, K, Pd and V, found that Zn was the best. Jun pointed out that Cr and Ga were better than Al, Al/Cr and Zr as additions to Cu/ZnO. Lee performed modification of Cu/ZnO/$Al_2O_3$ with Ag, Pt, Rh, Ru, Co, Mn, Mo, Ti and Zr.

Extensive research concerning methanol synthesis was conducted by Skrzypek and his team. After preliminary measurements, they decided to narrow down the search for the optimal catalyst for methanol synthesis to modify Cu/ZnO/$ZrO_2$ precursor (Lachowska and Skrzypek, 2004a; Lachowska and Skrzypek, 2004b; Lachowska et al., 2004; Słoczyński et al., 2001; Słoczyński et al., 2003; Słoczyński et al., 2004).

The study of the influence of oxide additives on the activity and structure of the Cu/ZnO/$ZrO_2$ catalyst in the synthesis of methanol from $CO_2$ and $H_2$ were performed by Skrzypek's team in cooperation with researchers from Jerzy Haber Institute of Catalysis and Surface Chemistry PAS. The oxide precursors CuO/ZnO/$ZrO_2$/(M) with an approximate composition of 62.4–65.8 wt.% CuO. 25–26.7 wt.% ZnO. 4.5–12.6 wt.% $ZrO_2$ and 0.7–12.6 wt.% (M) were obtained using two methods: (A) by decomposition of citrate and (B) co-precipitation. For method (A) – M = Ga, Cr, Pd, Mn, Mg, Au, Ag, for method (B) – M= Ga, B, In, Gd, Y, Mg, Mn. The catalytic activity was presented as stationary values, established after 10–20 days. Significant changes were caused by oxide additives in the activity of the Cu/ZnO/$ZrO_2$ precursor, in the reaction of the methanol synthesis from $CO_2$ and $H_2$. The highest yields of methanol were observed for Cr, Ga and Pd (for the upper range of studied temperatures) promoted catalysts. The addition of In and Mg decreased drastically catalysts' activity. Methanol yields are shown in Fig. 2 (method A) and in Fig. 3 (method B).

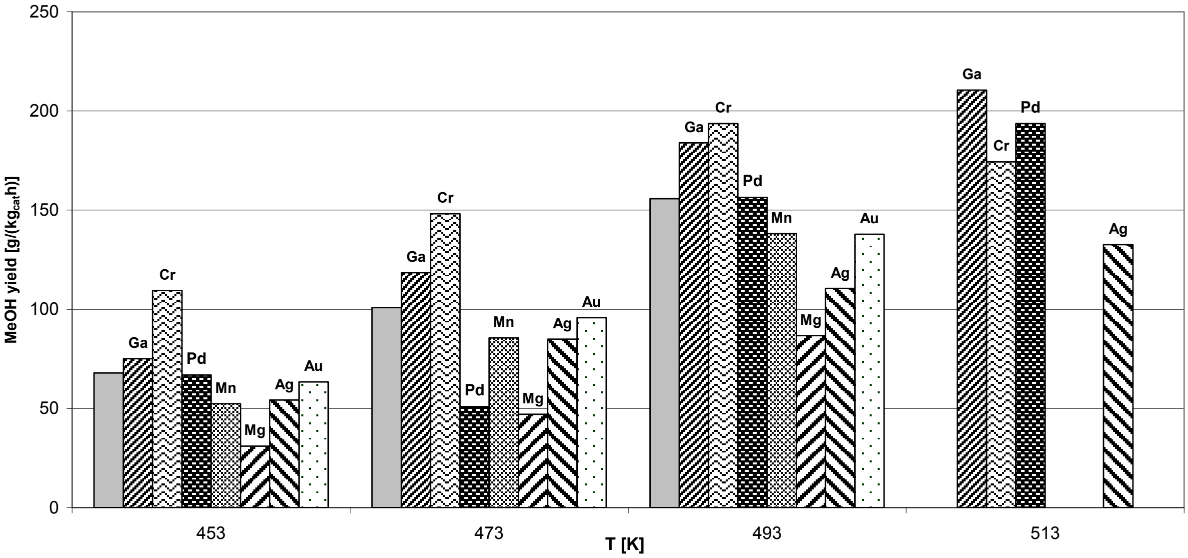


Fig. 2. Methanol yields for the modified CuZnZr catalysts obtained with decomposition of citrate method in comparison with non-modified CuZnZr catalyst (bar no. 1)

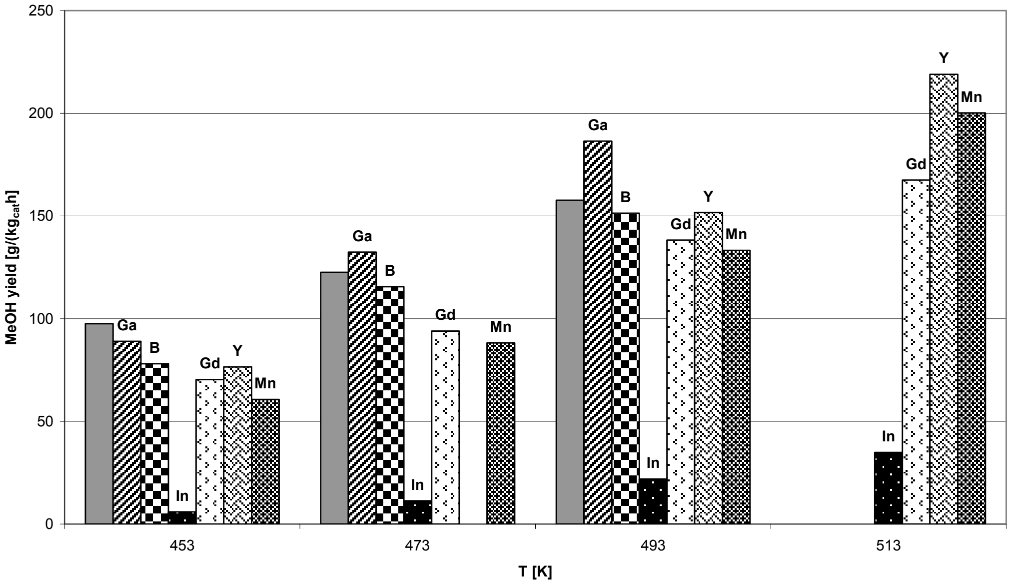


Fig. 3. Methanol yields for the modified CuZnZr catalysts obtained with co-precipitate method in comparison with non-modified CuZnZr catalyst (bar no. 1)

