

Radioisotopic tracing of methanol transformation using ^{11}C -labelled methanol over copper ion-exchanged H-ZSM-5, H-Beta and H-MCM-41

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Short half-life ^{11}C -radioisotope tracer in methanol form was used to study the transformation of methanol over copper ion-exchanged H-ZSM-5, H-Beta and H-MCM-41 catalysts. The progresses of adsorption and desorption as well as methanol transformation were followed by radiodetection. The reaction products were analyzed by radio-gas chromatography. The GC analysis was completed with a radiodetector that could distinguish the radiolabelled derivatives from other non-radioactive compounds, reagents or impurities. The radiodetector can be more sensitive to detect smaller amount of compound than the thermal conductivity detector or flame ionization detector since the intensity of a radio-signal is independent on thermal conductivity or ionization energy of compounds. The copper introduction into the catalysts had an inhibitory effect on the reaction to proceed further from the equilibration with the methanol and dimethyl ether resulting in hydrocarbons C_3 – C_6 . Presence of copper also allowed a possible reaction route for methanol to give formaldehyde and methyl formate.

KEY WORDS: methanol; ^{11}C -radioisotopic tracer study; ZSM-5; Beta; MCM-41; copper; ion-exchange.

1. Introduction

Several attractive products can be synthesized by converting methanol. For instance dimethyl ether (DME), obtained by dehydration of methanol, has received attention to be potentially used as a clean alternative fuel for diesel engines [1,2]. Conversion of methanol to light olefins is a possibility for economical utilization of natural gas resources, especially if the oil price increases considerably. In addition, methanol dehydrogenation to methyl formate (MF) is an interesting process, since the MF is an important intermediate for the production of formic and acetic acids, formaldehyde and dimethylformamide [3–6]. Molecular sieves are potential catalysts for these reactions [7,8] including Cu-modified ZSM-5 for formaldehyde formation [9] and Cu-modified MCM-41 mesoporous material for MF formation [10].

In order to improve the catalyst performance, the reaction over them should be accurately monitored. One possibility to do this is to utilize radioisotopic tracing technique. The advantage of its application is that adsorption, desorption and catalytic transformation can be followed directly by radiodetectors whereas GC-analysis is completed by radiodetector to distinguish the products from other compounds. The radioactive tracer

technique can easily and directly follow the conversion processes of small amounts of reactant molecule (methanol in this study) and, moreover, can distinguish reactant molecule and its derivatives from other natural carbon-contained compounds even at a very close retention time, detecting an increased thermal conductivity detector (TCD) signal compared to the TCD signal of the methanol derivative. Further advantage of radiodetector application is that the intensity of the radio-signal does not depend on the nature of the molecule, i.e. its thermal conductivity or ionization energy.

The radio-method can determine the methanol adsorption rate and the peak desorption temperature of products formed. The cyclotron produced ^{11}C -isotope ($T_{1/2} = 20.4$ min) is a commonly used positron emitter for the production of ^{11}C -labelled pharmaceuticals applied in Positron Emission Tomography (PET) investigations. During methanol conversion over catalysts the annihilation γ -rays of ^{11}C -isotope can be detected with higher efficiency by radiodetectors (starting at least from ~ 0.5 GBq radioactivity in this environment) than with TCD or flame ionization detector (FID) detectors used in gas chromatograph analysis. In addition, the method presented here can potentially be applied elsewhere; in radiopharmaceutical chemistry ^{11}C -labelled side chain methylation of different aromatics by ^{11}C -labelled methanol on Cu-catalysts could be an alternative to classical wet methods [11].

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Previously ^{11}C -labelled methanol was applied to study methanol transformation over proton forms of ZSM-5, Beta zeolites and MCM-41 [12,13]. The methanol labelling with ^{14}C isotope and ^{13}C stable isotope for investigation of methanol transformation over zeolites has been reported [14–16]. An advantage of ^{11}C -method is that the catalytic processes can be monitored on-line compared to the difficult off-line β^- measurements of ^{14}C isotopes and the NMR spectroscopy of ^{13}C stable isotope samples. The ^{11}C -radioisotope, as a positron emitter, has been introduced for measuring concentration profiles of hydrocarbons in zeolites [17]. The catalyzed dehydrogenation of ^{11}C -labelled methanol to ^{11}C -labelled formaldehyde has been studied over silver-containing ceramic catalyst [18].

