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The ^{11}C-radioisotopic study of methanol conversion on V-MCM-41: The influence of methyl iodide on the transformation

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ABSTRACT

The methanol conversion and a feasible methanol co-reaction with methyl iodide were studied on a vanadium incorporated MCM-41 type (V-MCM-41) mesoporous catalyst, which was prepared by a direct hydrothermal synthesis method. Adsorption/desorption as well as conversion derivates of radioactive methanol were easily followed by radioactivity detectors on V-MCM-41. The transformation and co-reaction products were analyzed by a gas chromatograph equipped with Radio/FID detectors. The radiodetector was applied to distinguish ^{11}C-derivates from the non-radioactive methyl iodide and its derivates. The radio-labeling method proved methanol transformation to methylal and, in the presence of methyl iodide, decided the roles of methyl group and iodide of methyl iodide in newly synthesized methyl iodide formation in the absence of oxygen gas.

1. Introduction

The methanol transformation products are mostly dimethyl ether (DME) and hydrocarbons [1] on proton form of mesoporous silica and alumino-silica, due to the Lewis and even Brønsted acid sites. Over transition metal modified MCM-41 catalysts, the main products are formaldehyde and methyl formate in oxidative environment. However in non-oxidative environment methylal (i.e. dimethoxy methane) and some dimethyl ether are expected to form in the temperature range of 473–623 K. Comparison of the methanol reaction pathways on pure vanadia (V_2O_5) [2,3], vanadia–silica [4], V-MCM-41 mesoporous silica [5–7] and mesoporous alumino-silica yielded interesting conclusions. Major products of methanol partial oxidation were formaldehyde and methylal with some CO_x on pure V_2O_5 and even on vanadia–silica [3]. Formation of hemimethylal (methoxy methanol, $CH_3O–CH_2OH$) intermediate was also detected. Vanadium incorporated MCM-41 (V-MCM-41) was reported to show higher activity than V_2O_5 supported on silica, due to the different sorption strengths [8]. Selective formaldehyde formation requires both weak acid and basic sites to limit the H abstraction and to prevent a too strong formaldehyde adsorption [6,7]. Functionality of the V–O–Si bridging bonds in selective oxidation of methanol was well illustrated [9,10]. In some recent studies it was reported that V^{4+} was active for selective oxidation through a redox cycle, while V^{5+} essentially yields total oxidation.

In the present experiments, vanadium incorporated MCM-41 type mesoporous silica catalyst, containing basically mild acid sites, was prepared by a low temperature direct hydrothermal synthesis procedure [11]. Vanadium was placed into the framework to obtain an oxidation catalyst. In the earlier paper of this work [12] it was shown that this novel V-MCM-41 with a V/Si ratio of about 0.04 showed very high activity in selective oxidation of ethanol to produce ethene, acetaldehyde and also some diethyl acetal and diethyl ether at low O_2/ethanol feed ratios. This is one of the main reasons of using this catalyst in methanol selective oxidation. Our earlier DRIFTS results also proved dissociative adsorption of ethanol and the formation of ethoxy species on the catalyst surface.

Methyl iodide may take effect for methanol conversion. Iodide can be oxidized to iodine hereby it can act as a reducer. On the other hand, the methyl group of methyl iodide can take part on co-production with methanol derivates. In the study of Qian et al. [13] on methanol conversion with methyl iodide (as iodide promoter) on Ag catalyst, the rate of methanol selective oxidation to formaldehyde was reported to be on the upgrade and CO_x was on the downgrade.

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In present work, the aim was to study the redox and the acidity properties of V-MCM-41, by methanol conversion and also to investigate the influence of methyl iodide on methanol conversion in oxygen-free medium, using ^{11}C-radiolabeling technique. Methanol, as a small polar molecule adsorbing easily on surface of V-MCM-41, was used for a catalytic test. Among methanol conversion products, dimethyl ether formation could correlate well with the acid character, while the formaldehyde formation could confirm the presence of redox sites of the catalyst. Non-radioactive methyl iodide (shortly $^{12}CH_3I$ or ^{12}C-methyl iodide) was added to ^{11}C-methanol and introduced into V-MCM-41 to study the influence of methyl iodide addition on product distribution, i.e. the roles of ^{12}C-methyl group and iodide (and/or V–I) as a possible promoter or reactant were investigated. This radio-method is suitable and perfect for detection of a possible "methyl-exchange" of methyl iodide.

