THE CATALYTIC DIRECT CONVERSION OF METHANE TO METHANOL WITH METAL-EXCHANGED ZSM-5

How does the different MO^+-ZSM-5 zeolites influence the methanol selectivity?

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Abstract

Methane gas is one of the greenhouse gases that contributes the most to global warming, and is an abundant resource that can be incorporated into the petrochemical industry by converting it into methanol. A more sustainable mechanism for conversion is done with metal-exchanged ZSM-5 zeolite, and the effect of using Copper, Cobalt and Iron is investigated in the report below. A selectivity towards methanol production and the methane activation has been suggested to be increasing the order of Fe<Co<Cu, while from experimental data the bimetallic Cu-Fe-ZSM-5 complex was found to be the superior catalyst for the methanol selectivity. Other aspects of the conversion have also been discussed where the effect Si/Al ratio, acidity, metal-complex and cyclic ability has been investigated as variables for the conversion.

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1   Introduction

Methane gas is one of the major culprits of global warming. It is the second most important anthropogenic greenhouse gas with a global warming potential (GWP)-value of 25, meaning one tonne of methane emitted to the atmosphere is equivalent to 25 tonnes of CO_2 [1]. This value excludes the production of CO_2 by the oxidation of methane in the atmosphere. The reduction in emissions of this greenhouse gas is essential for combating climate change and to ensure a sustainable future. The possibility of using the methane as an industrial resource can have an important impact on decreasing 60% of emissions which are caused by human activity such as cattle breeding, paddy fields, mining, landfills and biomass burning. The other 40% of the emissions originate from natural sources such as wetlands and termites, and can be trickier to capture for further conversion [2].

From the increased production of natural gas, we now have access to large and low-cost reserves of methane. One possible way of utilizing the methane industrially is to convert it into methanol that is an important reactant for the petrochemical industry in the production of high-quality chemicals such as formaldehyde, acetic acid, methyl methacrylate and others [3]. Methane is difficult to implicate in the chemical industry due to it being a reasonably inert gas with a low electron and proton affinity, low polarizability, weak acidity, a high C-H bond strength at 439kJ/mol, a high ionization energy and high symmetry [4, 5]. There are some catalysts that can oxidize methane as the activation of the C-H bonds are accessible at low temperatures, however, the challenge is to prevent the overoxidation of methane to carbon dioxide. This is due to the relatively lower bond strength of the oxidised products giving rise to further oxidation [3].

The most known and used commercial way of producing methanol today is through a process with a step using synthesis gas, also known as syngas, a mixture of CO and H_2 which is a dangerous and costly process that can often result in sulphur poisoning [6]. By utilising the direct conversion of methane to methanol, the syngas step can be avoided, which is beneficial as the syngas is known for being harmful to the environment [7]. The metal-exchanged ZSM-5 is one of the catalysts which is known for having high catalytic activity for the direct conversion of methane to methanol. Moreover, the zeolite ZSM-5 can be reutilized after conversion by oxidising the metal over and over again. This is often achieved by decomposing N_2O to N_2 or introducing O_2 as a sole oxidant

and generating the active metal site for another reaction [8]. This is again a more sustainable process with a minimum waste disposal and using the methane as the reactant.

In this project I will focus on the direct conversion of methane to methanol with metal-exchanged ZSM-5 through oxidation of methane. As the above challenges focus on the fact that methanol is a desirable product for such a conversion, I will base most of my discussion on results for the selectivity of methanol with different metal-ZSM-5. I will also look at the activation of methane, the effect of Si/Al ratio and acidity, as well as discussing other aspects of the conversion. There are many ways of introducing metals into zeolites in order to improve the catalytic properties, i.e., incorporation, ion-exchange or impregnation of metals, however I will mostly focus on ion-exchanged metals in ZSM-5. I will show only the comparison of ion exchanged and impregnated to demonstrate that methods of metal introduction also have an influence for the methanol selectivity. The metals I will focus on will be Copper, Iron and Cobalt as the majority of the papers are based on these metals. I will compare both experimental data and data calculated through density functional theory (DFT).

