Supporting Information

Hydrolytic Dehydrogenation of Ammonia Borane in Neat Water Using Recyclable Zeolite-Supported Cyclic Alkyl Amino Carbene (CAAC)-Ru Catalysts

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Content

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1. Preparation of impregnated catalyst 3

In a 100 mL round bottomed flask, 150 mg of ruthenium catalyst (**1**) was dissolved in 30 mL of methanol, and 5000 mg of mesoporous (CBV720) Y-zeolite was added. The mixture was stirred for 16 hours at room temperature. After completion, the suspension was transferred into centrifuge tubes, and centrifuged for 15 min at 4000 rpm. The separated zeolite was washed with 100 mL of methanol, and dried in high vacuum (cca. 0.2 mbar) for 24 hours. The dried zeolite was then placed into storage vial and was stored under nitrogen.

2. Preparation of impregnated catalyst 4

In a 100 mL round bottomed flask, 150 mg of ruthenium catalyst (**2**) was dissolved in 30 mL of methanol, and 5000 mg of mesoporous (CBV720) Y-zeolite was added. The mixture was stirred for 16 hours at room temperature. After completion, the suspension was transferred into centrifuge tubes, and centrifuged for 15 min at 4000 rpm. The separated zeolite was washed with 100 mL of methanol, and dried in high vacuum (cca. 0.2 mbar) for 24 hours. The dried zeolite was then placed into storage vial and was stored under nitrogen.

3. Dehydrogenation reaction of amino – borane (AB) using catalyst 3 or 4.

Reactions with 0.3 mol dm^{-3} **AB** solution

500 ppm reaction

1.6 mL of 0.3 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 25 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 4 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

100 ppm reaction

1.6 mL of 0.3 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 5 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 12 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

50 ppm reaction

3.2 mL of 0.3 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 5 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 24 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

10 ppm reaction

16 mL of 0.3 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 5 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 36 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

Reactions with 0.096 mol dm^{-3} **AB** solution

1000 ppm reaction

5 mL of 0.096 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 50 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 2 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

500 ppm reaction

5 mL of 0.096 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 25 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 4 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

100 ppm reaction

5 mL of 0.096 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 5 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 12 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

50 ppm reaction

10 mL of 0.096 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 5 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 24 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

20 ppm reaction

25 mL of 0.096 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 5 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 36 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

10 ppm reaction

50 mL of 0.096 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 5 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 36 hours. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask.

4. Catalyst recycling with 2000 ppm of catalyst 3 or 4

1.6 mL of 0.3 mol dm^{-3} **AB** solution in water was measured into a 3 mL screw cap septum vial equipped with a stirring bar. Into this solution, 100 mg of catalyst (**3** or **4**) was added, and the vial was sealed with a septum transfixed with a needle.This vial was placed in a 100 mL Schlenk flask, connected to a water-filled gas burette. The suspension was stirred until the produced hydrogen reached 3 equivalents, related to the amount of **AB**. After the reaction terminated, the vial was put into a centrifuge, in which the aqueous solution was separated from the zeolite. The supernatant was collected and measured for Ru with ICP-OES. Then a fresh portion of 1.6 mL of 0.3 mol dm^{-3} **AB** solution in water was added, and the vial was placed back to the Schlenk tube, connected to the gas burette. This procedure was repeated until the catalyst became inactive.

5. Catalyst recycling with 5000 ppm of catalyst 4

1.6 mL of 0.3 mol dm^{-3} **AB** solution in water was measured into a 5 mL vial with a septum, and together with a stirring bar. In this solution, 250 mg of **4** was suspended, and the vial was closed with a septum, with a needle, which allows the hydrogen gas to escape, and the whole vial with the needle was put into a 100 mL Schlenk flak, connected with a gas burette. The mixture was stirred until the produced hydrogen reached 3 equivalents. During this time, the generated hydrogen gas was collected in the gas burette, connected with the Schlenk – flask. After the reaction terminated, the vial was put into a centrifuge, where the water solution was separated from the zeolite. The supernatant was collected and measured for Ru with ICP-OES. Then, a fresh portion of 1.6 mL of 0.3 mol dm^{-3} **AB** solution in water was measured, and the vial was put back to the Schlenk tube, connected with the gas burette. The above procedure was repeated until the catalyst became inactive.

