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^{11}C-radioisotope labeled methanol conversion over H- and Cs- modified ZSM-5, Beta zeolites and MCM-41 mesoporous molecular sieve

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Abstract

The Na–MCM-41 mesoporous molecular sieve, Na–ZSM-5 and Na–Beta zeolites have been modified by Cs- and H- using ion-exchange method and characterized by XRD, SEM and nitrogen adsorption. The conversion of methanol was studied over H- and Cs- modified ZSM-5, Beta zeolites and MCM-41 mesoporous molecular sieve. Methanol was in ^{11}C-radioisotope labeled form in-order to follow its conversion during the catalytic process, since the radioactivity method provides a very sensitive detection possibility to investigate the conversion of small amounts of methanol and some intermediates at different reaction times and temperatures. The understanding of reaction mechanism is important for side-chain methylation over Cs–zeolite catalysts by methanol, as they are more selective than other alkali exchanged zeolites (Li, Na and K). The reaction pathway of the transformation of methanol to hydrocarbons and aldehydes has been elaborated.

Keywords: Methanol conversion; ^{11}C-labeled methanol; Catalyst; Cs–ZSM-5; Cs–Beta; Cs–MCM-41; Hydrocarbon

1. Introduction

Methanol compared to hydrocarbons is more suitable for the characterization of structural and chemical properties of zeolite catalysts [1–4]. Different hydrocarbon transformations are applied as test reactions to elucidate catalytic properties of microporous and mesoporous materials. During catalysis methanol with its bound oxygen has significantly different physical and chemical properties from hydrocarbons. The selectivity and the formation rates of reaction products give information about methanol dehydration on the acidic zeolite and methanol dehydration, and dehydrogenation on acid–base zeolites. The methanol conversion as a test reaction is sensitive to structures and chemical compositions of the different types of zeolite catalysts such as Cs modified ZSM-5, Beta zeolites and MCM-41 mesoporous molecular sieves. These zeolite catalysts have different properties for methanol adsorption and conversion.

The variations of Si/Al ratio and different exchanged cations can change the concentration of adsorption sites and the acid–base properties. The above mentioned zeolites have low Si/Al ratios, namely 20–35 and their modification with Cs metal ion leads to the increase of the polarities of zeolite lattices such as increase of base strength of lattice oxygen [1]. Two possible binding geometries of the methanol molecule towards Cs^{+}cation and acidic OH group of Cs-modified zeolites are given in Fig. 1.

On the acidic sites of the zeolite catalysts namely on H-modified zeolites methanol first reacts with zeolitic Brønsted acid sites to give surface methoxy group and then couple with another methanol molecule through dimethyl ether to produce hydrocarbons [2].

H- zeolite

$$CH_3OH \xrightarrow[-H_2O]{} CH_3O- \longrightarrow CH_3OCH_3 \longrightarrow C_2\text{-}C_4 \text{ hydrocarbon}$$

The effect of alkali metal in the zeolite for methanol conversion was investigated in [1,3 and 4]. On the basic–acidic sites of zeolite catalysts, namely on Cs-modified

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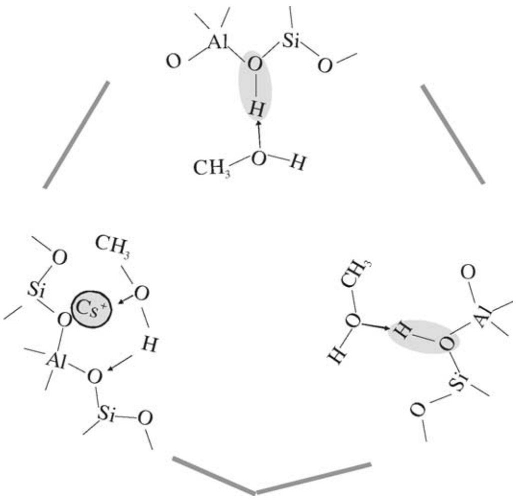
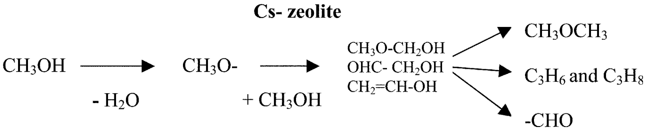


Fig. 1. Two possible binding geometries of the methanol molecule towards Cs^+cation and acidic OH group of Cs-modified zeolite.

zeolites methanol first reacts with zeolitic hydroxyl groups and the formed methoxy may combine with another methanol by dehydrogenation on Cs-ion to form an intermediate (methoxy methanol or glycolaldehyde, vinyl alcohol, etc.) which can further lead to dimethylether, formaldehyde or, -and acetaldehyde) and C_3 hydrocarbons at higher temperatures.