Here we present a study of methanol conversion over proton forms and copper ion-exchanged H-ZSM-5, H-Beta and H-MCM-41 catalysts using ^{11}C -labelled methanol. The results are compared with each other in order to demonstrate the influence of copper ion-exchange and consequent acid reduction on the catalytic properties.

2. Experimental

2.1. Synthesis and characterization of Cu-modified H-ZSM-5, H-Beta and H-MCM-41 catalysts

The synthesis of Cu-modified H-Beta and H-MCM-41 was carried out as described in Refs. [19–21]. The thorough characterization of the materials is also described in the aforementioned references. The synthesis of Na-ZSM-5 was carried out as described in Ref. [22] with the synthesis time of 48 h. Copper was introduced into Na-ZSM-5 by ion-exchange. After ion-exchange, the sample was washed thoroughly and filtered, followed by drying at 353 K for 12 h and calcined at 673 K. The details of the characterization of Na- and H-ZSM-5 are given in Ref. [22]. The Si/Al ratio was determined to be 31 for ZSM-5, 11 for Beta and 2.6 for MCM-41 and the copper content was determined to be 2.3% (Cu-H-MCM-41), and 1.5% (Cu-H-Beta) [19–21]. The copper content for Cu-H-ZSM-5 is 2% if full ion-exchange is assumed. The decrease in the amount of the Brønsted acid sites (BAS) and increase in the amount of the Lewis acid sites (LAS) was observed for Cu-H-Beta and Cu-H-MCM-41 according to the FTIR spectra of adsorbed pyridine compared to proton forms [19]. The presence Cu^+ and Cu^{2+} was revealed by FTIR spectra of adsorbed CO and adsorbed NO on oxidized Cu-H-MCM-41 and Cu-H-Beta [19].

2.2. Catalytic experiments

In the first step the ^{11}C -methanol was prepared by a classical method: $^{11}\text{C}\text{CO}_2$ was produced by cyclotron

using $^{14}\text{N}(\text{p}, \alpha)^{11}\text{C}$, $^{11}\text{C} + \text{O}_2 \rightarrow [^{11}\text{C}]\text{CO}_2$ process. The $^{11}\text{C}\text{CO}_2$ was reduced into radiomethylate complex with lithium aluminium hydride. After drying the radio-complex was hydrolysed into ^{11}C -methanol by dilute water [23]. Only just few μmol volume of ^{11}C -methanol product (radioactivity was approximately 400 MBq) was increased up by non-radioactive methanol for catalysis study i.e. ^{11}C -methanol was trapped by He flow into ca. 20 and 200 μmol of non-radioactive methanol. This mixture is denoted as “ ^{11}C -methanol”. It must be noticed, however, that in this environment with low concentration of radioactive isotope in methanol, radiolysis of reactants can be neglected and does not disturb the methanol transformation.

The radioactivity was measured in MBq by an ionization chamber (ATOMLAB 300, overall accuracy: $\pm 3\%$ or 10 kB) to evaluate the radioactivities of the adsorbed methanol (also intermediates and products), the remained compounds on catalyst as well as the sample before GC-injection. The ionization chamber was calibrated for ^{11}C -isotope.

The rates of radioactive compounds were measured after separation on GC, online with TCD, by a very sensitive (250 CPM (count per minute)) flow-count scintillation detector (RD, Bioscan, B-FC-3200, 5 cm diameter with 5 cm thick of NaI crystal). In the environment of the experiments the background is in the range of 1000–4000 CPS. Flow-Count's analogue data output is compatible with chart recorders, integrators and computer-based chromatography data systems. In the experiments relative measurements were applied for the calculation of yield-ratios of compounds from the ratios of the radioactivity peaks on the radio-chromatograms. The concentration of radioactivity (is expressed as the number of becquerels per unit volume) is in the range of few MBq/ μmol , i.e. the ratio of radioactive and non-radioactive methanol molecule is in range of $1/10^{11}$.

The reaction was carried out in a glass tube fixed-bed reactor as a closed static reactor constructed of a glass tube (4 mm i.d., 110 mm long). Quartz wool was used to hold approximately 20 mm long catalyst at the centre position. A thermocouple was located at the outside wall of the tube. For the catalyst pretreatment and catalysis process the apparatus was equipped with a He gas dosing system with flow controllers. The tubing and valve system of the reactor allowed the feed stream and, after catalysis, the product stream to be passed into a small gas syringe (1 ml) as a sample collector. Before catalysis, for pretreatment the catalyst was heated to 623 K with 5 K/min gradient and kept it for 2 h under He flow.

