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A novel radioisotope method for studying catalytic transformations over alumina, H-ZSM-5 and H-beta zeolite catalysts: investigation of conversion of ^{11}C-labeled methanol to ^{11}C-labeled dimethyl ether and hydrocarbons

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A novel radiochemical method for investigating the catalytic transformations of the ^{11}C-radioisotope labeled methanol over H-ZSM-5 and H-Beta zeolite catalysts has been introduced. The catalysis process was monitored by gamma detectors and the ^{11}C-labeled products were analyzed by radio-gas chromatography. The medium pore H-ZSM-5 and H-Beta zeolite catalysts were synthesized and characterized using X-ray powder diffraction, scanning electron microscope, nitrogen adsorption, X-ray fluorescency and FTIR spectroscopy. The investigations of ^{11}C-labeled product distributions and reaction mechanism of the conversion of [^{11}C]methanol over H-ZSM-5 and H-Beta zeolite catalysts have been elaborated in terms of structure and acidity of the catalysts. In microreactors the effect of natural carbon compounds from environment can be a disturbing effect for the detection of inactive carbon products. Applied radio detection method eliminates these disturbing effects and detects only ^{11}C-labeled compounds during the whole catalytic process. In the study of the transformations of carbon compounds, besides the well known ^{14}C tracer technique and ^{13}C MAS NMR spectroscopy investigation, the ^{11}C-method is a new, more sensitive and simple one to monitor the transformation of the starting ^{11}C-labeled compound by radio detectors (gamma detector) and for analyzing the ^{11}C-labeled products by radio-gas chromatography.

KEY WORDS: methanol conversion; zeolite; catalyst; hydrocarbon; ^{11}C-labeled methanol; ^{11}C-labeled hydrocarbon.

1. Introduction

The zeolite catalysts are used in oil-refinery and petro-chemical industry, and have potential applications for synthesis of fine chemicals and environmental catalysis [1–6]. The transformation of methanol to gasoline over H-ZSM-5 catalyst, also known as MTG process for the production of synthetic fuel, is well documented in literature [7, 8].

The framework of ZSM-5 zeolite contains two perpendicularly intersecting channel systems, one sinusoidal running parallel to (001), having near circular pore openings with free dimensions of 0.54 × 0.56 nm and an other one straight and parallel to (010), having an elliptical shape with dimensions of 0.51 × 0.54 nm. The size of the channel intersection is 0.8 nm [9]. The structure of Beta zeolite consists of polymorph A, which has straight channels of 0.73 × 0.6 nm and tortuous channels of 0.56 × 0.56 nm, and the polymorph B, which has straight channels of 0.73 × 0.68 nm and tortuous channels of 0.55 × 0.55 nm [10]. Both zeolite types have common property with their strong Brønsted acid sites which govern the adsorption and conversion of methanol during the catalysis.

While the alumina catalyst is active only for dehydration of methanol by removing water, the H-ZSM-5 and H-Beta zeolite catalysts are active and selective with their strong Brønsted acid hydroxyl groups and other chemical environment for the formation of dimethyl ether and hydrocarbons:

$$CH_3OH \xrightarrow[-H_2O]{\text{aluminaorzeolite}} CH_3OCH_3 \xrightarrow{\text{zeolite}} C_2 - C_5 \text{ olefins}$$

$$\xrightarrow{\text{zeolite}} \text{paraffins}$$

The aim of this work was the investigation of transformation of methanol over alumina, H-ZSM-5 and H-Beta zeolite catalysts using ^{11}C-labeled methanol (shortly [^{11}C]methanol); to study the reaction mechanism of methanol to hydrocarbon conversion [11–13]. This novel ^{11}C-method has high sensitivity over the ^{14}C tracer technique [14] by using several order of magnitude higher radioactive concentrations in the very low inactive (carrier) region. It makes possible to detect very low amounts of radio-methanol and other radio-products. As for the detection of radioactivities the annihilation γ-rays of ^{11}C isotope can be measured with much higher efficiency with a simple technique. Another advantage is that with this ^{11}C-method 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 [15].