The radioisotope method provides possibilities to follow the chemical processes with gamma detectors, which are able to detect very small amounts of methanol as well as intermediates and products [5]. This radio-method also makes possible to demonstrate the participation of ^{11}C-labeled carbon of ^{11}C–methanol in the formation of products during reactions of ^{11}C–methanol with other inactive carbon compounds. In this work we have investigated ^{11}C-radioisotope labeled methanol conversion over H- and Cs-modified ZSM-5, Beta zeolites and MCM-41 mesoporous molecular sieve.

2. Experimental

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

The Na–ZSM-5 (Si/Al = 31), Na–Beta (Si/Al = 11) and Na–MCM-41 (Si/Al = 20) catalysts were synthesized and converted to proton forms (H–ZSM-5, H–Beta and H–MCM-41) by ion exchange with NH_4Cl solution followed by drying and calcination.

Synthesis of ZSM-5 zeolite was carried out in a 300 ml autoclave (Parr) at 423 K, according to the method outlined in Ref [6] with some modification. The reagents used in the synthesis were fumed silica (Aldrich), NaOH (Merck), $Al(OH)_3$ (Aldrich), tetrapropylammonium bromide (Fluka) and distilled water. After the completion of synthesis, the autoclaves were quenched in cold water and the materials synthesized were filtered and washed thoroughly with distilled water. The Na–ZSM-5 sample was dried at 373 K and the removal of organic templates was carried out at 813 K in the presence of air. The samples were converted to proton form by ion exchange with 1 M NH_4Cl solution at room temperature for 48 h. After ion exchange the samples were washed with distilled water to remove chloride ions, dried at 373 K and calcined at 813 K to obtain H–ZSM-5.

Synthesis of the parent form of Na–Beta zeolite was carried out as mentioned in Ref [7] with some modifications. Ludox AS 40 (Aldrich), sodium aluminate (Riedel de Häen) and tetraethylammonium hydroxide (40% aqueous solution, Fluka) were used as sources of silica, alumina and organic template, respectively. The gel was prepared by mixing the above reagents and transferred into a teflon cup inserted into a stainless steel autoclave. The autoclave was kept in an oven heated at 423 K and the synthesis was carried out under static condition. The products obtained after the synthesis was filtered and washed thoroughly with distilled water. The zeolites were dried at 373 K and the organic template was removed by heat treatment at 823 K. The Na–Beta zeolite was transformed to H–Beta by ion-exchange with 3 M NH_4Cl solution, followed by drying and calcination at 823 K.

Synthesis of Na–MCM-41 mesoporous molecular sieve was carried out using a method as mentioned in references [8,9] with some modifications. The reagents used in the synthesis were fumed silica (Aldrich), tetramethylammonium silicate (Sachem), sodium silicate (Merck), cetyltrimethylammonium bromide (Aldrich), aluminium isopropoxide (Aldrich) and distilled water. A gel mixture was prepared and introduced in a 300-ml autoclave (Parr). The synthesis was carried out in an oven at 373 K for 24 h. Subsequently, the autoclave was quenched and the mesoporous material was filtered and washed with distilled water. Drying of the sample was carried out at 383 K and calcination at 823 K. The Na–MCM-41 mesoporous molecular sieve was ion-exchanged with 1 M NH_4Cl solution, washed with distilled water to remove chloride ions and dried at 383 K. The H–MCM-41 catalyst was obtained by calcination of NH_4–MCM-41 at 803 K.

The Cs–ZSM-5, Cs–Beta and Cs–MCM-41 catalysts were prepared by repeated ion-exchange using aqueous solution of cesium nitrate. The catalysts were dried at 373 K and calcined at 673 K. The characterization of Beta, ZSM-5 zeolites and MCM-41 mesoporous molecular sieve was performed using X-ray powder diffraction, scanning electron microscope, X-ray fluorescency and nitrogen adsorption.