I will not focus on the actual capture of methane and the possible applications of this mechanism on an industrial level, as this will exceed the focus of the functional properties of the zeolite ZSM-5. Today there does not exist a synthetic catalyst that can convert methane to methanol at an industrial scale only using oxygen in one-step oxidation [3], thus discussing this part of the problem will be difficult.

2 Theory

2.1 Zeolites

Zeolites are inorganic crystalline framework oxides containing micropores of molecular dimensions usually smaller than 2 nm [9], giving them their large surface area. Zeolites can contain one, two or three dimensional pores and are well known for being excellent heterogeneous catalysts. The fundamental building blocks of zeolites are tetrahedral SiO_4 and AlO_4 that are corner sharing with one common oxygen in between [10], making the distinct three-dimensional framework. The net formula of the building blocks gives a negative charge on the tetrahedron with aluminium in the centre as AlO_4^- [10] giving the zeolite its acidic property. The aluminosilicate

framework of zeolite are said to have high cation-exchange capacity, high adsorption, as well as having hydration and dehydration properties all contributing to the zeolite being an excellent catalyst in many contexts [11].

2.2 The ZSM-5 zeolite and its synthesis

ZSM-5 is a high-silica zeolite with a MFI framework, which is a three-dimensional porous structure containing 4-, 5-, 6- and 10-membered-ring micropores. The three-dimensional porous system consists of straight one-dimensional channels parallel to the [101] direction with parameters approximately from 0.53 to 0.56 nm and sinusoidal two-dimensional channels in the [100] and [010] directions approximately from 0.51 to 0.55 nm [10]. It is known for its unusual hydrophobicity giving it an advantage in separating hydrocarbons from polar compounds [12]. ZSM-5 also known as silicalite-1, has gained significant fame as a catalyst and is used in industry within the synthesis of ethylbenzene, the isomerization of xylenes and is viewed as the prototype of shape-selective catalysts [10]. The chemical formula for the framework structure is $[Na_n(H2O)_{16}][Al_nSi_{96-n}O_{192}]$-MFI, with $n < 27$ giving it its high-silica ratio [13], with the aluminium giving it its acidic character.
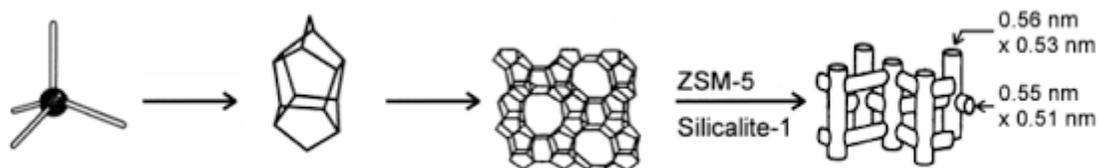
Figure 1: The synthesis of ZSM-5, from tetrahedra to pentasil units to MFI framework with the 10-membered-ring pores [10].

Zeolites can be synthesised by dispersing silica and aluminium tetrahedra sources in water, then adding inorganic cations for an alkali source and an organic structure-directing agent [14]. The organic materials are used as templates for the structure, as the inorganic zeolite structures form around the organic materials [15]. The batch is stirred into a gel, crystallized under autogenous pressure, washed and further calcinated in air at high temperatures to remove template [14]. For ZSM-5 zeolite, the Si and Al tetrahedra build pentasil units, creating the 10-membered-ring pores, straight and sinusoidal [10]. One synthesis used to produce microporous ZSM-5 involves the mixing of tetraethyl orthosilicate (TEOS) and sodium aluminate ($NaAlO_2$) as the Si and Al sources,

tetrapropylammonium hydroxide (TPAOH) and water [16]. TPAOH is a common structure-directing agent used for various synthesis procedures of MFI-framework zeolite [17]. The variables that can influence the formation of the specific zeolite are the batch composition, Silicon and Aluminium source and their ratios, alkalinity, water content, inorganic cations, organic templates and crystallization conditions such as temperature, time, aging and seeding [14].