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The application of the ^{11}C-radioisotope, as a positron emitter, has been investigated for measuring concentration profiles of hydrocarbons in zeolite [16]. The cyclotron produced ^{11}C-isotope ($T_{1/2} = 20.4$ min) is a commonly used positron emitter for the production of ^{11}C-labeled pharmaceuticals used in positron emission tomography (PET) investigations. Here the γ-radiation, resulting from annihilation of the positron, is detected. The application of this "no carrier added" (that means "no natural carbon compounds added") [^{11}C]methanol precludes the disturbing effect of natural carbon impurities (from air, catalyst, tube wall), it means, that the ^{11}C-labeled products are distinguished from the other, so-called disturbing inactive carbon compounds. The radio-gas chromatography is a safe method to verify with accuracy the ^{11}C-labeled products formed only from [^{11}C]methanol. At the same time, it is sensitive enough to detect very low amounts of methanol or hydrocarbon products (μmol amounts). The ^{11}C-labeled products are then analyzed by radio-gas chromatograph equipped with a thermal conductivity detector (TCD) and coupled on-line with a radioactivity flow detector.

Although the ^{11}C-radioisotope was measured here with a simple gamma detector, in PET investigation the position of ^{11}C-labeled radiopharmaceuticals are monitored by gamma detectors in coincidence. The [^{11}C]methanol, as intermedier, is applied very frequently in the radiopharmaceutical chemistry. The zeolite catalysis can be used as a novel, one-step method for production of ^{11}C-labeled hydrocarbons and ^{11}C-labeled methylated aromatics in the future.

2. Experimental

2.1. Synthesis and characterization of Na-ZSM-5, H-ZSM-5 Na-Beta and H-Beta zeolite catalysts

Synthesis of ZSM-5 zeolite was carried out in a 300-mL autoclave (Parr) at 423 K according to the method outlined in Ref. [17] 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. [18] 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.

The synthesized ZSM-5 and Beta zeolites were characterized using X-ray powder diffraction, scanning electron microscopy, nitrogen adsorption and X-ray fluorescency. The acidic property of the H-ZSM-5 and H-Beta catalysts was investigated by FTIR of adsorbed pyridine. The details of the acidity measurements are given in reference [10–19]. The schematic presentations of Na-ZSM-5 and Na-Beta zeolites showing the channel systems are given in figures 1 and 2. The geometry of single methanol adsorption on ZSM-5 zeolite is given in figure 3.

2.2. Transformation of ^{11}C-labeled Methanol to ^{11}C-labeled Hydrocarbons over H-ZSM-5 and H-Beta Zeolite Catalysts

The reaction was carried out in a micro-flow reactor constructed of glass tube (4 mm i.d., 110 mm long). Quartz wool was used to hold approximately 20 mm long catalyst at the center 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 gas dosing system with flow controllers (for He and air). 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. For pretreatment the catalyst was heated to 623 K with 5 K/min gradient under He flow followed by airflow for 2 h.

In the first step the [^{11}C]methanol was prepared by a classical method: [^{11}C]CO_2 was produced by cyclotron

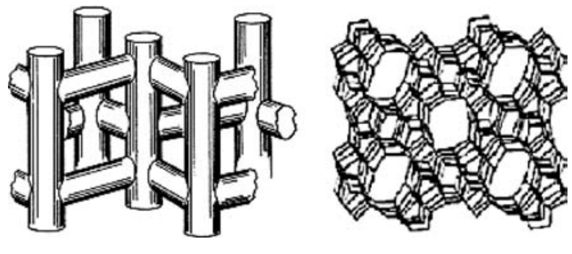

Figure 1. Channel systems and framework structure of Na-ZSM-5 zeolite.

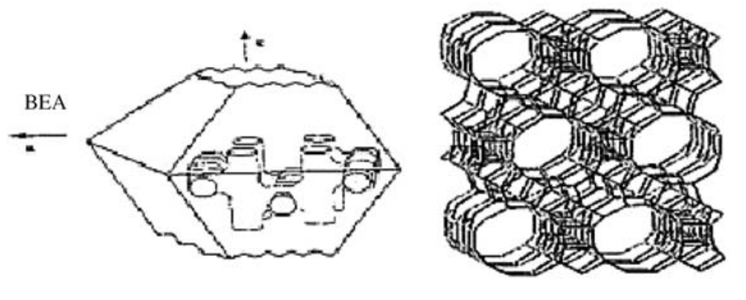

Figure 2. Channel systems and framework structure of Na-Beta zeolite.