2.2. Conversion of ^{11}C-labeled methanol to ^{11}C-labeled hydrocarbons and dimethyl ether over H- and Cs-modified MCM-41, Beta and ZSM-5 catalysts

The reaction was carried out in a micro-flow reactor constructed of a glass tube (4 mm i.d., 110 mm long) in which approximately 20 mm long catalyst was placed at the centre position between quartz–wool holders. During the catalyst pre-treatment and catalysis a gas dosing system with flow controllers (for He) was used. The feed stream and, after catalysis, the product stream was transformed into a small gas syringe (1 ml as a sample collector) with He flow by operating the reactor valves. For the pre-treatment the catalyst was first preheated to 423 K for 30 min then up to 623 K with 5 K/min ramp for 2 h under He flow. The ^{11}C-radioisotope ($T_{1/2} = 20.4$ min) as a gamma emitter (by annihilation of its positron) was produced in cyclotron. The ^{11}C-labeled methanol was synthesized by a classical method [10]. The catalytic experiments were started by introducing the ^{11}C-labeled methanol with He as a carrier gas (the He flow rate was 50 ml/min) over H- and Cs-modified ZSM-5, Beta and MCM-41 catalysts packed into a micro-reactor at 393 K. The rate of [^{11}C]methanol adsorption and, after the reaction, the rate of desorption of the remaining [^{11}C]derivatives on catalysts was continuously detected by a lead shielded (less sensitive Geiger–Müller type) gamma detector. After [^{11}C]methanol adsorption, the valves were closed and the catalyst was heated up to the required temperature (533–603 K) and kept for given reaction times. The products of the catalytic conversion of the ^{11}C-labeled methanol were analyzed by a radio-gas chromatography (gas chromatograph with thermal conductivity detector (TCD) coupled on-line with a radioactivity detector) [5]. The radioactivity sensor of the radio-gas chromatograph was a sensitive scintillation detector with lead shielding. The TCD was applied for the identification of the radioactive products by their equivalent inactive carbon compounds. The oven of the PLOT Q capillary column (30 m × 0.53 mm × 40 μm, Alltech) of the gas chromatograph was programmed to hold the temperature at 333 K for two minutes and then to elevate the temperature up to 523 K with 40 K/min while keeping He carrier gas constant.

After catalysis all of the ^{11}C-labeled volatile products were removed from catalysts by He gas flow at the reaction temperatures. The remaining radioactivity was compared to the initial radioactivity. The radioactive products were injected together with its equivalent inactive compound into radio-gas chromatograph in order to identify the radioactive compounds. All the inactive compounds were commercially available except the intermediate found mainly in experiments with Cs-modified zeolites. This radioactive intermediate was identified by synthesising the possible reaction intermediates in the laboratory, since they are not commercially available due to their unstability.

3. Results and discussion

3.1. Characterization results

The X-ray powder diffraction patterns of ZSM-5, Beta and MCM-41 catalysts were similar to those reported in the literature [5,11]. The modification with Cs did not influence the parent structures of the Na–ZSM-5, Na–Beta zeolites and Na–MCM-41 mesoporous molecular sieve. The surface area of the Na–MCM-41, Na–ZSM-5 and Na–Beta zeolites were determined to be 1291, 477 and 730 m^2/g, respectively. The scanning electron micrographs of Na–ZSM-5, Na–Beta zeolites and Na–MCM-41 mesoporous molecular sieve were similar to those mentioned in references [12,13]. The Si/Al ratio of the Na–MCM-41, Na–ZSM-5 and Na–Beta were determined to be 20, 31 and 11, respectively.

3.2. Transformation of ^{11}C–methanol over H-modified ZSM-5, Beta and MCM-41 catalysts

The transformation of methanol was investigated using ^{11}C–methanol over H-modified ZSM-5, Beta zeolites and MCM-41 mesoporous molecular sieve at 603 K for 5 min reaction time. The ratio of ^{11}C–methanol adsorption was high enough (∼90%) at 393 K. The main products were ^{11}C-labeled C_3–C_4 alkane and alkene and dimethyl ether over H–ZSM-5 and Beta zeolites (Fig. 2). The conversion of ^{11}C–methanol over H–MCM-41 was quite different. The highest yield for ^{11}C-labeled propane-propene and the minimal unreacted ^{11}C–methanol were over H–MCM-41. It should be noted here that, only over H–MCM-41 catalyst, a small amount of not previously observed ^{11}C-labeled intermediate was detected at 533 K.