2.3 The ion-exchange of ZSM-5 with metals

The aluminium sites on the surface of the 10-ring pore of ZSM-5 creates a negative charge which is balanced by a proton giving rise to the Brønsted-acid site. At this site a metal will be ion-exchanged with a proton by stirring the material with an aqueous solution containing the desired metal, favourably under conditions that promotes mass transfer at around 90°C [10]. In one case, the ion-exchange of Cobalt was achieved by dispersing 1 gram of ZSM-5 to a 0.1 M Co(II) solution [17]. The metal cations introduced by ion-exchange can form different complexes at the site and will therefore vary in their catalytic properties. For example, the site of Cu-ZSM-5 can be a dicopper complex [18], and one paper stated that the most promising complexes for methane activation and the selective oxidation of methane was Fe(IV)=O and Cu(III)-O-Cu(III) for respective Iron and Copper exchanged ZSM-5 [3].

These metal-complexes contain what is called an α-site, and when the complexes are further oxidised by decomposing of N_2O or introducing O_2 it gives rise to a form of surface oxygen referred as α-oxygen [19]. This α-oxygen has a high reactivity that can react with methane at room temperature. The α-oxygen has been proven experimentally to have similar reactivity and chemical properties as the active oxygen for methane monooxygenase [19].

2.4 Mechanism and procedure for conversion to methanol

The specific mechanism for the conversion of methane differs from metal to metal-complex used in the activation. However, a more general description of the process can be described by the partial oxidation of methane with the α-oxygen [19]. The simplified reaction is:

$$CH_4 + (O)_\alpha \rightarrow CH_3OH \tag{1}$$

This reaction excludes the important role of the metal in the methane activation and conversion, and a more detailed description of the oxidation is needed. Unfortunately, the specific mechanism for methane activation is relatively unknown, but a theoretical mechanism has been suggested in a DFT calculation study with simple mononuclear metal-complexes MO^+-ZSM-5, see Figure 2. Here, the mechanism of direct conversion of methane to methanol involves a catalytic cycle with two transition states and reoxidation of M^+ back to M^{3+} by N_2O decomposition [8]. As the CH_4 approaches the metal-complex it is activated and one of its C-H bonds weakens, enabling the H-atom to detach and approach the α-oxygen, simultaneously as the CH_3 approaches the metal centre, all in the first transition step (TS1). This results in covalent bonds between H-O and M-CH_3 as the hydroxo intermediate complex $[HOM-CH_3]^+$-ZSM-5. In the second step (TS2), a recombination of the CH_3 and the metal-bound OH to form a methanol complex that dissociates from the metal [8].
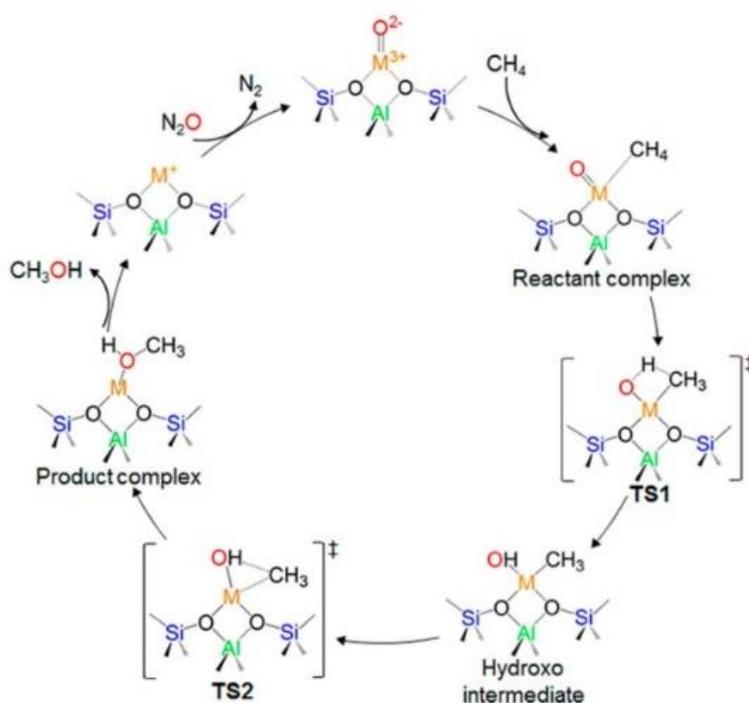
Figure 2: Mechanism for direct conversion of methane to methanol and the reoxidation of the α-site through decomposition of N_2O [8].