The ^{11}C-labeled radioactive methanol has already been applied for the determination of adsorption/desorption rates and product selectivity in methanol conversion on H- and Cu-modified MCM-41 alumino-silica catalysts [14]. The great advantage of this radiolabeling method is that the ^{11}C-methyl group of ^{11}C-methanol can be distinguished from the ^{12}C-methyl group of ^{12}C-methyl iodide by radiolabeling. The possible co-reaction products can be detected excellently by Radio/FID–GC.

2. Experimental

The V-MCM-41 catalyst was prepared by direct hydrothermal synthesis method [11,12,15]. In the preparation of MCM-41 and V-MCM-41 materials, an aqueous solution of sodium silicate (27 wt% SiO_2 and 14 wt% NaOH, Aldrich) was used as the silica source and cetyltrimethylammonium bromide (CTMABr, 99% pure powder, Sigma) was used as the surfactant. The vanadyl sulfate hydrate ($VOSO_4{\cdot}xH_2O$, Aldrich) was used in the synthesis of V-MCM-41 type materials. Besides these chemicals, sulfuric acid (4N) and sodium hydroxide (1 M, Merck) were used in the synthesis of V-MCM-41 type materials to adjust the pH. Hydrothermal synthesis was carried out in a Teflon-lined stainless steel autoclave at 393 K for 96 h. The product was washed until the pH of the filtrate was about 7, dried in vacuum and calcined in a flow of dry air. During calcination, the furnace temperature was increased to 823 K at a rate of 1 K/min, and afterwards kept at this temperature for 6 h. The synthesized V-MCM-41 material was characterized and its surface area and its average pore diameter were found as 390 m^2/g (BET) and 2.8 nm (BJH), respectively. The V/Si mole ratio of V-MCM-41 was 0.07 (EDS) and the formation of V-MCM-41 structure was characterized by XRD analysis [12].

For catalytic ^{11}C-methanol conversion test, a glass tubular fixed-bed reactor was used as a closed static reactor. The cyclotron produced ^{11}C-radioisotope ($T_{1/2} = 20.4$ min) was used for ^{11}C-labeled methanol production by radiochemical process. The catalytic experiments were started by preparing ^{11}C-labeled methanol (shortly ^{11}C-methanol, radioactivity ca. 370 MBq). The required volume of ^{11}C-methanol was warmed up in a vessel to 373 K and transported into ~250 mg of catalyst (flow system) at an ambient temperature by pure He gas flow (50 ml/min), in the absence of oxygen gas. The radioactivity of non-adsorbed ^{11}C-methanol was measured on P_2O_5 trap at the outlet. After the reactants were transported into the reactor, the valves were closed and the catalytic experiments were carried out in a closed static mode. The sample was heated up to the required temperatures (10 K/min heating rate and 10 min reaction time) and He gas flow was used to remove the gas phase ^{11}C-methanol and its derivates for GC analysis, i.e. the valves of the reactor were opened and a small volume of gaseous products was transported by He gas flow to Radio/FID–GC for analysis (the same experiment was for each of the test temperature).

In these experiments, two fixed radiodetectors (lead shielded gamma detectors, i.e. Geiger–Müller tubes) were used to follow the radioactivity rates of the adsorbed and the desorbed methanol and its derivates, continuously. The dose of the remaining radioactivity was compared to the initial radioactivity on the catalyst, using Dose Calibrator (Atomlab 300) which was used for radioactivity measurement. After catalysis, the volatile products were removed from the catalyst by He gas flow at the required reaction temperature and their radioactivities were measured by Dose Calibrator for calculation of conversions. The catalytic conversion products of ^{11}C-methanol, additionally co-reaction products with ^{12}C-methyl iodide were analyzed by Radio/FID–gas chromatograph (H-P 6890 GC system with flame ionization detector (FID) coupled on-line with a Bioscan flow count as radioactivity detector). The FID detector was used to identify every one of the reagents and their derivates (except carbon monoxide and carbon dioxide), irrespectively of radiolabeling. The radioactivity detector was used to identify the radioactive compounds. 100 μmol volume of (^{11}C-methanol + ^{12}C-methyl iodide) mixture was injected into the reaction chamber containing the catalyst. Experiments were repeated with different ratios of methanol to methyl iodide (6/1, 1/1, 1/2 and 1/100 vol.%) to investigate its effect on the co-products and product distribution. During analysis, formaldehyde was also identified by a sensitive reaction with DNPH (2,4-dinitrophenyl hydrazine) reagent and analyzed on HPLC (C_{18} column, 50:7 acetonitrile–water mobile phase with UV detection at 360 nm).