3.3. Transformation of ^{11}C–methanol over Cs-modified ZSM-5, Beta and MCM-41 catalysts

The conversion of methanol was investigated over Cs-modified ZSM-5, Beta and MCM-41 catalysts at two different temperatures and at three different reaction times. The ratio of ^{11}C–methanol adsorption was less (∼40%) than at the H-modified zeolites at 393 K. ^{11}C-labeled gas

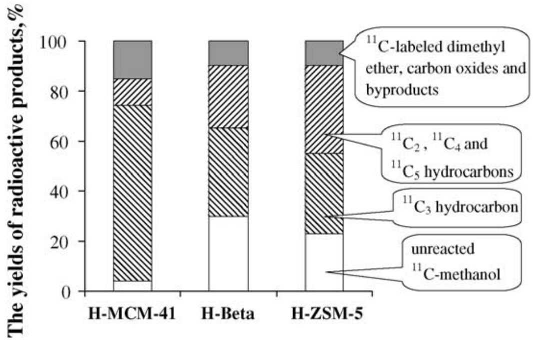


Fig. 2. Radioactive gas products of ^{11}C–methanol conversion on H-modified MCM-41, Beta and ZSM-5 zeolite catalyst at 603 K.

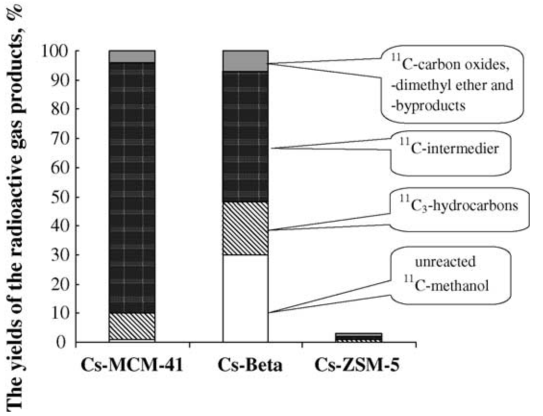


Fig. 3. Radioactive gas product of ^{11}C–methamol conversion on Cs-modified MCM-41, Beta and ZSM-5 zeolites at 533 K.

products were detected over Cs–Beta and Cs–MCM-41 catalysts but not over Cs–ZSM-5 catalyst at 533 K after 5 min reaction time (Fig. 3). ^{11}C-labeled intermediate was also detected with high yields together with radio-gas products over Cs–Beta and Cs–MCM-41 catalysts at 533 K.

At higher temperature i.e at 603 K, the ^{11}C-labeled intermediate was detected over Cs–Beta and Cs–MCM-41, after 5 min reaction time (Fig. 4) but it was partly converted to other ^{11}C-labeled compounds (Fig. 5). At longer reaction times (~1 h) the compounds were converted to ^{11}C-labeled carbon oxides as final products. In the case of Cs–ZSM-5 catalyst, only the ^{11}C-labeled intermediate was detected as radio-gas products at 603 K in the first minutes. At longer reaction time the ^{11}C-intermediate decomposed to ^{11}C–dimethyl ether and ^{11}C–aldehyde (formaldehyde or acetaldehyde).

From the above results of ^{11}C-labeled methanol conversion the reaction mechanism can be advanced. The ratio of ^{11}C–methanol adsorption was quite different for H- and -Cs modified zeolites. More specifically introduction of Cs^{+} cation decreases the active surface of zeolite for adsorption. The formation of ^{11}C-labeled C$_3$ product was more favourable over weakly acidic H–MCM-41 than over strongly acidic H–ZSM-5 and H–Beta zeolite catalysts. The selectivity and the yield of ^{11}C-labeled C$_3$ hydrocarbon product increased proportionally to the decrease of acidity (H–ZSM-5 > H–Beta > H–MCM-41) [12]. The results are similar to those obtained in the literature [2,14].