One experimental procedure for the conversion involves the activation of the catalyst at high temperature and flushing with nitrogen gas to remove organic contaminants, water and excess

oxygen, before the reaction is carried out at low temperature in a stainless steel vessel. The highest results from this experiment was with a methane pressure of 38 kPa and the produced methanol was extracted from ZSM-5 with ethanol [17].

3 Discussion and Results

3.1 Effect of catalytic metal for selectivity of methanol

Panov and his co-workers were among the first ones to explore the catalytic effect of Iron-exchanged ZSM-5 in the conversion of methane to methanol, and discovered the highly reactive properties of the α-site. In their first experiments they achieved a methanol yield of 100% as well as a methanol selectivity from 80-100% [20]. Here the reaction was carried out at room temperature at a pressure of 0.07-0.1 kPa and no other products that methanol was detected, while experiments with no loaded α-site found no methanol products [20]. After this discovery, the same catalytic conversion has been extensively investigated for other metals, and a variety of methanol yields and selectivities have been found. In a study from 2015, it was found that Fe-ZSM-5 gave a methanol selectivity of only 12.6% with reaction conditions of 50°C at 3050 kPa [21] . This is a significant decrease from the findings of Panov, however the study underlines the high catalytic activity of introducing Iron-cations to ZSM-5 as it had a significantly high production of oxygenated product [21]. These oxygenates include a variety of products such as methyl hydroperoxide (MeOOH), formic acid (HCOOH) and CO_2. The production of other oxidized products is an issue for the conversion of methane throughout the different catalysts as methanol is more prone to oxidation than methane [4]. This results in yields of other products and it is therefore challenging to reach high selectivities of methanol.

The earlier introduced α-oxygen present on oxidised transition metals is said to be the underlying cause of the methane activation when there is an interaction between the two, and the formation of such a α-oxygen have been shown to relate to the presence of ions [22]. In the study with methanol selectivity of 12.6% for Iron it was suggested that the high activity was due to Iron impurities in the ZSM-5 that reacted with other catalyst compositions used i.e. H_2O_2 and N_2O [21]. Another study found a similar selectivity of methanol at 12% with reaction conditions identical to the one at 12.6% [23]. Although the pressure used in Panovs experiment is significantly lower than for the later experiments, it seems from the studies I have found that a selectivity of methanol

similar to the one on Panov at 100% has not been achieved later, and it may question the credibility of Panovs work.

For Copper, studies are more unanimous in methanol selectivity, where in one study investigating the effect of SiO_2/Al_2O_3 ratio observed a methanol selectivity of 74% with a Cu-ZSM-5 exchanged zeolite with a Si to Al ratio of 23 [21]. In this result only 6 μmol of CO_2 was observed while 17.1 μmol of methanol was produced. In another study, a selectivity for methanol at 83% was observed with Copper-exchanged ZSM-5 also with small amounts of other oxygenated products such as CO_2 and MeOOH [23]. The reaction conditions for both experiments were a temperature of 50°C and a methane pressure of 3050 kPa [21, 23].

An alternative catalyst for the conversion has investigated in both the above studies, where a Fe–Cu bimetallic exchanged-ZSM-5 gave methanol selectivity higher than for Iron-only and Copper-only exchanged ZSM5 with identical reaction conditions as bare Cu-ZSM-5 [21, 23]. One study observed a selectivity of 77.8% [21] while the other reported to be 85% [23]. In both cases small amounts of CO_2 was produced, however it was suggested that the high activity of the Cu-Fe/ZSM-5 for methanol selectivity correlated with the strength and high concentration of acid sites that accommodated for extra-framework Iron species [21] which again suggested that the Al^{3+} within the framework is very valuable for the activity of the ZSM-5. It was also suggested that the addition of Cu^{2+} either as a component in the catalyst or added in the reaction mixture drastically decreased the over-oxidation process of the methane, resulting in much higher methanol yields [23]. From these results it can be suggested that ZSM-5 with both Fe and Cu species are the best catalysts for this reaction.