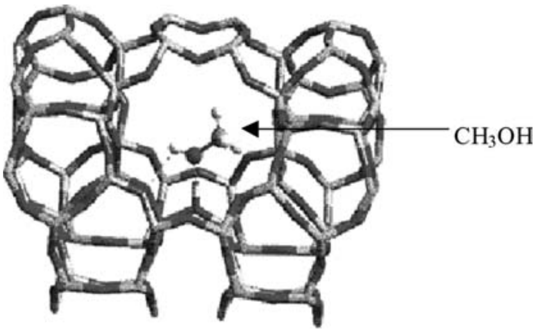

Figure 3. Geometry of single methanol adsorption on ZSM-5 zeolite.

using $^{14}N(p, \alpha)^{11}C$, $^{11}C + O_2 \rightarrow [^{11}C]CO_2$ process. The $[^{11}C]CO_2$ was reduced into radiomethylate complex with lithium aluminium hydride. After drying the radiocomplex was hydrolyzed into [^{11}C]methanol by dilute phosphoric acid [20].

In the second step the [^{11}C]methanol was removed from the production unit by He flow into the reactor containing 250 mg alumina (neutral, Merck) or H-ZSM-5 or H-Beta zeolite catalysts in separate experiments. The catalytic experiments were performed and the rate of [^{11}C]methanol adsorption on catalysts was continuously detected by a lead shielded gamma detector (less sensitive Geiger–Müller type was used because of the high radioactivity). At the maximum grade of radioactivity the transportation was stopped (approximately 4 min). The [^{11}C]methanol adsorption rate was measured at different temperature (300–450 K). The ratio of adsorption was high enough (~90%) even at 410 K compared to room temperature. After [^{11}C]methanol adsorption at 410 K, the valves were closed and the catalyst was heated up to the required temperature that was 473–673 K (figure 4). After reaction time (3–20 min) the valves were opened again to remove the gas products from the catalyst by He flow for analysis. The residual radioactivity on the column was also monitored by radiodetector. After catalysis the radioactivity of the gas products in the gas syringe was measured before and after injection to radio GC in order to know how much radioactivity was really injected.

The identification of the ^{11}C-labeled products and the checking of the radiochemical purity of the starting [^{11}C]methanol were completed by radio-gas chromatography (figure 4) within 1 h (because of the short lifetime of ^{11}C-radionuclide). In this work the ^{11}C-labeled products were not analyzed for ^{11}C-labeled aromatics. The radioactivity sensor of the radio-gas chromatograph was a sensitive scintillation detector with lead shielding. Specifically, the TCD of the gas chromatograph, which was used for the identification of the radioactive products, was applied for determination of retention times with a calibrated gas mixture of hydrocarbons (Supelco, Scott Specialty Gases). The oven of the PLOT Q capillary column (30 m × 0.53 mm ×

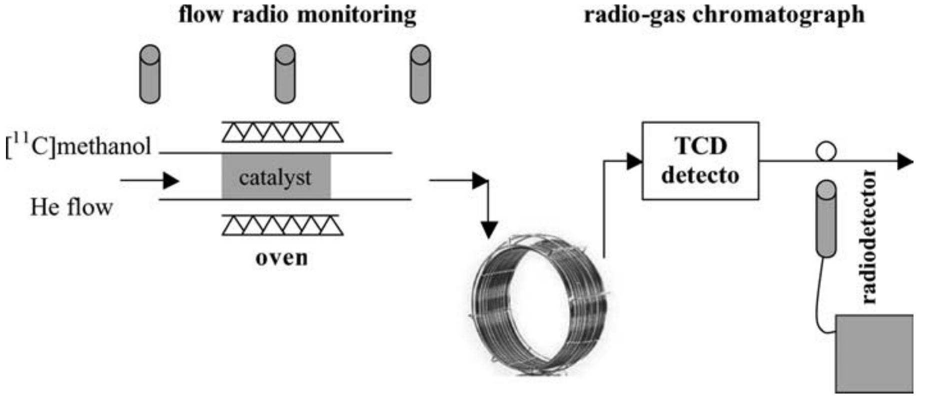

Figure 4. Schematic diagram of the catalysis and subsequent analytical setup.