3. Results and discussion

The surface of V-MCM-41 is expected to be completely covered by ^{11}C-methanol at ambient temperature. After methanol trap, radioactivity did not leave the reactor until 473 K, i.e. all the radioactive molecules were adsorbed and bonded to the catalyst structure. In the case of using a mixture of ^{12}C-methyl iodide and ^{11}C-methanol, the temperature was again close to 473 K at the beginning of a desorption run. With an increase of temperature to 553 K, conversion of methanol sharply increased to 40%, while methyl iodide conversion remained at a low value (~5%), at any volume ratio of methanol to methyl iodide in the temperature range between 513 and 553 K.

In the experiments carried out by introducing 1 μmol of radioactive methanol into the reactor, the main radioactive products were observed as hemimethylal and methylal, between 473 and 523 K. However, CO and CO_2 became the dominant products above 533 K (Figs. 1a and 2a, Table 1). By increasing the volume of methanol injected into the reactor to ~100 μmol, the hemimethylal product disappeared and only methylal was formed (Figs. 1b and 2b). Formaldehyde formation increased with an increase of temperature from 503 to 533 K. With a further increase of temperature above 553 K, increase of formation of CO and CO_2 were detected which was considered to be due to the further transformation of formaldehyde to carbon oxides. The conversion of 100 μmol ^{11}C-methanol in the absence of methyl iodide was between 40 and 50%, while in the presence of methyl iodide its conversion increased up to 55–65%, at 1/1–1/100 volume ratios of ^{11}C-methanol and ^{12}C-methyl iodide, respectively, between 523 and 623 K (Table 1).

These results confirm the presences of vanadyl species ($[VO]^{2+}$ redox sites) and weak acid sites and their roles in formaldehyde intermediate formation. The formaldehyde may react with another

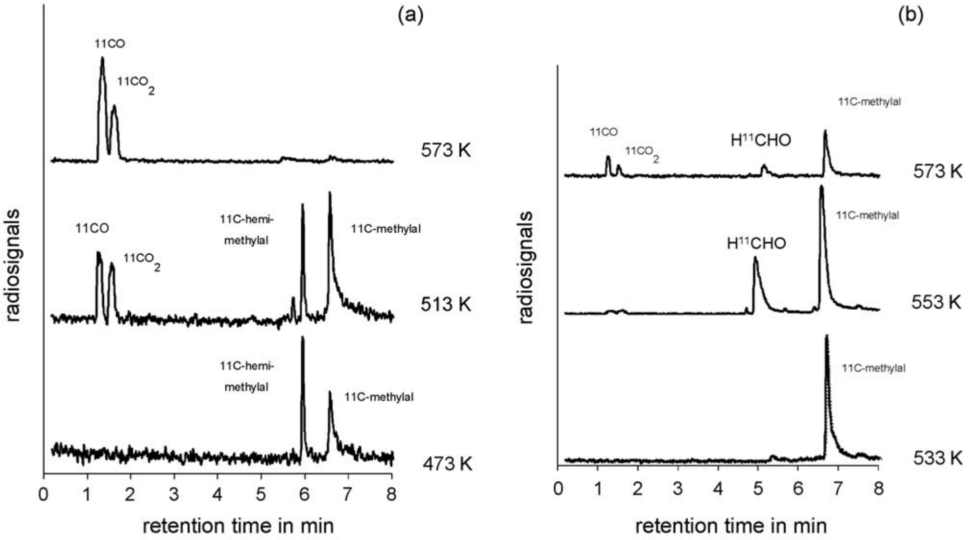
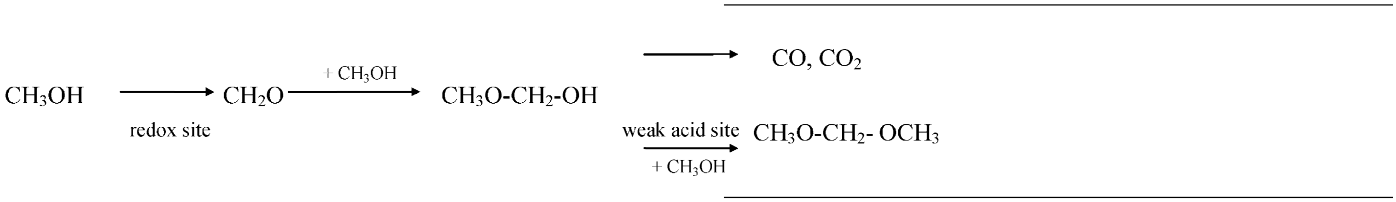