 An experiment of methane conversion with Cobalt-exchanged ZSM-5 observed a methanol selectivity at 45% at the highest. The two materials with the highest selectivity contained Cobalt of 2.7 and 1.7wt%, with methanol selectivity of 45 and 40% respectively [24], whereas having a selectivity towards formaldehyde at 60% and 55%. The favourable conversion towards formaldehyde was suggested due to the type of Cobalt species present, which I will discuss later. Another study that used hierarchial Cobalt-exchanged ZSM-5, synthesised by using a secondary template, Poly Diallyl Dimethyl Ammonium Chloride (PDDA), to obtained a higher surface area, observed a methane conversion of 7.56% [17], however no selectivity of methanol was calculated.

Table 1: Experimental values of methanol selectivity, methane conversion and the reaction conditions, as well as DFT calculated values of binding energies of methane, relative activation energies for a C-H methane bond dissociation and the relative energies for methanol formation via TS2, of the methane to methanol conversion for Copper, Iron and Cobalt-exchanged ZSM-5.

	Metal exchanged	Methanol selectivity (%)	Methane conversion (%)	Calcination temperature, reaction temperature and pressure		
Experimental data	Copper	74[21] 83[23]	- -	550°C, 550°C,	50°C, 50°C,	3050 kPa 3050 kPa
	Iron	100[20] 12.6[21] 12[23]	100[20] - -	897°C, 550°C, 550°C,	25°C, 50°C, 50°C,	0.07-0.1 kPa 3050 kPa 3050 kPa
	Cobalt	45[24] -	- 7.56[17]	550°C, 300°C,	150°C, 150°C,	- 38 kPa
	Copper and Iron	77.8[21] 85[23]	- -	550°C, 550°C,	50°C, 50°C,	3050 kPa 3050 kPa
	Metal complex	Binding Energy Methane	Activation energy for C-H bond	Energy for methanol formation via TS2		
Theoretical data DFT calculated[8] (kcal/mol)	Copper (CuO$^+$)	-1.1	6.4	-27.7		
	Iron (FeO$^+$)	-4.5	17.3	9.8		
	Cobalt (CoO$^+$)	-3.5	12.9	14.9		

As for the theoretical data calculated by DFT, there were no selectivity calculated, however, they compared binding energies of methane, relative activation energies for a C-H methane bond dissociation and the relative energy for methanol formation in TS2. The two relative activation energies were calculated for the two transition states of the cyclic mechanism for conversion. The binding energies and the adsorption of methane is said to be related to the confinement effect of ZSM-5 and will be further discussed with the ZSM-5 structure, as well as the activation energies of the C-H bond [8]. Binding energies and activation energies will be discussed in a later chapter.

As for the evaluation of the methanol selectivity, they have compared the relative energy for methanol formation in the TS2 low-spin state, at 9.8, 14.9 and -27.7 kcal/mol for Fe, Co and Cu, see Table 1, to the formation of a radical methyl by-product that have relative formation energies of 14.9, 19.3 and 1.1 kcal/mol for Fe, Co and Cu respectively. The difference in energy for the two formations are calculated to 0.6, 9.5 and 28.8 kcal/mol [8]. This indicates that for both Cobalt and Copper, formation of this methyl radical is significantly disfavoured as the energy for methanol formation is much lower. However, for Iron, the relatively small energy difference indicates that formation of methanol and methyl radical is energetically competitive, meaning it will hypothetically result in a lower methanol selectivity [8]. This trend corresponds well with most of the experimental data for methanol selectivity discussed above, where we see a trend for metal-ZSM-5 of Cu>Co>Fe indicating a high dependence on the metal for methanol formation.