## 3. STEAM REFORMING OF METHANOL (SRM)

The hydrogen obtained in methanol steam reforming process can be used to power fuel cells – efficient and environmentally friendly energy source (Agrell et al., 2003; Apanel and Johnson, 2004; Leszczyński 2001; Sá et al., 2010; Spivey, 2005). The combustion of hydrogen in fuel cell is regarded as a clean process, releasing energy and providing only water as an exhaust material (Mastalir, 2005). The fuel cell technology is being carefully evaluated for use in stationary power and transportations (Spivey, 2005).

Methanol steam reforming is a catalytic process. The catalysts which are used in the process should be characterized by a high activity and selectivity. This is particularly important in terms of minimising the amount of carbon monoxide formed as a by-product. Carbon monoxide is a strong poison for the platinum catalyst of the fuel cell with a polymer proton exchange membrane ((Peppley et al., 1999, Samms and Savinell, 2002; Spivey, 2005). Copper catalysts used in the methanol steam reforming are in fact similar to those used in the "low-pressure" methanol synthesis process in installations for large industrial scale. However, in this case, there are other mechanisms of the reaction and they can vary substantially and require separate examination. The major products of methanol steam reforming process are $H_2$ and $CO_2$ with the minor quantities of CO. Thanks to the selectivity of the copper–based catalysts, methane formation can be completely avoided. Then, the two main reactions occur:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \tag{4}$$

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

Many papers concerning Cu-based catalysts performance (Frank et al., 2007; Huang and Wainwright, 2009; Idem and Bakhshi, 1995; Wu et al., 2009;) describe their activity, selectivity and stability and show the ways to improve them. In order to achieve the optimum catalyst, authors suggest to introduce changes in the composition of the catalyst, changing the contents of copper and metal oxide (promoters) introduced into the Cu precursor as well as the methods of preparation and activation of the catalyst (Agrell et al., 2003; Breen and Ross, 1999; Cheng et al., 2003; Liu et al., 2003; Mastalir et al., 2005; Matter et al., 2004; Oguchi et al., 2005; Suwa et al., 2004;Takezawa and Iwasa, 1997; Yao et al., 2006).

The modification of the ternary CuZnOZrO$_2$ catalyst with one or more promoters was performed under Skrzypek's supervision. As a result, there were more than 20 CuZnZr catalysts developed with promoters: Ga, Ag, Au, Cr, Ce, Mg, La, Mn, Pd (Madej-Lachowska, 2012; Lachowska 2004a, Lachowska, 2007; Lachowska, 2010). The activity of catalysts was evaluated in terms of the values of product yield and selectivity. The selectivity is of a great significance from the fuel-cell applications point of view, because even the traces of CO (>20 ppm) in the reformed gas deteriorate a Pt electrode and the cell performance is lowered dramatically. The stability of the studied catalysts was also taken into consideration.

The catalysts were prepared using the thermal decomposition of citrates method. The measurements of the specific surface area determined with the BET method and active surface of copper did not allow to draw any correlation with the activity of the examined catalysts. The differences between the catalysts result from the temperature at which they reached the maximum (the highest hydrogen yield) for these parameters. Incorporating promoters to the "base" Cu/ZnO/ZrO$_2$ (bar no.1) catalyst strongly improves its activity in the methanol steam reforming process. The methanol conversion, hydrogen yield and selectivity of the studied catalysts are shown on Figs 4–6.