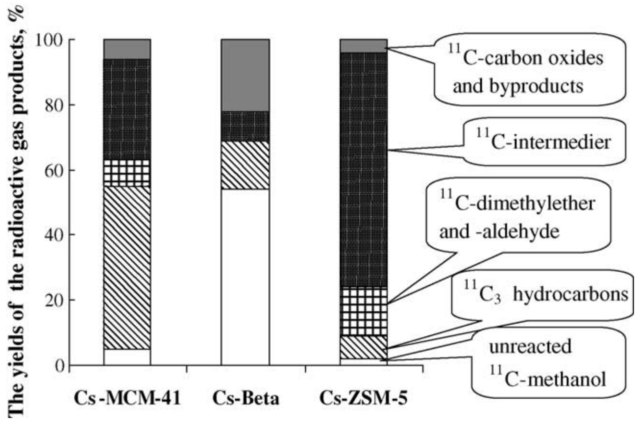


Fig. 4. Radioactive gas products of ^{11}C–menthol conversion on Cs modified MCM-41, Beta and ZSM-5 zeolites at 603 K.

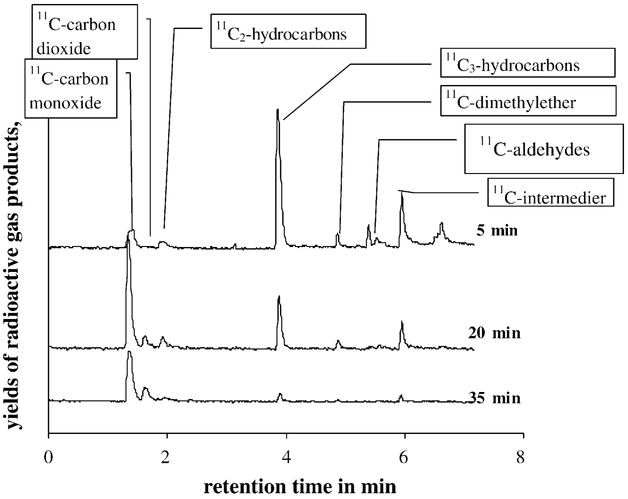


Fig. 5. Radio-gas chromatogram of ^{11}C–methanol conversion on Cs–MCM-41 at 603 K and different reaction times.

Over the acid–basic Cs–MCM-41, Cs–Beta and Cs–ZSM-5 catalysts, the yields and the selectivities of ^{11}C-labeled gas products have changed essentially and a previously unidentified intermediate product was detected. In the case of Cs–MCM-41 and Cs–Beta zeolite this new intermediate was detected already at 533 K, while over the Cs–ZSM-5 zeolite it appeared only at 603 K. This intermediate was the only product at short reaction times over Cs–ZSM-5 zeolite catalyst. The Cs–MCM-41 and Cs–Beta catalysts have similar behaviour with respect to methanol conversion compared to Cs–ZSM-5 zeolite at 533 K.

A possible molecule is the methoxy methanol or glycolaldehyde or vinyl alcohol as an intermediate during methanol conversion mostly over basic–acidic sites of Cs-catalysts. During the reaction the intermediate can decompose to hydrocarbons, dimethyl ether and,- or aldehydes. The detection of this intermediate molecule is important for understanding of the mechanism of methanol conversion. The retention time of this ^{11}C-labeled intermediate compound on the column of the gas-chromatograph is equal with the retention time of the methoxy methanol.

4. Conclusions

The Na–MCM-41 mesoporous molecular sieve, Na–ZSM-5 and Na–Beta zeolites have been modified by Cs- and H- using ion-exchange method and characterised by XRD, SEM and nitrogen adsorption. The introduction of Cs^{+} cation decreases the capacity of MCM-41, ZSM-5 and Beta zeolites for methanol adsorption. The catalytic experiments with ^{11}C–methanol demonstrated that formation of ^{11}C-labeled C_3 product was more favourable over weakly acidic H–MCM-41 mesoporous molecular sieve than over strongly acidic H–ZSM-5 and H–Beta zeolite catalysts. Elucidation of the chemical structure of this intermediate is important for understanding of the reaction mechanism. Several compounds, like methoxy methanol, glycolaldehyde or vinyl alcohol could be considered as possible intermediates. Comparison of the retention time of this ^{11}C labelled intermediate with retention time of the potential candidates revealed, that it is equal to the retention time of methoxy methanol.

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