3.2 Methane activation and the effect of ZSM-5 structure

In the DFT study, they calculated the binding energies of methane to -4.5, -3.5 and -1.1 kcal/mol for Fe, Co and Cu respectively [8]. These binding energies were compared with the O-M-C angles in the binding of the carbon upon the metal, and it was pointed out that they followed the same trend, where the weakest binding energy, with the $[CuO(CH_4)]^+$ -ZSM-5 complex had the smallest angle of 85°, $[CoO(CH_4)]^+$ -ZSM-5 with 108° and $[FeO(CH_4)]^+$ -ZSM-5 with 111° [8]. The difference in angle from each metal suggests that the angle is dependent on the nature of the metal, and comparing them to the methane binding energies implies that the angle affects the reactivity of the complex. It is also suggested that the angles of these reactant complexes is related to the confinement effect put forth by the ZSM-5 which affected the strength of methane adsorption. The confinement effect of ZSM-5, investigated by Zicovich-Wilson and Corma [8], suggests that when a methane molecule approaches the active site on the surface of the 10-ring pore of ZSM-5, nanoparticles of the ZSM-5 confines the free space of the interaction with the MO^+ species, resulting in a destabilisation of methane adsorption and a significant lowering of the activation energy of the C-H bond dissociation [8]. The result of the effect of confined space for the activation and adsorption of methane is explored by comparing values calculated for bare MO^+ in gas-phase. Here methane is adsorbed to the metal with a O-M-C angle of approximately 180° for all metals, with binding energies of -22.8, -25.4 and -45.8 kcal/mol for Fe, Co and Cu, respectively, giving a much stronger adsorption than with ZSM-5. This indicated that the bent structure formed on the

surface of the ZSM-5 10-ring pore weakens the adsorption energy of methane. When looking at the relative activation energies for the C-H bond dissociation for the ZSM-5 complexes, see Table 1, they are 9.2, 13.6 and 26.4 kcal/mol lower than for gas-phase bare MO^+ for Fe, Co and Cu respectively [8], indicating that the ZSM-5 structure promotes the high catalytic activity of the MO^+ species for methane.

3.3 Effects of Si/Al ratio, acidity and ZSM-5 metal-complex

An experimental study that has compared the methanol production with Si/Al ratios with Copper-exchanged ZSM-5 concluded with one exception that a lower Si/Al corresponds with a higher yield of methanol. Cu-ZSM-5 with ratios of 20, 30, 50, 80 and 200-400 produced 2.8, 26.6, 12.5, 10.8 and 3.2 $\mu mol \cdot gcat^{-1}$ of methanol in reaction conditions of 200°C and pressure 101 kPa, a trend suggesting that more aluminium present increases the methanol yield [25]. The Cu-ZSM-5 with ratio of 20 was the only material that showed the presence of Copper nanoparticles with a diameter of around 5 nm on the surface. These are said to not be active for reaction conditions as in this study, suggesting that little of the Copper introduced has formed the desirable complexes for reaction, resulting in the low methanol yield at this ratio [25]. Apart from this, the trend suggests that the hydrophilicity of the ZSM-5 affects the methanol production, where the yield decreased exponentially with increasing ratio. Another study investigating the effect of Si/Al ratio on methane oxidation to methanol, tested the effect for Fe-ZSM-5, Cu-ZSM-5 and Cu-Fe-ZSM-5 with Si/Al ratios of 23, 30 and 80, resulting in the same trend where the lower ratio gave highest methanol yields, see Figure 3[21]. The reaction conditions were at 50°C and pressure 3050 kPa. Here, the catalyst with the overall highest yield was the bimetallic complex Cu-Fe-ZSM-5, with 126.3 μmol at ratio 23, approximately 79 μmol higher than the other two catalysts. However, all catalysts had approximately the same yield at a ratio of 80, suggesting that the type of metal complex in the materials with such a high ratio did not affect the methanol yield to a significant degree[21].

In general, the concentration of metal-complexes have been linked quantitatively to the yield of the methanol produced [18]. Although the metal-complexes studied in the theoretical DFT study above were all MO^+-ZSM-5, this is not the case for most experimental studies. As mentioned in the theory of this report, the metal introduced at the Brønsted-acid sites can form many different