The ^{11}C -methanol was introduced by He gas flow (the He flow rate was 50 ml/min) into ~ 250 mg of catalysts at ambient temperature. After adsorption, the valves were closed and the catalyst was heated up to the required temperatures.

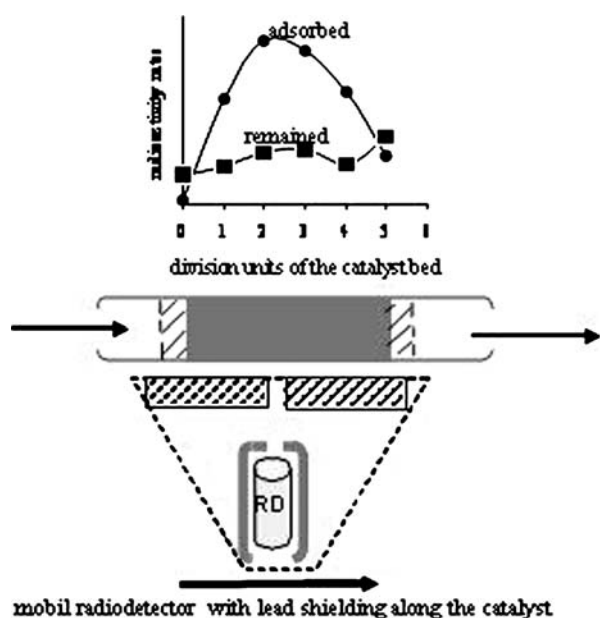


Figure 1. Distribution of adsorbed and remained radioactivity along Cu-catalyst bed.

In an experiment the distribution of adsorbed ^{11}C -methanol was determined along the catalyst bed by a mobile radioactivity detector (gamma detector i.e. Geiger-Müller tube, RD) at ambient temperature (figure 1). After catalysis at 530 K (for 20 min with 30 K/min gradient) and removal all of the volatile products, the distribution of remained radioactivity was scanned in the direction of the He-flow.

During experiments two fixed radiodetectors (lead shielded RD1, RD2) were used to follow continuously the radioactivity rates of different volumes of adsorbed ^{11}C -methanol (20 and 200 μmol) in centre position of the catalyst (RD1) and the removed volatile ^{11}C -derivates behind the catalyst bed (RD2) as a function of reaction temperature. The temperature was increased to 450 K by 30 K/min gradient, thereafter, uniformly increased further to 530 K with 10 K/min gradient. The

rates of RD1 and RD2 were represented as a function of catalyst temperature (figure 2).

The products of catalytic conversion of ^{11}C -methanol were analyzed by radio-gas chromatography (gas chromatograph with TCD coupled on-line with a radioactivity gamma-flow detector). The radioactivity sensor of the radio-gas chromatograph was a sensitive scintillation detector with lead shielding. TCD was applied to identify the radioactive products by determination of retention times of their equivalent inactive carbon compounds. All chemical compounds were commercially available. The ^{11}C -hydrocarbons were identified by added inactive standard $\text{C}_1\text{--C}_5$ olefins and paraffins gas mixtures (Scott Specialty Gases, Supelco) during radio-GC analysis. The oven of the PLOT Q capillary column (30 m \times 0.53 mm \times 40 μm , Alltech) of the gas chromatograph was programmed to hold the temperature at 333 K for 2 min and then the temperature was elevated up to 523 K with 40 K/min while keeping He carrier gas constant at 1.7×10^5 Pa pressure.

The glass tube with catalyst was removed after ^{11}C -methanol adsorption and after ^{11}C -methanol transformation (without volatile ^{11}C -products) and put into Dose Calibrator (Atomlab 300) for radioactivity measuring. The remaining radioactivity was compared to the initial radioactivity on the catalyst for calculation of conversion rate.

During experiments the aromatics usually were not detected in the range of 503–623 K used with 5–20 min reaction time. During analysis the radio signals were decay corrected. The alumina catalyst as a standard was also used to demonstrate the transformation pathway of methanol over a material containing only Lewis acid sites.