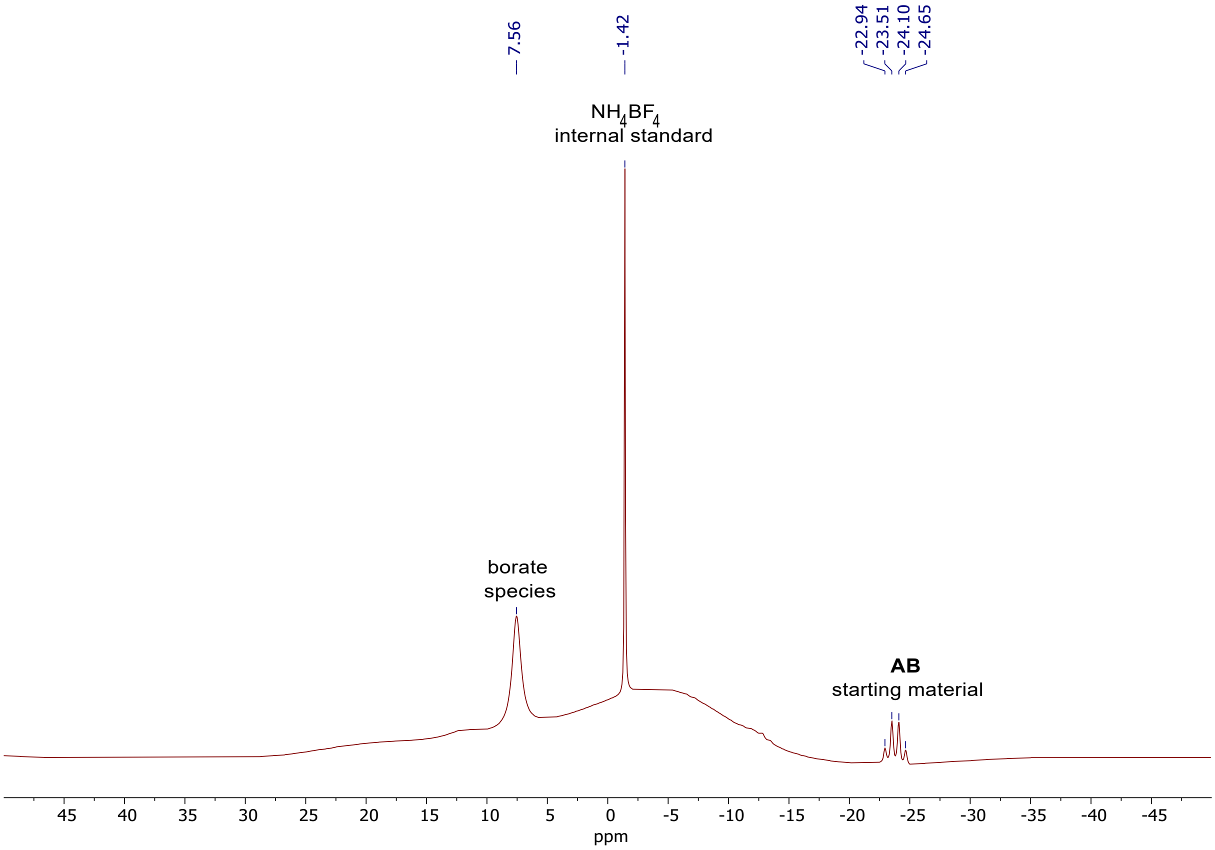

Figure S1. Representative example of the ^{11}B-NMR specrta of the **AB** hydrolysis

6. Determination of the amount of ruthenium in supported zeolite samples

For each analysis, a 50 mg sample of the zeolite was measured in a teflon tube, and 6 mL of cc. HNO_3, 2 mL of cc. HCl, and 1 mL of cc. HF was added to the zeolite. The teflon tube was then closed and placed into a microwave oven and kept at 200 °C for 60 min under pressure. After this treatment, 10 mL of concentrated boric acid was added to each sample, and placed back to the microwawe oven, and again kept at 200 °C for another 60 min.