complexes depending on the metal and the precursor material used for the ion-exchange [21]. In addition, it is also suggested that the Si/Al ratio influences the type of metal-complexes for Copper, where in materials with higher Si/Al ratios, the probability of creating mono-copper species is drastically higher than for materials with lower ratios [25]. This was suggested in the earlier experimental study where they found a larger population of multi-copper species in the Cu-ZSM-5 with ratio 30:1 than for the 50:1 and 80:1 ratio materials, concluded from the methanol/Copper production [25]. When comparing this to the methanol yields of the three ratios, 26.6, 12.5 and 10.8 μmol·gcat^{-1} for ratio 30, 50 and 80, it is evident that the multi-copper species found in the lowest ratio are more reactive than the mono-copper species.
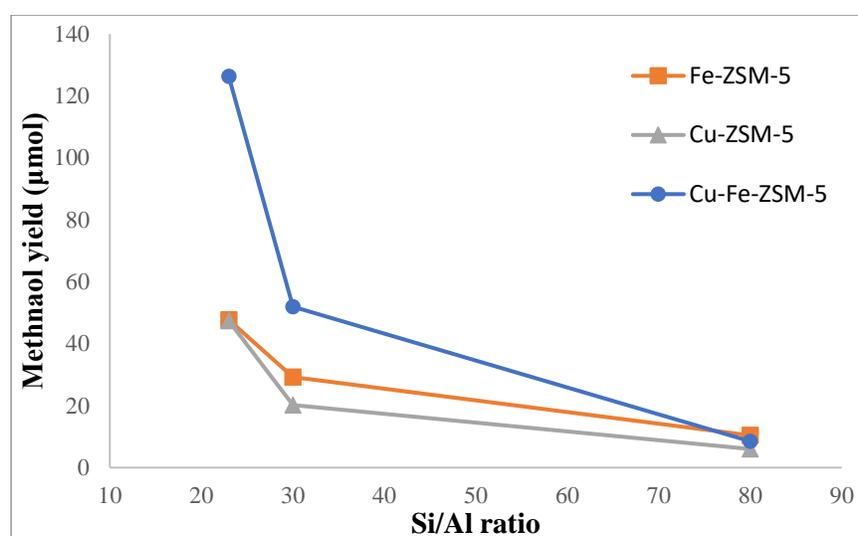
Figure 3: Graph illustrating the effect of Si/Al on methanol yield (μmol) for ion-exchanged Fe-ZSM-5, Cu-ZSM-5 and Cu-Fe-ZSM-5, data taken from [21].

3.4 The ion-exchange method for Cobalt

Without performing a detailed analysis of the catalytic use of metal-impregnated ZSM-5, it is worth mentioning that for using Cobalt as the transition species, many studies have concluded that impregnation gives much higher methanol selectivity and methanol yield. In the previously discussed study that calculated a methanol selectivity of 45%, and a formaldehyde selectivity of 55% also did the same experiment with Cobalt-impregnated ZSM-5, where they calculated a methanol selectivity of 100% [24]. Here the two catalysts were both calcinated at the same temperature of 550°C and the reactions were done in 150°C under same pressure [24]. In another

study they came to the same conclusion where they observed that more active Co-oxide particles were created by the impregnation method than in the ion-exchange method, where it was suggested that it was the larger Co-oxide particles that led to the formation of methanol [26]. In the study investigating Co-ZSM-5 where a methane conversion of 7.56% was obtained with ion-exchanged, a methane conversion of 42% was obtained with the use of wet impregnation [17]. It was suggested that the difference in conversion percentage was due to the fact that impregnated Co-ZSM-5 that was calcinated at 549.85°C formed Cobalt-oxides that were active, while the ion-exchange method followed by calcination at 299.85°C appeared not to completely turn the Cobalt(II) ions into active oxides as they had to counteract the negative formal charge of the ZSM-5 structure, resulting in a lower presence of the necessary active Cobalt-oxides [17]. This shows that not only does the method of introducing the metal affect the methanol yield, but also the calcination conditions.