Fig. 1. Radio-GC chromatograms of ^{11}C-methanol transformation products on V-MCM-41 at different temperatures using 1 μmol (a) and 100 μmol (b) ^{11}C-methanol.

adsorbed methanol to hemimethylal and afterwards may directly decompose to carbon oxides, or with surplus adsorbed methanol to methylal in non-oxidative environment, according to the proposed scheme below:



These results of the methanol transformation to hemimethylal and methylal are in analogy with the previous observations of the role of redox and Lewis acid site in Cu as transition metal modified ZSM-5, β zeolites or MCM-41 alumino-silica [14,16,17]. Since the reaction was carried out in the absence of oxygen gas, only the redox site with frame oxygen can take part in the formation of formaldehyde during oxidative dehydrogenation of methanol. Dimethyl ether was not detected, due to the absence of medium acid sites which were required for direct methanol dehydration. In methanol conversion, like in ethanol conversion, the result of the decreased formaldehyde yield (like acetaldehyde yield) with respect to time indicates and confirms the use of lattice oxygen of catalyst.

Product selectivities of the reaction were found to depend upon the ratio of methanol to methyl iodide introduced into the reaction chamber containing V-MCM-41. The reaction route and the selectivities of side products of the reaction were slightly modified at 6/1 ratio (methanol to methyl iodide) (Figs. 3a and 4a, Table 1). However, they were drastically changed at 1/1, 1/2 and 1/100 ratios (Figs. 3b and 4b, Table 1) and a newly formed radioactive ^{11}C-methyl iodide product was detected by Radio/FID–GC analysis

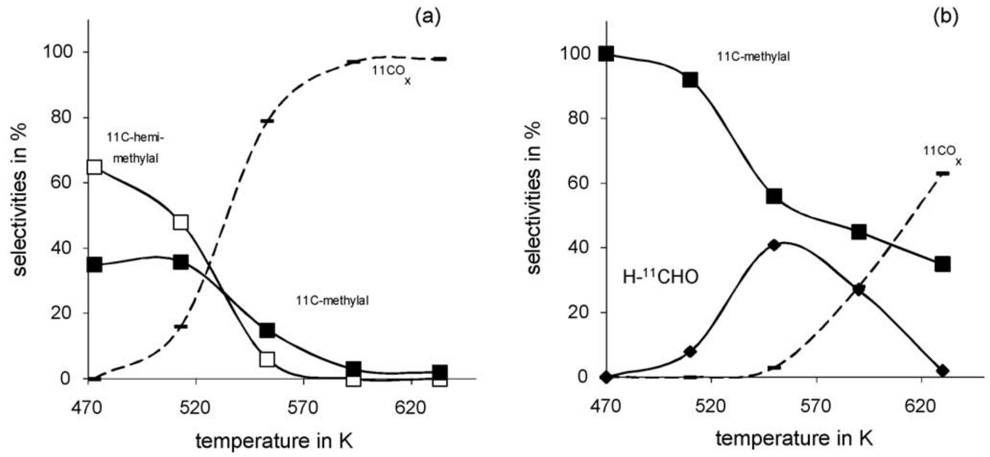


Fig. 2. Product selectivities of ^{11}C-methanol transformation over V-MCM-41 in function of temperature using 1 μmol (a) and 100 μmol ^{11}C-methanol (b). Calculation was by radioactivity data.

Table 1
Summary of conversion and selectivity of ^{11}C-methanol without and with ^{12}C-methyl iodide on V-MCM-41 (10-min duration test).