Summarizing, the advantage of application of radioisotope tracer is the direct follow of adsorption, desorption and transformation of methanol on catalysts by radiodetectors whereas GC-analysis is completed by radiodetector to distinguish the products from other compounds. The drawback of this ^{11}C -tracer method is

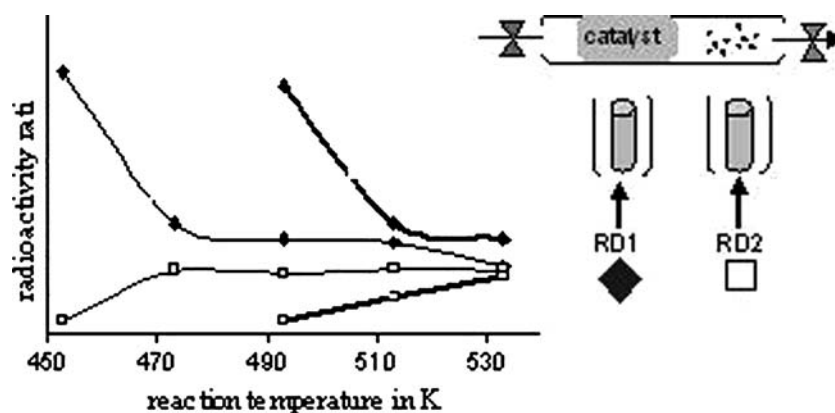


Figure 2. Radioactive ratios of adsorbed ^{11}C -methanol (including intermediates and products) (RD1) and desorbed ^{11}C -derivatives (RD2) as a function of reaction temperature.

its short half life in the case of longer reaction time (more than 2 h) and the fact that the ^{11}C -radioisotope can be produced only by cyclotron accelerator.

3. Results and discussion

3.1. Investigation of distributions of adsorbed and desorbed ^{11}C -methanol and reaction products along the catalyst bed

High adsorption rates of methanol, varying between 80% and 90%, were measured for Cu-modified catalysts. Since the radiochemical detector is not species dependent, besides adsorbed compounds also intermediates and products could be formed. Therefore the results, discussed in this section and presented in figures 1 and 2, in fact, refer not only to ^{11}C -methanol, but also to ^{11}C containing intermediates and products, both in the gas phase and adsorbed on the surface. The radioactivity of adsorbed ^{11}C -methanol corresponds to the initial volume of methanol and the difference of the radioactivities of adsorbed ^{11}C -methanol and remained ^{11}C -derivates on catalyst equals with the total volume of volatile ^{11}C -products. The distribution of adsorbed ^{11}C -methanol (and products of its transformations) was determined along the catalyst bed by a mobile radioactivity detector (RD) at ambient temperature (figure 1). The maximum of the radioactivity rate was measured at about 1/3 length of the catalyst bed. After the catalytic reaction the distribution of remained radioactivity (figure 1) proves that methanol transformation was extended over whole catalyst bed after desorption.

Two fixed RD1 and RD2 radiodetectors were used to follow continuously the radioactivity ratios of adsorbed ^{11}C -methanol (as well as ^{11}C intermediates and products) to volatile ^{11}C -derivates as a function of reaction temperature (figure 2). Desorption of 20 μmol ^{11}C -methanol (also ^{11}C intermediates and products) started above 450 K. The rate of adsorbed ^{11}C -methanol (including ^{11}C intermediates and products) decreased (RD1) deeply in the range of 450–470 K while the desorption rate of volatile ^{11}C -derivates increased in the same temperature range (RD2). Desorption of 200 μmol ^{11}C -methanol (intermediates and products) started at higher temperature approximately with 40–50 K. There was no change in the radioactivity rates, when the same initial radioactivity of [^{11}C]-methanol with higher volume of non-radioactive methanol was used.