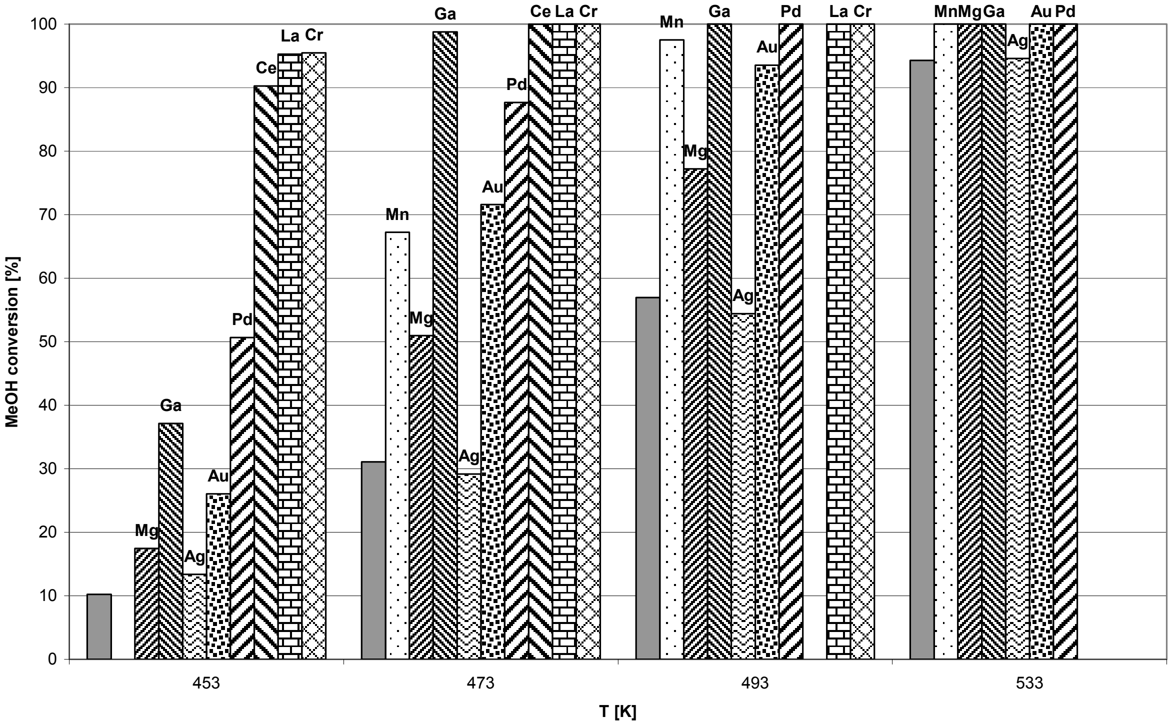


Fig. 4. Methanol conversion for the modified CuZnZr catalysts in comparison with non-modified CuZnZr catalyst (bar no. 1)

The best of the tested promoters were: chromium, cerium, lanthanum and gallium. However, it was difficult to choose the best (performing) of these catalysts as the differences in their activity are small and could be attributed to the measurement error. Thanks to performed investigations a significant increase in the methanol conversion in the temperature range 433–473 K was reached. The most important achievement was a reduction of the optimal operating temperature for the catalysts. The best catalysts reached their maximum hydrogen yields at the temperature as low as 473 K. A thermodynamic analysis showed that an increase in the temperature of the process above 480 K caused a strong increase of the equilibrium conversion of a side reaction, whose product, carbon monoxide, is highly undesirable, in terms of the application of the produced hydrogen in the fuel cells (Lachowska, 2004b).

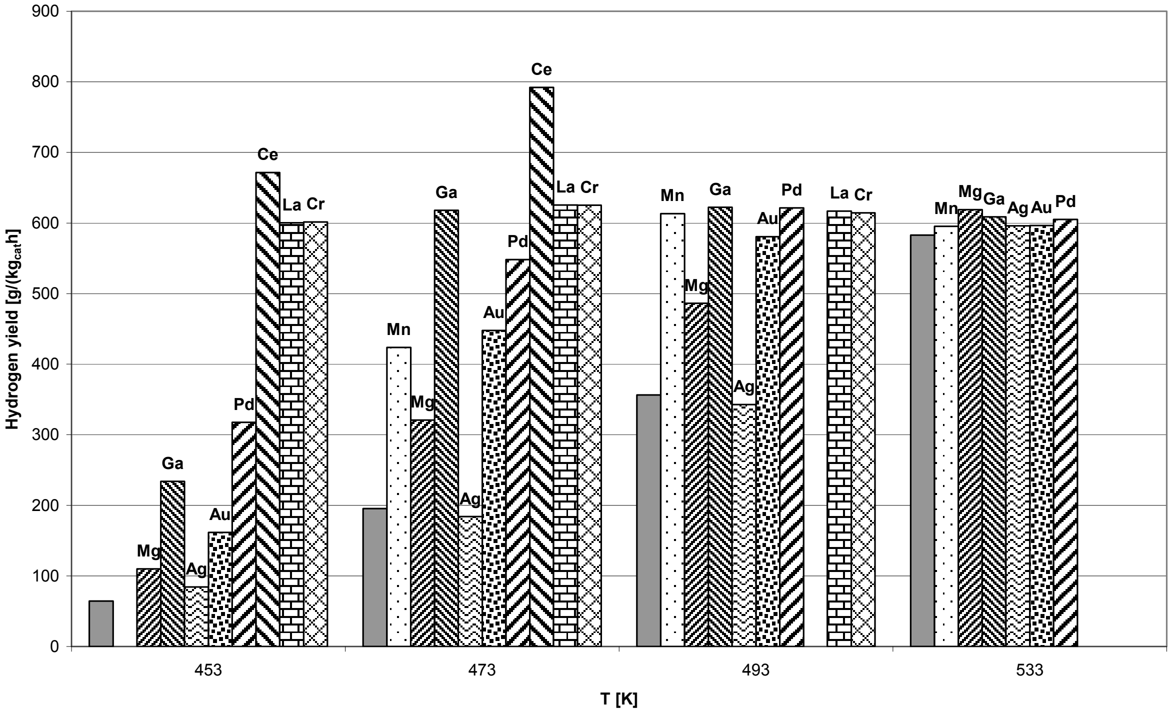


Fig. 5. Hydrogen yield for the modified CuZnZr catalysts in comparison with non-modified CuZnZr catalyst (bar no. 1)