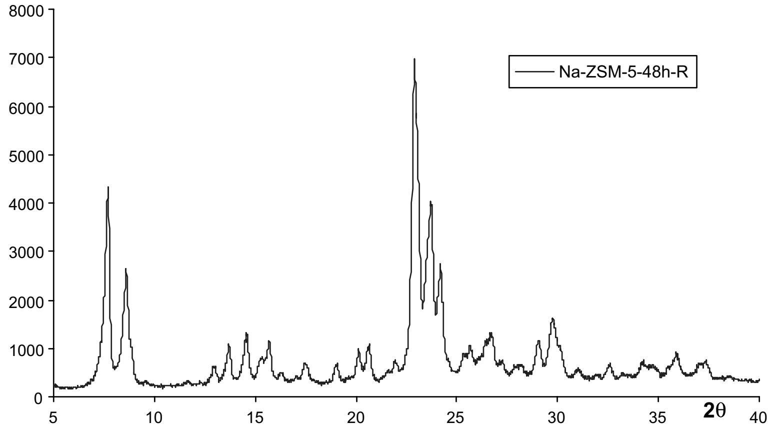

Figure 5. X-ray powder diffraction pattern of Na-ZSM-5 zeolite.

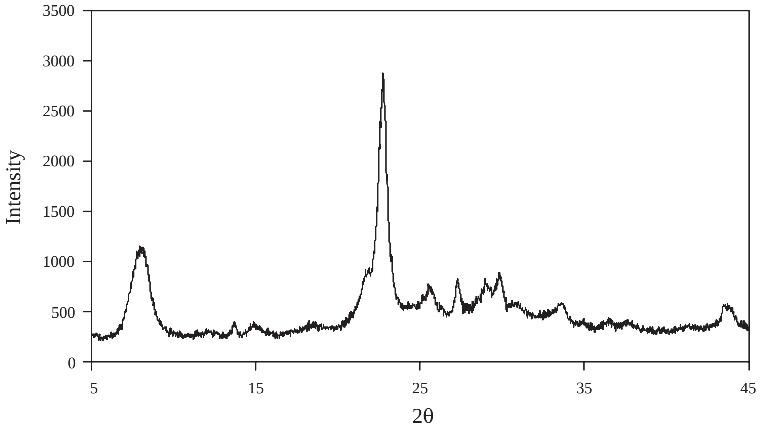

Figure 6. X-ray powder diffraction pattern of Na-Beta zeolite.

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. For dimethyl ether and water, the calibration started at 303 K (5 min) followed by ramping with 40 K/min to 523 K with 11 mL/min He carrier gas flow rate.

After catalysis all of the ^{11}C-labeled volatile products were removed from zeolites by He gas flow at 653 K. The remaining radioactivity on the catalyst was on average 20% to the initial radioactivity (decay corrected value). The identification of the ^{11}C-labeled volatile products was carried out under the same conditions.

3. Results and discussion

3.1. Catalyst synthesis and characterization results

The X-ray powder diffraction patterns of Na-ZSM-5 and Na-Beta zeolites were similar to those reported in the literature, indicating the presence of ZSM-5 and Beta phases. The X-ray powder diffraction patterns of highly crystalline phase pure Na-ZSM-5 and Na-Beta zeolites are given in figures 5 and 6. The surface area of H-ZSM-5 and H-Beta zeolite catalysts were determined to be 477 and 730 m^2/g, respectively. The crystal shape and size of Na-Beta and Na-ZSM-5 zeolites were similar to those reported in the literature indicating the phase purity, absence of amorphous materials and authenticity of the samples. The scanning electron micrograph of Na-ZSM-5 zeolite is given in figure 7. The presence of Brønsted and Lewis acid sites in H-ZSM-5 and H-Beta catalysts were determined by FTIR. The Si/Al ratio of Na-ZSM-5 and Na-Beta zeolites, determined by X-ray fluorescency was found to be 31 and 11, respectively.

3.2. *Transformation of ^{11}C-labeled methanol to ^{11}C-labeled hydrocarbons over H-ZSM-5 and H-Beta zeolite catalysts*

The transformation of methanol was investigated using [^{11}C]methanol for study of conversion of methanol