3.2. Transformation of methanol

The transformation of 20 μmol of methanol vapour was investigated over copper modified catalysts at 503 and 573 K. During analysis by radio-GC, the TCD signals were compared with radioactivity signals. Dimethyl ether was the only product after 10 min of the reaction (see figures 3, 5). At higher temperature

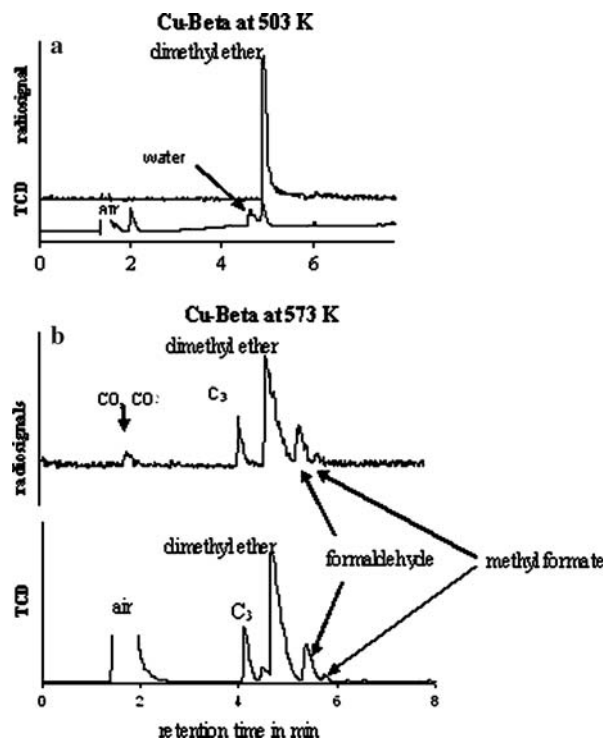


Figure 3. Radio-GC analysis of transformation products of ca. 20 (a) and 200 (b) μmol of ^{11}C -methanol over Cu-Beta.

(573 K), transformation of methanol to formaldehyde and carbon oxides (CO_x) started to occur in addition to the DME formation. It is notable that no hydrocarbons were produced.

The reaction was also investigated with an increased volume of methanol (200 μmol) over copper modified and proton forms of the H-MCM-41, H-ZSM-5 and H-Beta catalysts (see table 1 and figures 3–5). The selectivities were calculated on the basis of radio-chromatograms. Over the proton forms hydrocarbons were the main products: the selectivity was 69%, 82% and 91% over H-MCM-41, H-Beta and H-ZSM-5, respectively. These results are very much in line with those reported in the literature for methanol transformations over zeolites. In particular, a range of hydrocarbons was obtained over H-ZSM-5 [24] with C_3 being the predominant product. The selectivity to DME was low, below 10% for the zeolites and 23% for H-MCM-41. Some CO_x were also obtained as products. Among the hydrocarbons, selectivity to C_3 (i.e. propane and propene) was app. 40% on the proton forms of zeolites but much higher (75%) on H-MCM-41. The propene/propane ratio was also different on zeolites (app. 1:2) while in case of H-MCM-41 almost all C_3 was in form of propene.

The copper ion-exchange had a dramatic effect on the product distribution over the zeolites being less pronounced for H-MCM-41. The formation of hydrocarbons C_3 – C_6 was greatly hindered, the selectivity being

Table 1

Summary of characterization of H- and Cu-modified ZSM-5, Beta and MCM-41 catalysts and alumina in addition transformation products of 200 μmol methanol at 573 K

Catalyst	Conversion	Selectivity to radioactivity %					
		C ₃ -C ₆	C ₃ among C ₃ -C ₆ (C ₃ = /C ₃) ^a	DME	Formaldehyde	Methylformate	CO _x
H-ZSM-5	78	91	42 (35/65)	3	0	0	6
Cu-H-ZSM-5	51	23	36 (65/35)	41	12	9	15
H-Beta	70	82	40 (32/68)	9	0	0	9
Cu-H-Beta	54	21	25 (67/33)	51	20	3	5
H-MCM-41	88	69	75 (96/4)	23	0	0	8
Cu-H-MCM-41	61	7	87 (93/7)	57	31	2	3
Alumina	87	0	0	~100	0	0	0

^a Propene to propane ratio given in the parantheses

over 20% for zeolites but only 7% for Cu-H-MCM-41. Furthermore, the conversion level was slightly lower after Cu ion-exchange. The selectivity to DME was considerably increased varying from 41% to 57%. Formation of formaldehyde and MF was also observed.

Selectivity to C₃ products did not change significantly, but the propene/propane ratio was approximately 2:1 over Cu-modified zeolites, while it was 1:2 for the parent proton forms. Interestingly, copper ion-exchange did not affect the propene/propane ratio on Cu-H-MCM-41, which was similar to H-MCM-41. Methanol conversion was also carried out over alumina leading only to formation of DME with ~100% selectivity.