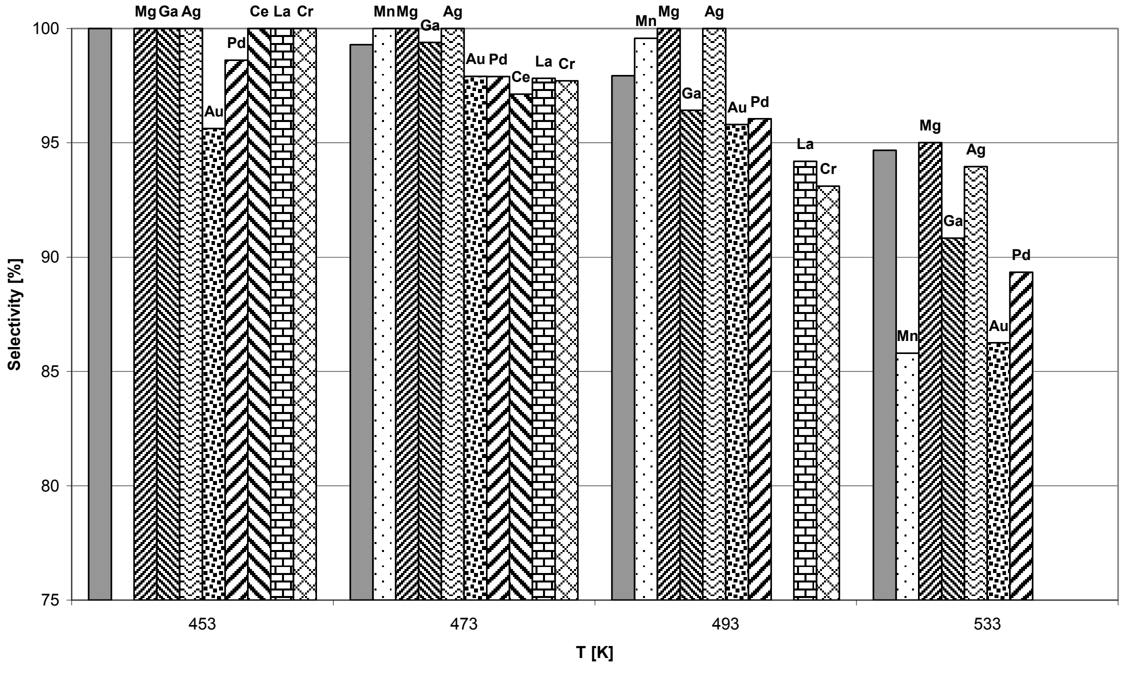


Fig. 6. Selectivity for the modified CuZnZr catalysts in comparison with non-modified CuZnZr catalyst (bar no. 1)

## 4. HIGHER ALCOHOL SYNTHESIS (HAS)

The mixture of methanol and higher alcohols is an interesting product either as direct antiknock agent in gasoline or in production of ethers (methyl–*tert*–butyl ether, MTBE, and ethyl–*tert*–butyl ether, ETBE), which are antiknock agents as well. At present, modification to refining process of oil and the use of oxygenated petrochemical compounds are the means to enhance the octane number of gasoline. Therefore, there is a great demand for these products. Since methanol is the only product with a serious potential for mass production and high yield and low cost, the higher alcohol synthesis has been conducted only in pilot plants. The process requires special, composite catalysts working in severe conditions. The main reaction system follows the general formula:

$$n\,CO + 2nH_2 \leftrightarrow C_nH_{2n+1}OH + (n-1)\,H_2O \tag{6}$$

where n = 1 for methanol, higher values of n for respective higher aliphatic alcohols. Simultaneously the water-gas shift reaction occurs:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{7}$$

Undesired side reactions of hydrocarbon formation occur, especially that of methane:

$$n\,CO + (2n+1)\,H_2 \leftrightarrow C_nH_{2n+2} + n\,H_2O \tag{8}$$

Formation of other oxygenates, methyl esters, ethers, aldehydes and ketones can also proceed. All the above reactions are reversible, exothermic and proceed with volume contraction; except water gas shift reaction, that is assumed to be in thermodynamic equilibrium at this process conditions. Therefore, from the thermodynamic point of view, lower temperatures and higher pressures are desirable.

Active sites should be homogenously distributed as far as possible. Any disturbance of the optimum distribution of active sites leads to suppression of the selectivity and activity of the catalysts. The hydrogenation catalysts origin from two main classes; that for methanol synthesis and that for Fischer–Tropsch synthesis. The mechanism of alcohol synthesis is catalyst specific. The overall combination of experimental techniques in a suitably wide range could give insight into the reaction mechanism. It is believed that modified Fisher–Tropsch catalysts promote CO insertion mechanism leading to the formation of linear alcohols only. Ethanol is the dominant higher alcohol (in the case of cobalt–based modified Fisher–Tropsch catalysts it constitutes ~20 wt.%, molybdenum–based 25 – 40 wt.%, iron–based ~70 wt.% in the liquid phase); in the case of rhodium catalysts the synthesis is selective to only ethanol. In the presence of methanol synthesis catalysts, higher alcohols are formed via an addition of hydrogen in $CH_2$ group in the α or β position relative to OH group. The addition in the β- position occurs faster than the α- addition and leads to the formation of branched alcohols. Modified low-temperature methanol synthesis catalysts seem a good choice. Only these catalysts allow the production of monomethyl branched primary alcohols, mainly 2-methyl-1-propanol (isobutanol) and 2-methyl-1-butanol (isopentanol). The formation of branched alcohols comprises up to 60 wt.% of isobutanol. If higher alcohols are the major desired product then a promoter containing alkali or alkali earth species should be used. Efficient synthesis requires temperatures by about 100 K higher than those for methanol synthesis, a feed gas ratio distinctly lower ( $y_{H_2}^0 / y_{CO}^0$ about 1/1), and a longer contact time.

The advantage of copper catalysts is their high activity and mild reaction conditions. The disadvantage is their sensitivity to the poisoning with sulphur, chlorine and phosphorus; the susceptibility to sintering; the gradual deterioration of the support in the presence of alkali metals. Synthesis gas obtained from coal, natural gas or biomass usually contains hydrogen sulphide ($H_2S$). The values of the yield of alcohol mixture differ distinctly in spite of the same composition of catalyst. The average values lie in the range 0.2 – 0.4 $kg/kg_{cat}/h$. (Spivey, 2005; Herman, 2000). The values up to 0.98 $kg/kg_{cat}/h$ have also been claimed in patents (Keim and Falter, 1989). The content of methanol in a raw mixture usually goes beyond 50 wt.%; it should be minimised, because the production of pure methanol is large, cheap and efficient.