3.5 Catalytic cyclic conversion

As suggested the methane to methanol conversion with ZSM-5 can be reused in a cyclic manner, where the metal-complex is oxygenated again after methanol is produced. A study that explored the isothermal cycling of Copper-exchanged ZSM-5 compared the methanol yield of two Cu-ZSM-5 with Si:Al ratio 30:1 and 200-400:1 respectively. They discovered that the cyclic conversion does not only rely on the activation of the C-H bond, but also physical properties such as hydrophobicity [25]. The experiment showed a low conversion in the second cycle for Cu-ZSM-5(30:1) and it is proposed that this is because the active oxygen species created during calcination at 600°C cannot reactivate under activation at milder conditions in the later cycles at 200°C. In addition, with the high hydrophilicity of the 30:1 ratio material does not allow all the water from the extraction of methanol from the first cycle to leave the material, resulting in its inability to complete the conversion for a second time [25]. While in the 200-400:1 ratio material all the water was removed during the extraction treatment of the first cycle, and gave a relatively stable methanol production for five cycles. This also suggests that the active oxygen species were somewhat regenerated during the reactivation at 200°C [25]. They therefore concluded that more active materials such as the 30:1 ratio showed worse cycling abilities, while the less active were better suited, and that all parts of the conversion, the activation, reaction and extraction must be optimal for cyclic capabilities. The results also indicated that the activation temperature and the hydrophobicity influence the catalytic cycling of the methane to methanol conversion [25], as well

as concluding that the catalyst needs to be activated at high temperatures before the next cycle begins.

In an experiment with Cobalt-exchanged ZSM-5 a second cycle of the conversion was also carried out, where they observed similar results in the second run as the first. As in the first run the material was dried and calcinated at 550°C for reactivation of the oxygen species [24]. The ZSM-5 material used in this experiment all had a Si:Al ratio of 35:2 [24], giving it an even more active material, and still the same results were observed for a second cycle. Comparing this to the above study that got a poor result in the second run, it highlights the fact that high activation temperatures is the essential part of the cycling process as the first Copper experiment lowered the calcinating temperature for their second run, while the Cobalt used the same temperature.

The extraction process of the Copper experiment was done by exposing the materials to 5 vol.% steam balanced in argon at 200°C [25], while for the Cobalt experiments extraction procedure was done by stirring 0.2 g of the sample in 0.5 mL ethanol for 1 h [24]. As explained above, water inhibited the cyclic ability of the Copper material, and as the Cobalt experiment does not use water it may be a factor for good cycling abilities.

4 Conclusion

The metals discussed in this report have all shown great promise for ion-exchange ZSM-5 catalytic conversion, however by comparing values of methanol selectivity from different experimental studies it has been made evident that a mix of Copper and Iron transition metals is the superior metal-complex for methanol selectivity at 85%. Although the innovative results from Panov and co-workers with methanol selectivity of Iron-exchanged at 100%, it was insinuated by the later studies that such selectivity for Iron were hard to accomplish.

A trend for methanol selectivity for the different metals was suggested by the DFT study that well suited the values I found in the experimental studies, as Cu>Co>Fe, where Copper had a selectivity at 83%, Cobalt at 45% and Iron at 12%. A trend for the activation of the methane C-H bond was also suggested by the DFT study where they compared values calculated for bare MO^+ species with those for ZSM-5 complexes, and found that the activation energy for the C-H bond was

lowered with an increasing degree from Fe<Co<Cu, as well as indicating that the ZSM-5 material promoted the activation of the methane bond, with the highest effect for Copper.

The effect of Si/Al ratio on the yield of methanol was also discussed, where a higher ratio corresponded with a lower yield of methanol, peaking at a ratio of 30:1 for the study on Cu-ZSM-5 study and at 23:1 for another study comparing different metal-complexes where the Cu-Fe-ZSM-5 showed the highest overall yield. This indicated that the hydrophilicity of the zeolite affected the production of methanol. It was also suggested that the methanol production was influenced by the type of complex found on the Brønsted-acid sites, where the multi-Copper complexes showed greater promise for higher methanol yields.

The use of the ion-exchange method was also discussed in relation to Cobalt, where it was suggested by a handful of studies that the impregnation method gave much higher methanol selectivity as it created more active Co-oxides. In the end, the use of the catalytic conversion in a cyclic matter was discussed, where it was suggested that higher Si/Al ratios showed better cycling abilities, and that higher activation temperature is a significant variable for better cyclic abilities in the conversion.

I have not discussed and compared the reaction conditions, and how these may influence the conversion in a detailed manner. By comparing the conditions for the reactions it could also indicate what reactions are more likely to be applied at an industrial level, as they would influence the cost and extent of the conversion.

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