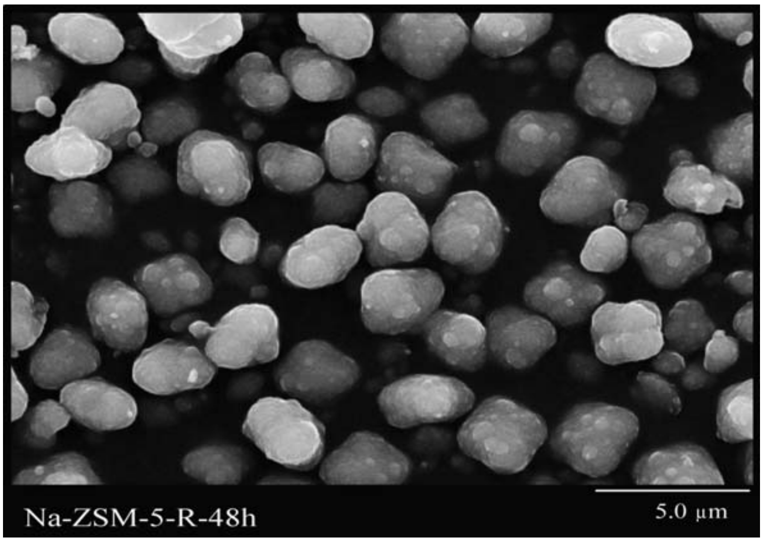

Figure 7. Scanning electron micrograph of Na-ZSM-5 zeolite.

to hydrocarbon over alumina, H-ZSM-5 and H-Beta catalysts. The yields of the ^{11}C-labeled products were calculated from the chromatograms corrected by the decay of the ^{11}C-radioisotope. During the conversion of [^{11}C]methanol on alumina, the main product was [^{11}C]dimethyl ether (figure 8). The yield of [^{11}C]dimethyl ether on alumina did not increase above 510 K (figure 9). The yield of [^{11}C]dimethyl ether formation decreased in the presence of water hence the temperature of the catalyst was kept at 413 K during the trapping of the [^{11}C]methanol. The yields of the [^{11}C]C_3 among the [^{11}C]hydrocarbons undesired products notably increased at 563 K. [^{11}C]CO and small amounts of [^{11}C]CH_4 and [^{11}C]HCHO were also detected as by products.

During the conversion of [^{11}C]methanol over H-ZSM-5 and H-Beta zeolite catalysts, predominantly [^{11}C]C_3, but also [^{11}C]C_4 hydrocarbons were detected up to 573 °K (figure 10 for H-ZSM-5 catalyst). Further

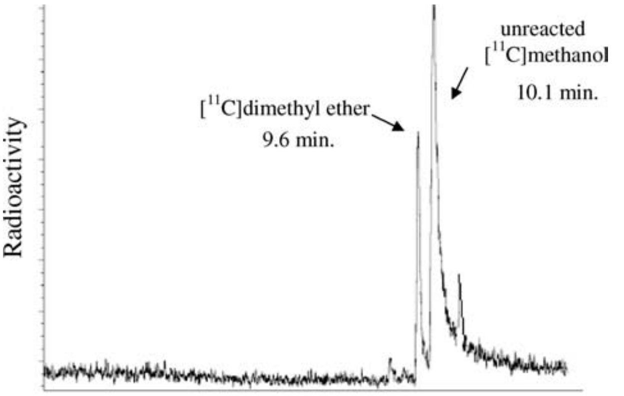

Figure 8. GC radiochromatogram of the conversion of [^{11}C]methanol to [^{11}C]dimethyl ether over alumina at 523 K.

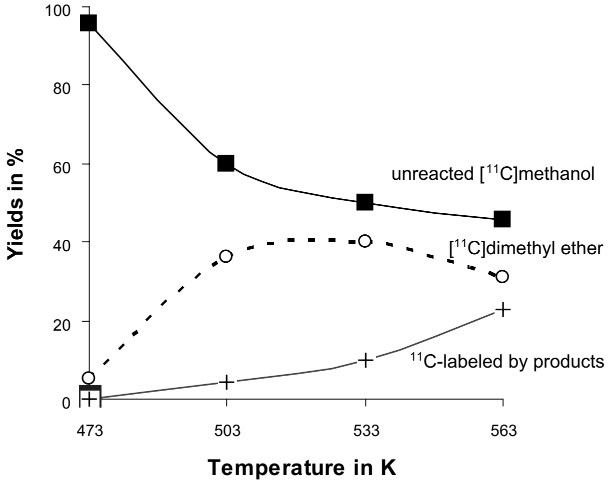

Figure 9. Yields of [^{11}C]dimethyl ether and ^{11}C-labeled by products after the conversion of [^{11}C]methanol over alumina as a function of temperature.