Many series of composite catalysts containing mainly copper and zinc oxides promoted with varying amounts of aluminium, iron, molybdenum and thorium oxides have been worked out by Skrzypek et al. (Kulawska and Skrzypek, 2001; Skrzypek et al., 2000; Skrzypek et al., 2001). The range of parameters investigated was P = 4 – 10 MPa, T = 593 – 650 K, $y^0_{H_2} / y^0_{CO}$ = 0.46 – 3.17, GHSV = 1800 – 7000 1/h.

The oxide precursors were obtained using different preparation methods. The method of complex formation of metals by citric acid and decomposition of citrate complexes (Courty et al., 1973) proved the best in our laboratory. The mixture of metal oxides is perfectly mixed because of branched structure of citrates. The use of citrate complexes gives perfect homogeneity and fully repeatable properties of prepared catalyst (Skrzypek et al., 2000; Skrzypek et al., 2001), which cannot be obtained using conventional coprecipitation method, even though the latter is usually used, as known from literature (Herman, 2000; Mahdavi et al., 2005). Other components and many dopants towards higher aliphatic alcohol synthesis have been investigated. The selected promoters used are potassium and caesium. All catalysts have varied in composition, following the general formula $CuO/ZnO/ZrO_2(Al_2O_3)/Fe_2O_3/MoO_3/ThO_2(UO_2)/KOH(Cs_2O)$.

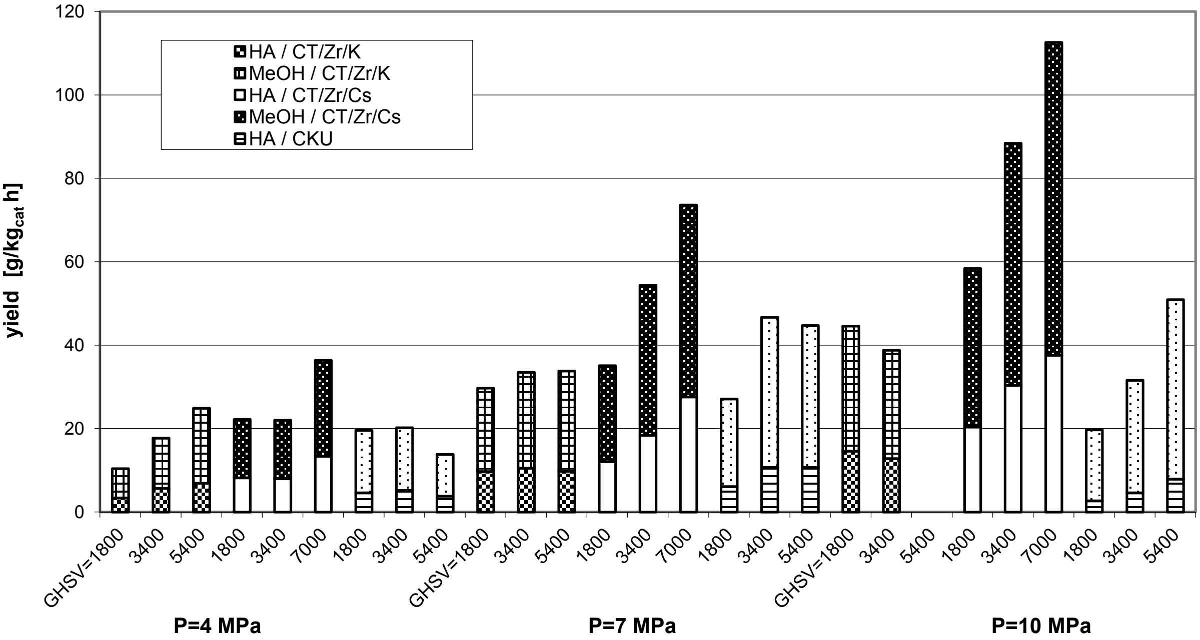
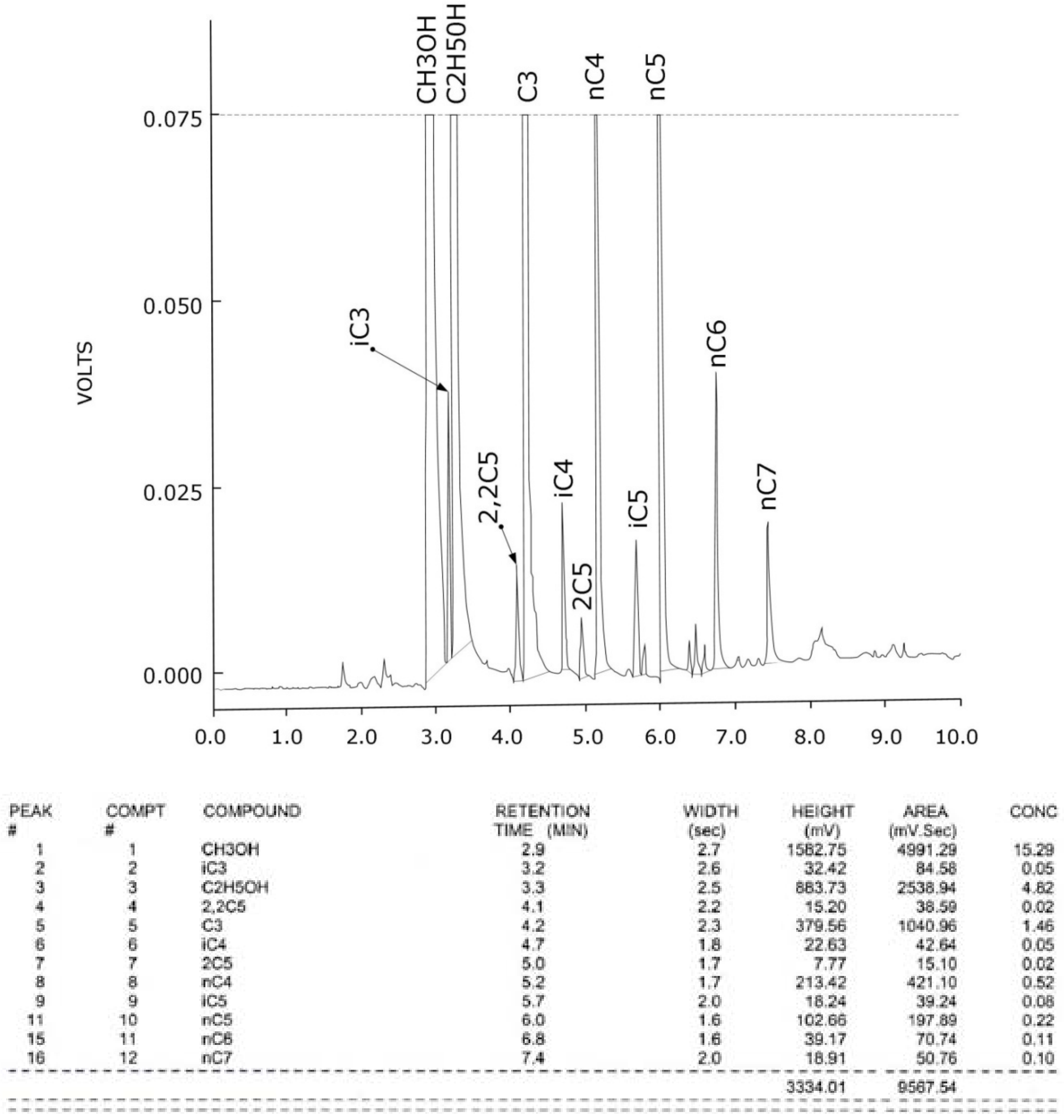