Reactant	Volume (μmol)	Temp. (K)	Conver. % $^{11}CH_3OH$	Selectivities to radioactive products (%)			
				$H^{11}CHO$	$^{11}CO_x$	^{11}C-Hemimethylal	^{11}C-Methylal
$^{11}CH_3OH$	1	523	45	1	37	32	30
		623	51	0	96	1	3
	100	523	45	28	0	0	72
		623	47	12	41	0	47

Reactants	Ratio of $^{11}CH_3OH$ and $^{12}CH_3I$	Temp. (K)	Conver. % $^{11}CH_3OH$	Conver. % $^{12}CH_3I$	Selectivities to radioactive products (%)				
					$H^{11}CHO$	$^{11}CO_x$	^{11}C-Hemimethylal	^{11}C-Methylal	$^{11}CH_3I$
$^{11}CH_3OH + ^{12}CH_3I$ (100 μmol)	6/1	523	51	5	6	1	0	92	1
		623	51	7	41	8	0	50	1
	1/1	523	53	6	2	0	0	50	48
		623	54	8	2	0	0	88	10
	1/100	523	60	4	0	0	0	0	100
		623	65	7	31	2	0	50	17

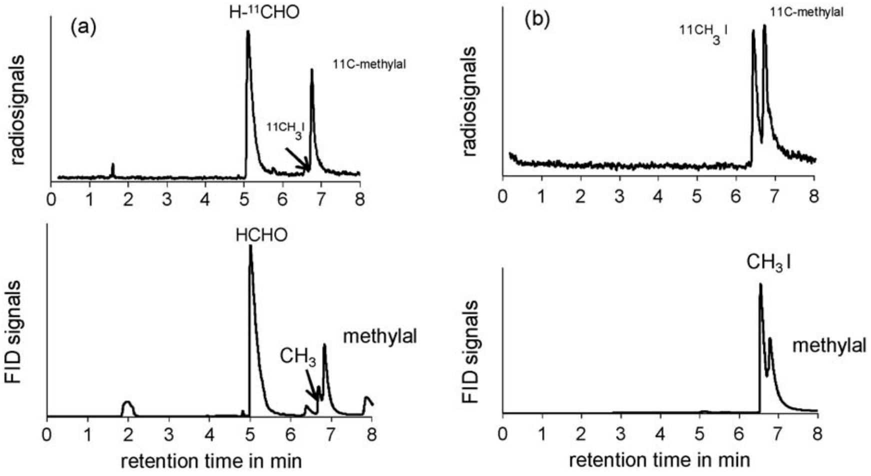


Fig. 3. Radio-and FID–GC chromatograms of co-products of ^{11}C-methanol and ^{12}C-methyl iodide on V-MCM-41 at 553 K using 6/1 (a) and 1/2 (b) ratios of ^{11}C-methanol/^{12}C-methyl iodide (total volume: 100 μmol).

at lower and higher temperature ranges, indicating the basic scheme below:

$$
\begin{array}{lll}
 & \xrightarrow{>{}^{12}CH_3I} {}^{11}\text{C-methylal} & \longrightarrow {}^{11}\text{C-methylal, } {}^{11}CH_2O\text{, small } {}^{11}CH_3\,I \\
{}^{11}CH_3OH \;+ & \xrightarrow{<\,{}^{12}CH_3I} {}^{11}\text{C-methylal, } {}^{11}CH_3\,I & \longrightarrow {}^{11}\text{C-methylal, } I_2 \\
 & \xrightarrow{<\,<\,{}^{12}CH_3I} {}^{11}CH_3\,I & \longrightarrow {}^{11}CH_3I\text{ , } I_2
\end{array}
$$

If the ^{11}C-methanol/^{12}C-methyl iodide ratio was ~1/100, only the single, newly formed ^{11}C-methyl iodide product would be detected as the co-product. Iodides can bind onto a fraction of the Brønsted acid sites, decreasing the acidity of the catalyst, and those may even bound to V-cation, explaining the sharp decrease of formaldehyde selectivity at higher methyl iodide/ methanol ratios. The newly formed ^{11}C-methyl iodide product was instable and decomposed above 573 K. Transformation of formaldehyde to methylal was again dominant at higher temperatures and CO_x formations were suppressed by iodide ions, in agreement with earlier observations [13]. Summarizing, the selectivity of newly formed methyl iodide decreased while the methylal selectivity ascended with increasing temperature (Fig. 4b).