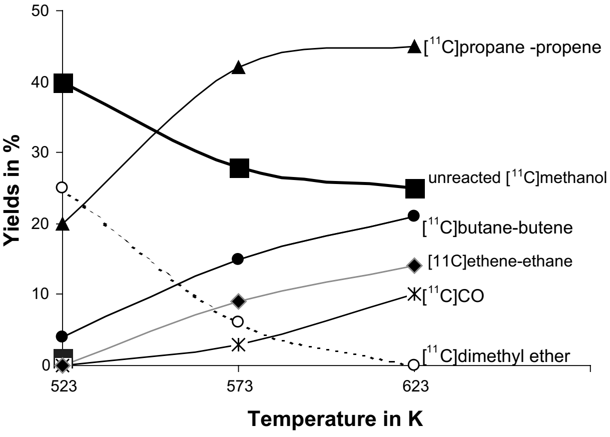

Figure 10. Yields of ^{11}C-labeled products after conversion of [^{11}C]-methanol over H-ZSM-5 zeolite as a function of temperature.

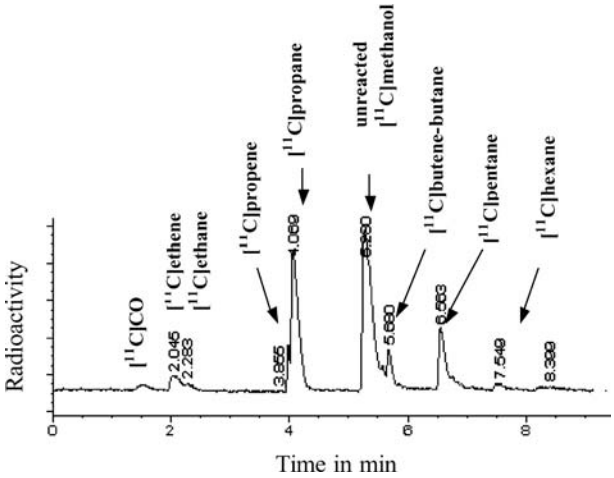

Figure 11. GC radiochromatogram of [^{11}C]hydrocarbons and unreacted [^{11}C]methanol over H-ZSM-5 zeolite catalyst at 653 K.

increasing the temperature of the catalyst to 653 K resulted in [^{11}C]C_3 as the main product, in addition [^{11}C]C_4 and [^{11}C]C_5 also increased, causing the [^{11}C]dimethyl ether to disappear (figure 11). The yields of ^{11}C-labeled products in the figure 11 were calculated from the chromatogram by decay correction. At the temperature of 653 K [^{11}C]C_6 hydrocarbons and some other ^{11}C-labeled compounds were detected together with [^{11}C]CO as a side product. The [^{11}C]C_2H_4 and [^{11}C]C_2H_6 hydrocarbons were also detected.

The results for the H-Beta catalyst fundamentally were similar to the results of H-ZSM-5 zeolite. For the definite identification of the more dominant [^{11}C]iso-butane product on H-Beta zeolite, a phosphorous pentaoxide trap was applied to remove the unreacted [^{11}C]methanol after the reaction. In such a way the [^{11}C]iso-butane, the retention time of, which is very close to the [^{11}C]methanol, could be detected by the same chromatographic column (figure 12). By increasing the reaction time from 3–5 min to 15–20 min or applying high temperature (673 K), the amount of [^{11}C]CO could be considerably increased and [^{11}C]CO_2 has definitely appeared on both of H-ZSM-5 and H-beta zeolites, for the latter case see figure 12.

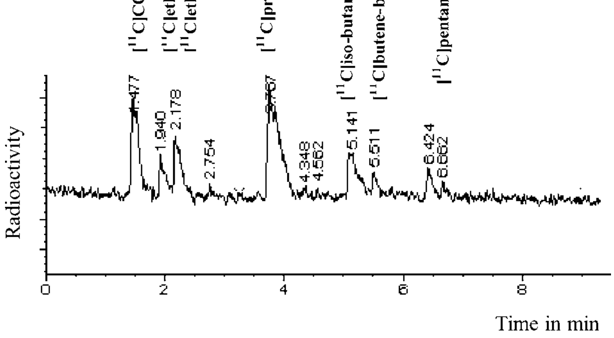

Figure 12. GC radiochromatogram of [^{11}C]hydrocarbons after removing the unreacted [^{11}C]methanol over H-Beta zeolite catalyst at 673 K.