Fig. 7. Comparison of effect of process parameters on the yield of methanol (MeOH) and higher aliphatic alcohols (HA) over various catalysts at selected substrate ratio $c = H_2/CO$.
$T$ = 623K. (1) K/Cu/Zn/Zr/Fe/Mo/Th, $c$ = 1.32; (2) Cs/Cu/Zn/Zr/Fe/Mo/Th, $c$ = 1.32;
(3) Cs/Cu/Zn/Al/Fe/Mo/U, $c$ = 1.0

Restricted technological regime has been maintained to avoid the preparation effect on the properties of catalysts. The yield obtained was 130–170 g/kg$_{cat}$/h of liquid product that contained about 40 wt.% of methanol and 25–35 wt.% of higher aliphatic alcohols. Practically no by-products were formed, only traces of methane were detected. Higher aliphatic alcohols included ethanol 51–64 wt.%, propanol 23–32 wt.%, and $C_4$–$C_7$ aliphatic alcohols. Branched alcohols (isopropanol, isobutanol, isopentanol) constituted up to 10 wt.%. We found the composition of liquid product was practically independent of process parameters. The yield of aliphatic alcohols was strongly dependent on process parameters, see Fig. 7. An increase in both temperature and pressure caused an increase in yield obtained (Kulawska, 2004; Kulawska and Moroz, 2007). The optimal process parameters were temperature about 620 K, pressure 10 MPa, initial substrates ratio $y^0_{H_2} / y^0_{CO} \sim$ 1.3, gas hourly space velocity GHSV ~ 3800 1/h over Cs-promoted catalyst. Interaction of so many components gave beneficial properties. No sintering has been observed though the reaction temperature was slightly higher than that at typical conditions over low-temperature modified methanol catalysts, (but lower than that at typical conditions over high-temperature modified methanol catalysts). We have obtained very selective catalysts towards alcohols. It was an important improvement. Practically no hydrocarbons have been detected, traces of methane were the only side product in a few series performed using a catalyst promoted with potassium. All oxygenates were aliphatic alcohols, occasional traces of acetone have been found. It is shown in Fig. 8.



| PEAK # | COMPT # | COMPOUND | RETENTION TIME (MIN) | WIDTH (sec) | HEIGHT (mV) | AREA (mV.Sec) | CONC |
|---|---|---|---|---|---|---|---|
| 1 | 1 | CH3OH | 2.9 | 2.7 | 1582.75 | 4991.29 | 15.29 |
| 2 | 2 | iC3 | 3.2 | 2.6 | 32.42 | 84.58 | 0.05 |
| 3 | 3 | C2H5OH | 3.3 | 2.5 | 883.73 | 2538.94 | 4.82 |
| 4 | 4 | 2,2C5 | 4.1 | 2.2 | 15.20 | 38.59 | 0.02 |
| 5 | 5 | C3 | 4.2 | 2.3 | 379.56 | 1040.96 | 1.46 |
| 6 | 6 | iC4 | 4.7 | 1.8 | 22.63 | 42.64 | 0.05 |
| 7 | 7 | 2C5 | 5.0 | 1.7 | 7.77 | 15.10 | 0.02 |
| 8 | 8 | nC4 | 5.2 | 1.7 | 213.42 | 421.10 | 0.52 |
| 9 | 9 | iC5 | 5.7 | 2.0 | 18.24 | 39.24 | 0.08 |
| 11 | 10 | nC5 | 6.0 | 1.6 | 102.66 | 197.89 | 0.22 |
| 15 | 11 | nC6 | 6.8 | 1.6 | 39.17 | 70.74 | 0.11 |
| 16 | 12 | nC7 | 7.4 | 2.0 | 18.91 | 50.76 | 0.10 |
|  |  |  |  |  | 3334.01 | 9567.54 |  |