In reverse of the methyl radiolabeling, the results of co-reaction of ^{11}C-labeled methyl iodide and non-radioactive methanol showed that mostly ^{11}C-methane was formed in small degree on V-MCM-41, even at elevated temperatures, i.e. the methyl group of methyl iodide did not take part in methanol conversion in this environment.

Here it is noticed that, after conversion, iodine vapour was visible inside glass wall of the reactor, due to iodide oxidation to iodine. If non-radioactive ethyl iodide was used instead of non-radioactive methyl iodide as co-reactant, the reaction pathway was similar but with lower selectivity to ^{11}C-methyl iodide. In ^{11}C-methanol co-reaction with methyl iodide, a part of methanol was formed with iodide to ^{11}C-methyl iodide. This newly formed methyl iodide was distinguished by radiodetection. Summarizing, during methanol conversion with methyl iodide, formaldehyde formation decreased or even nearly disappeared, but new methyl

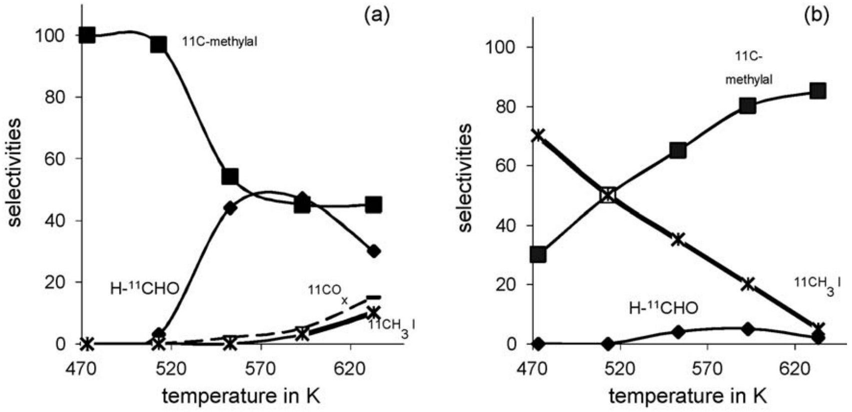


Fig. 4. Selectivities of ^{11}C-methylal, ^{11}C-formaldehyde and newly formed ^{11}C-methyl iodide in co-reaction of ^{11}C-methanol and ^{12}C-methyl iodide where the ^{11}C-methanol/^{12}C-methyl iodide ratio is 6/1 (a) and 1/1 (b) over V-MCM-4. The product selectivities were calculated from radioactivity data.

iodide formation appeared by iodide (or by V–I), compared to the single methanol conversion products.

4. Conclusion

In methanol partial oxidation on V-MCM-41, the reaction pathway was to formaldehyde and methylal in non-oxidative environment. As it was discussed in the earlier study in ethanol selective oxidation, that intrinsic activity of vanadium incorporated into SiO_2 framework was much higher than that of nonincorporated vanadium. In that work [12] simultaneous involvement of vanadyl (V═O) and V–O–Si groups in the lattice structure was considered in the formation of dimethyl ether, while formation of formaldehyde was generally considered to be due to the vanadyl groups. A similar mechanism is expected in methanol selective oxidation.

In the case of the added methyl iodide, selectivity to methylal decreased and the methyl iodide was recomposed by methyl group of methanol in methanol conversion at low temperature. The radiolabeling method was an excellent method for the detection of the "exchange" of methyl groups. Increasing the temperature, the methyl iodide transformed back while the iodide upgraded the methylal formation and suppressed the CO_x production. Summarizing, the iodide plays a remarkable role in the catalytic process. Iodide-induced change of the reaction performance was reversible. The experimentally observed effects are in agreement with the hypothesis that the addition of methyl iodide leads to a repopulation of different oxygen species on the catalyst surface. On the basis of results it was concluded that, the addition of methyl iodide lead to a change in the selectivity of reaction. Two reactants compete for the same sites of catalyst and methyl iodide inhibits the complete oxidation of methanol. Summarizing, the product distribution of methanol transformation was influenced by methyl iodide addition and this influence was excellently detected (as ^{11}C-methyl iodide) by Radio/FID–GC method.

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