3.3. Effect of copper ion-exchange

It is widely accepted [7] that the first step of the methanol conversion initially proceeds through equilibration with DME. The experimental value of conversion over alumina is very much in line with thermodynamic equilibrium data from literature [25]. Light olefins are then the initial hydrocarbon products, followed by heavier olefins, paraffins and aromatics. Analysis of the product distribution reveals that the results presented here are well in line with this reaction network. Zeolites like H-ZSM-5 and H-Beta are materials with a considerable amount of acid sites, especially strong Brønsted acid sites (defined as their ability to retain chemisorbed pyridine at 723 K), but the number of the strong acid sites can be lost after an introduction of a metal into the zeolite [26,27]. On the other hand, H-MCM-41 is considered as a mildly acidic material having negligible amount of the strong Brønsted acid sites [28]. Furthermore, it is clear that the number of Brønsted acid sites is remarkably decreased after the Cu ion-exchange [19,21]. The difference in the acidity between H-MCM-41 and proton forms of the zeolites is the probable reason for the observed difference in the product distribution. Less hydrocarbons were produced in the reaction over H-MCM-41 due to the lack of the strong Brønsted acid sites as well as lower acid site density, indicating that strong acid sites are important to carry out the hydrogenation and dimerization steps effectively. Furthermore, among the hydrocarbons mostly propene (app. 72% among the hydrocarbons, app. 50% overall) was formed over H-MCM-41, but over the

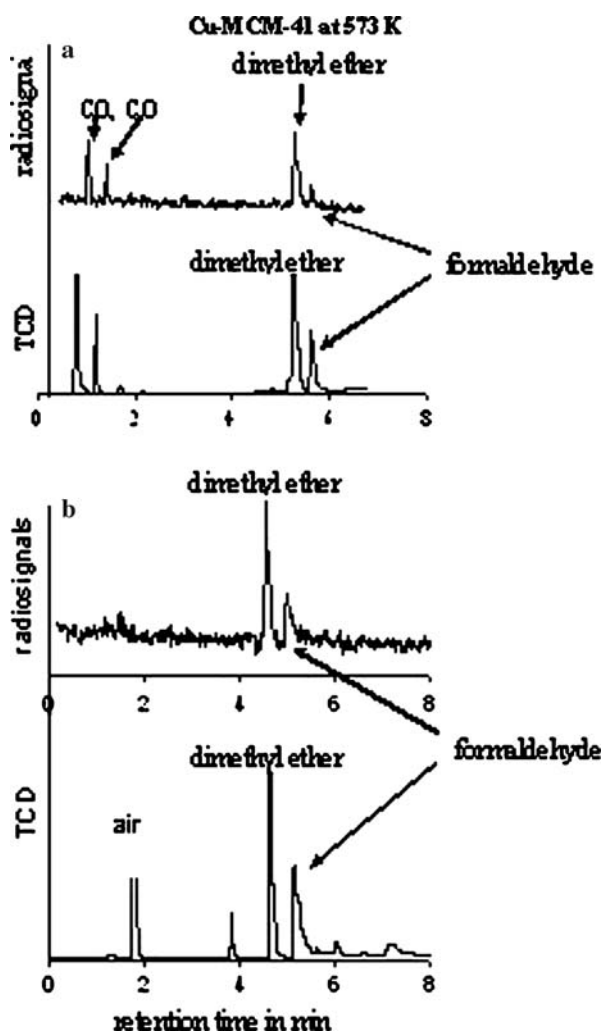


Figure 4. Radio-GC-analysis of transformation products of ca. 20 (a) and 200 (b) μmol of ^{11}C -methanol over Cu-MCM-41.