Fig. 8. An example of gas chromatography analysis of liquid product

Many new investigations aimed at development of the catalysts for production of higher aliphatic alcohol synthesis have been carried out and some improvements were made. Molybdenum-based catalysts are attractive for production of linear alcohols (Surisetty et al., 2011; Surisetty et al., 2012). An extremely high resistance to sulphur and chlorine is a distinctive advantage of this type of catalyst. The second advantage is nearly water–free product; the water–gas shift reaction is greatly enhanced making carbon dioxide the main by–product. Selectivity to hydrocarbons is still greater than to alcohols, even over carbides of transition metals with $Mo_2C$ being the most promising (Wang et al., 2010; Xiang et al., 2008). Other catalysts proposed by various research teams are in fact variants of the catalysts developed by Institut Français du Pétrole. The combined cobalt – copper system has more complex composition, at least with trivalent metal as a third component. Metal ratios Cu/Co = 1/1, (Cr,V,Fe,Mn)/Co = 0.1/1 are commonly used with potassium doping. It must be noted that these catalysts cannot be considered as being modified methanol catalysts with cobalt addition. The doping of Co to typical copper catalysts even in very low amounts (under 1 wt.%) reduces the yield even by more than one order of magnitude (Sugier and Freund, 1978; Sugier and Freund, 1980; Xiaoding et al., 1987). Methanol is the main product, the good higher alcohol formation is obtained for copper – rich compositions. Similar trends were observed in the systems containing $Al_2O_3$ or ($Al_2O_3$ + ZnO). Some substitutions or modifications were made, e.g. by replacing Co with other Fe group metals (Ni, Fe) or by replacing alkali elements with other basic elements. However, no substantial improvement in either selectivity or yield has been observed (Yang et al., 2011). In the reaction over potassium promoted iron/copper catalyst ( without zinc) unfortunately many hydrocarbons are formed (Ding et al., 2012).

Further improvement of this complicated process is possible by modification of a reactor set. Slurry reactors have been expected to be a good industrial solution because of fast exchange of reaction heat and higher surface area. Their application did not produce the expected results (Nowicki and Ledakowicz, 1998; Sun and Roberts, 2003), though Nowicki and Ledakowicz (1998) used caesium-promoted copper/zinc catalyst, the maximum alcohol formation was only 40 g/kg$_{cat}$/h at T = 593 K, P=6.4 MPa, $y_{H_2}^0 / y_{CO}^0$ = 2. Both olefins and paraffins were formed in significant amounts affected by Vesto wax SH–105 as a slurry liquid. The syngas composition had a distinct effect on the product distribution giving an increase in total both alcohol and hydrocarbon production followed by increase of hydrogen content. Probably the kind of slurry liquid is also important. Sun and Roberts, 2003 used decahydronaphtalene at 13.9 MPa, 648 – 673 K. The maximum selectivity to higher alcohols was 0.15 over Cs-promoted zinc chromite – it was not copper catalyst.

Tandem bed reactors have been applied with beneficial results. Lower alcohols produced in the low temperature (598 K) bed were supplied to the higher temperature (613 K) bed to form higher alcohols. High yield of 200 g/kg$_{cat}$/h of 2-methyl-1-propanol was obtained in a double bed configuration with caesium- promoted copper/zinc/ chromium trioxide catalyst in both beds at pressure 7.6 MPa, at constant initial substrates ratio $y_{H_2}^0 / y_{CO}^0$ = 0.75, and gas hourly space velocity 18 375 l/kg$_{cat}$/h (Burcham et al., 1998). Earlier attempts in a tandem bed with only one packed with copper catalyst were not so successful at the same process conditions (Beretta et al., 1996).

The synthesis of higher alcohols requires special, composite catalysts working in severe conditions. It makes catalysts age fast; catalysts last several months, whereas in other catalytic processes up to several years. The proper preparation of catalysts i.e. the homogeneity of components during each step of pre–treatment is very important in safeguarding good performance, as well as the method of preparation itself.

It should be stressed that all these investigations were concerned with obtaining a mixture of methanol and higher aliphatic alcohols, to be used as gasoline addition. Synthesis of higher aliphatic alcohols (having mole masses in range 50 – 120) individually is conducted with different chemical technologies.

## 5. SYNTHESIS GAS TO DIMETHYL ETHER (STD)

Application of dimethyl ether is very interesting due to environmental protection; it is not a greenhouse gas, it is relatively non-toxic, not corrosive to any metal and not harmful to human beings. Easily liquefied, it is easy in transport and largely it is currently used as a substitute for propane in LPG. The infrastructure of LPG can be used for DME. With a high cetane number equal to 55 it is a substitute for conventional diesel fuel; it contains no sulfur or nitrogen. It is a colourless gas that is a useful precursor to other organic compounds, an aerosol propellant and a refrigerant also applicable to special laboratory procedures. Its world production approaches 150 000 tonnes. A new demonstration plant of DME in Piteå, Sweden, is based on renewable feedstocks (European Biofuels Technology Platform).