4. Conclusions

A novel radiochemical method for the monitoring of catalytic transformation of [^{11}C]methanol to [^{11}C]dimethyl ether and [^{11}C]hydrocarbons over alumina, H-Beta and H-ZSM-5 zeolite catalysts using radio detectors (gamma detector) have been developed. Lewis acid-base pair (weak sites) on alumina is responsible for dehydration, therefore the products obtained from the catalytic transformation of ^{11}C-labeled methanol were dominantly ^{11}C-labeled dimethyl ether. Brønsted acid sites are required for the transformation of alcohol to hydrocarbons. The presence of both Brønsted and Lewis acid sites in H-ZSM-5 and H-Beta catalysts could be the reason, ^{11}C-labeled light hydrocarbons such as ^{11}C-labeled alkanes and olefins were formed.

The yield of [^{11}C]C_3 hydrocarbon products enhanced with increase in temperature over H-ZSM-5 and H-Beta catalysts in the range of 523–673 K. The novel method offers a simple way to follow the conversion of ^{11}C-labeled methanol and to analyse the ^{11}C-labeled products by radio detectors, there by eliminating the addition effect of environmental natural carbon sources at TCD detection. In the future, on the basis of the performed experiments, the zeolite catalyst could be suitable for the conversion of ^{11}C-labeled methanol to ^{11}C-labeled hydrocarbons and for ^{11}C-methylation of aromatics in the radio pharmaceutical chemistry (for investigation by positron emission tomography).

Acknowledgments

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References

[1] C. Naccache and Y.B. Tarrit, in: *Zeolite Science and Technology*, eds. F.R. Ribeiro, A.E. Rodrigues, L.D. Rollmann and C. Naccache (The Hague, 1984) p. 373.
[2] T. Inui, G. Takeuchi and Y. Takegnami, Appl. Catal. 4 (1982) 201.
[3] E.G. Derouane, J.P. Gilson and Z. Gabelica, Appl. Catal. 1 (1981) 201.
[4] N. Kumar, L.-E. Lindfors and R. Byggningsbacka, Appl. Catal. A: Gen. 139 (1996) 189.
[5] R. Byggningsbacka, N. Kumar and L.-E. Lindfors, J. Catal. 178 (1998) 611.
[6] A. Corma, J. Catal. 216 (2003) 298.

[7] C.D. Chang and A.J. Silvestri, J. Catal. 47 (1977) 249.
[8] J.R. Anderson, K. Foger, T. Mole, R.A. Rajadhyaksha and J.V. Sanders, J. Catal. 58 (1979) 114.
[9] G.T. Kokotailo, S.L. Lawton, D.H. Olson and W.M. Meier, Nature 272 (1978) 437.
[10] N. Kumar, M. Vainio, V. Nieminen, R. Byggningsbacka, L.-E. Lindfors, T. Salmi, D.Y. Murzin and E. Laine, Stud. Surf. Sci. Catal. 135 (2001) CD-ROM 24-P-16.
[11] M. Xu, J.H. Lunsford, D.W. Goodman and A. Bhattacharyya, Appl. Catal. A: Gen. 149 (1997) 289.
[12] M. Stöcker, Micropor. Mesopor. Mater. 29 (1999) 3.
[13] Ø. Mikkelsen and S. Kolboe, Micropor. Mesopor. Mater. 29 (1999) 173.
[14] J.G. Lo, Appl. Radiat. Isot. 38 (1987) 689.
[15] Ø. Mikkelsen, P.O. Rønning and S. Kolboe, Micropor. Mesopor. Mater. 40 (2000) 95.
[16] B.G. Anderson, N.J. Noordhoek, D. Schuring, F.J.M.M. de Gauw, A.M. de Jong, M.J.A. de Voigt and R.A. van Santen, Catal. Lett. 56 (1998) 137.
[17] T.A.J. Hardenberg, L. Martens, P. Mesman, H.C. Muller and C.P. Nicolaides, Zeolites 12 (1992) 685.
[18] R.L. Wadlinger, G.T. Kerr and E.J. Rosinski, U.S. Patent: 3308069 (1975).
[19] N. Kumar, V. Nieminen, K. Demirkan, T. Salmi and D.Y. Murzin, Appl. Catal. A: Gen. 235 (2002) 113.
[20] E. Sarkadi, Radiochim. Acta. 76 (1997) 197.