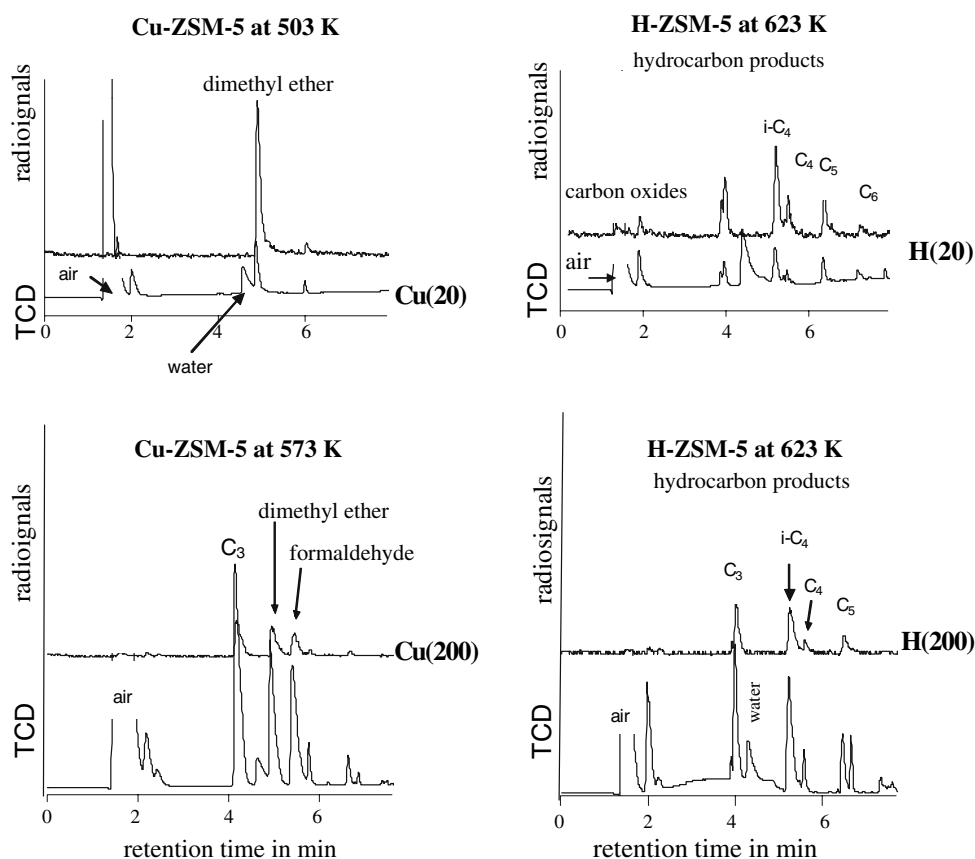


Figure 5. Comparison of transformation products: 20 and 200 μmol of ^{11}C -methanol over H- and Cu-modified ZSM-5 by radio-GC analysis.

proton forms of zeolites the selectivity to propene among the hydrocarbons was below 15%. Propene can be considered as the initial light olefin product. The impact of the acid sites is further evidenced by the copper ion-exchange. Obviously after the Cu-exchange and a subsequent reduction in the acid site density the reaction will not proceed from the equilibrium between methanol and DME further to olefins and paraffins at the same rate. Similarly the selectivity to hydrocarbons is lower and the selectivity to DME is higher over H-MCM-41 than over H-ZSM-5 and H-Beta. In the same way the reduced number of strong acid sites leads to lower amounts of propane formation from propene. In addition to the changes in the acidity, copper introduction allows a possible reaction route for methanol to form formaldehyde by dehydrogenation, which was not detected in the reactions without copper. Methyl formate is also formed only over copper ion-exchanged catalyst. Thus, formation of formaldehyde and MF must be due to the presence of copper. In the reaction over alumina it is demonstrated that the Lewis acid sites can effectively convert methanol to DME, but Brønsted acid sites are needed to carry out the reaction further to form hydrocarbons

as alumina contains practically only Lewis acid sites [2].

4. Conclusions

A radiochemical method has been developed for the monitoring of catalytic adsorption, desorption and transformation of methanol traced with ^{11}C -radioisotope on Cu-modified ZSM-5, Beta and MCM-41 catalysts. The ^{11}C -radiolabelling is an excellent and exact analysis method for methanol derivatives alone with determination of ratios of volatile and remained derivatives on catalysts by radiodetectors. The radiodetector completed the GC analysis since it was possible to distinguish the radio labelled derivatives from other non-radioactive compounds (reagents or impurities). It was possible even for compounds with the same retention time which often happens. The radio-method was more sensitive to detect smaller amounts of compounds than thermal conductivity detector (TCD) and even FID whereas the intensity of radio-signal (RD) is independent on nature of compounds, i.e. thermal conductivity or ionization energy of molecules.

The copper introduction into the catalysts inhibited the reaction to proceed further from the equilibration with the methanol and DME to produce hydrocarbons C₃–C₆. Furthermore, presence of copper also allowed a possible reaction route for methanol to produce formaldehyde and MF.

Acknowledgments

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