The main reaction system follows the following formulas:

$$2\ CO + 4\ H_2 \leftrightarrow 2\ CH_3OH \tag{9}$$

$$2\ CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \tag{10}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{11}$$

Synthesis process of gas-to-dimethyl ether (STD) has been developed for the direct synthesis of DME in a single reactor with hybrid catalysts. The main advantage of a single step synthesis is the lower thermodynamic limitation and the fact that it can be performed at higher temperatures and lower pressures. Typical hybrid catalysts used in this process are composed of a methanol synthesis copper catalyst and a methanol dehydration catalyst, mechanically mixed. After development of methanol synthesis catalyst the investigations are steered in two main directions: improvement of dehydration catalysts and development of mixing both elements of hybrid catalyst. A balance should be obtained between two main catalytic functions. It is known that hydrocarbons are formed on the strong acid sites on the surface of catalysts. In order to avoid it the strength of acid sites must be reduced. The acidic functions can be modified either through adjusting the acid strength or the quantity of acid sites. The former gives a risk of undesired product formation, the latter requires larger amounts to be used. Beneficial effect gave sodium loading making the catalyst more resistant towards hydrocarbon formation and towards water. It is may be due to blocking of active sites by molecular water. In an industrial plant, the tolerance level of water in the methanol feed for DME is well below a few hundred ppm level (Vishwanathan et al., 2004). High activity of CuZnAl/HZSM-5 catalyst at relatively low temperature 470 K and a great loss in activity of CuZnAl/$\gamma$ - $Al_2O_3$ catalyst has been observed by (Abu-Darieh et al., 2012). It may be attributed to zeolitic water adsorbed at the surface of the acid function but could also be due to other more strongly adsorbed basic molecules. Magnesium oxide addition to hybrid catalysts involves basic sites (Mao et al., 2005) if MgO content is less than 5 wt.%. Further investigations on CuZnAl / HZSM-5 hybrid catalysts are conducted (Abu-Darieh et al., 2012; García-Trenco and Martínez, 2012). SAPO (microporous silicoaluminophosphate molecular sieves) catalysts mixed with commercial Cu/Zn/Al are used (Travalloni et al., 2008; Yoo et al., 2007). SAPO-5 and SAPO -11 showed significant stability, whereas SAPO-34 and SAPO -18 showed low stability probably because of unfavorable pore structure (pore expansion caused accumulation of carbonaceous material in supercages and coke formation). These catalysts were performed to maintain good catalytic activity in Exxon patents (US 7 241 713, 10.07.2007, US 7 241 716, 10.07.2007). Many studies are conducted on finding a proper amount of dehydration component (Abu-Dahrieh et al., 2012; Fei et al., 2006; Osman et al., 2012; Ptaszek et al., 2012). Catalytic performance of bifunctional catalysts can be improved through enhancing the fine dispersion of the two kinds of active components. The incorporation of $ZrO_2$ in CuO lattice caused formation of copper in the state $Cu^+$ and $Cu^0$ active sites for methanol synthesis (Sun et al., 2003). In slurry reactors catalyst particle size is an important factor, it should be 220-250 mesh, not finer (Jia et al., 2005; Tan et al., 2005).

In our laboratory investigations concerning utilisation of greenhouse gas – carbon dioxide have been conducted. Direct synthesis of dimethyl ether from carbon dioxide and hydrogen over hybrid catalysts has been carried out. We selected Cu/Zn/Zr/Ga methanol catalyst as an active component of the bifunctional hybrid DME catalyst. The active form has been obtained after reduction with hydrogen diluted in nitrogen. As dehydration component a zeolite of H-ZSM-5 type has been chosen from our early investigations. It revealed weak acidic centers of Broensted type, it was highly crystalline without impurities (Grzesik et al., 2012). The effect of gas composition, temperature, pressure and contribution of dehydration catalyst has been investigated (Ptaszek et al., 2012). Recently, investigations performed in collaboration with researchers from Institute of Catalysis and Surface Chemistry Polish Academy of Sciences are focused on the application of natural and synthetic hydrotalcites as precursors and catalysts. Hydrotalcite compounds reveal unique properties, they are anionic clays with a lamellar structure composed of brucite-like layers. Isomorphous substitution of Mg $^{2+}$ to Al $^{3+}$ results in the formation of an excess positive charge on the clay lattice, which is compensated by mobile inorganic anions situated in the interlayer region, together with water molecules. Thermal decomposition of them results in the formation of basic mixed oxides that have also proved to be efficient catalysts (Plona et al., 2010; Skrzypek et al., 2010).

Modification of natural Iranian clinoptilolite zeolite to an efficient MTD catalyst (Royaee et al., 2008) is a good example of application of natural zeolites. Reuse of attrition particles of zeolites in new catalyst is also claimed (US 6 605 749).

More economic methanol dehydration catalysts are of great industrial interest. Methanol to dimethyl ether process is also a part of methanol to olefin (MTO) and methanol to gasoline (MTG) processes.

## 6. SUMMARY

Composite catalytic systems containing mainly copper and zinc with various additions can be applied with a good outcome in hydrogenation of carbon oxides towards synthesis of methanol, mixture of higher aliphatic alcohols and dimethyl ether or reforming of methanol. There is no possibility to indicate the best catalytic system. It depends on the main criterion used i.e. either yield or selectivity in connection with further applications of the product. Also, investigations carried out by various research teams in various experimental sets are not similar and direct comparison is not possible. The mechanism of the reaction of hydrogenation of carbon oxides is different for different catalytic systems depending on the metal, the support, the promoter and reaction conditions. The surface area of all copper/zinc catalysts investigated by Skrzypek et al. was relatively small, in the range of 15 – 30 $m^2/g$ using BET method. Surprisingly, these catalysts revealed very good activity and selectivity, contrary to known literature data. A proper choice of many components gave such good results. The catalysts also exhibited remarkable stability during experiments that lasted several months, so “good stability” in our experiments has different meaning than “good stability’ of catalysts tested only in a few days, e.g. about 212 h (Abu-Darieh, 2012), 500 h (Beretta, 1996) and 16 h stabilised catalyst before activity measurements (Huang et al., 2004). These positive properties distinctly set them apart from other catalysts, known from published studies. The improvement of active and selective catalysts is an outcome of long experimental experience along with a research intuition. Designing real catalysts based on literature knowledge, physicochemical properties and process data is so far not possible. It could be possible for a single reaction only.

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