After the programme terminated, each sample was diluted with 50 mL of distilled water, and sent for analysis. Elemental composition of these samples has been determined by Spectro Genesis axial plasma observation inductively coupled plasma optical emission spectroscopy, including the ability for simultaneous and multi element determination. The same proceeding was used in the case of the used catalyst analysis.

7. Leaching test with ICP-OES technique

Leaching tests were carried out once every catalyst loading test, with different catalyst loadings, meaning one for the 10, 50, 100, 500 ppm tests. In the case of 100 and 500 ppm tests, the exhausted catalyst was filtrated and the filtrate was diluted to a volume of 5 mL with distilled water. In the case of 10, 20 and 50 ppm tests, after filtration, the liquid phase was concentrated to a 5 mL sample. These samples were sent to ICP-OES analysis. All of them showed Ru content below detection limit (1 ppb).

8. Leaching test with catalyst filtration technique

1.6 mL of 0.3 mol dm^{-3} **AB** solution in water was measured into a 10 mL Schlenk tube equipped with a stirring bar. Into this solution, 5 mg of catalyst (**3** or **4**) was added, and the suspension was stirred for 1 hour. During this time, the generated hydrogen gas was collected in a water-filled gas burette, connected to the Schlenk flask. The reaction mixture was then filtrated with a 0.45 μm filter. After filtration, the hydrogen evolution was completely stoped.

9. BET surface determination

Nitrogen physisorption measurements were carried out using Thermo Scientific Surfer automatic, volumetric adsorption analyser. All measurements were carried out at a temperature of -196 °C. Before adsorption measurements, each sample were outgassed at 250 °C for 2 h.

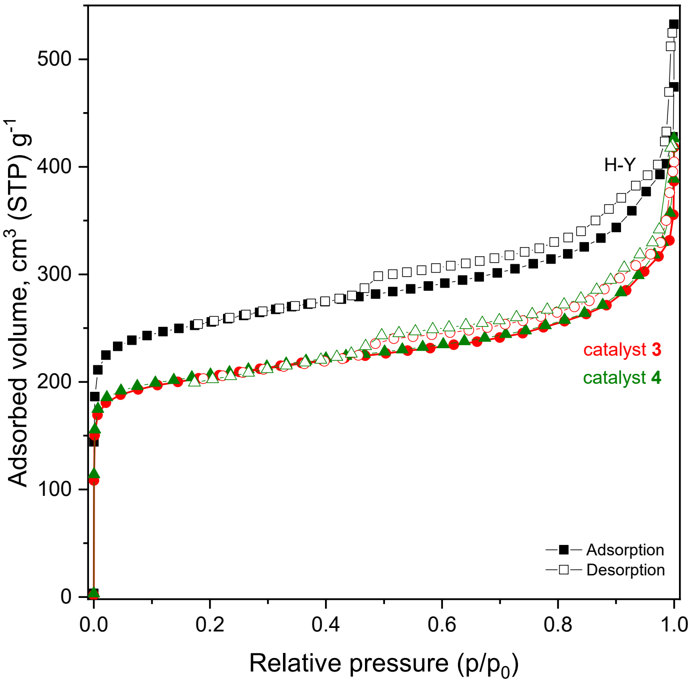

Figure S2. Nitrogen adsorption and desorption isotherms of (■) parent H-Y zeolite, (●) fresh catalyst **3**, and (▲) fresh catalyst **4**, determined at -196 °C.

10. Temperature programmed ammonia evolution

The NH_4-exchanged Y zeolite sample was characterized by temperature-programmed ammonia evolution (TPAE) measurement. About 300 mg of sample were heated from 150 to 600 °C at a rate of 10 °C/min in a 20-mL/min flow of dry nitrogen. From the effluent NH_3 was absorbed in distilled water. The pH of the absorbing solution was kept between pH 5.5 and 6.0 by automatically titrating the absorbed ammonia with 0.1 M HCl solution. The ammonia, evolved from the sample between 180 and 650 °C during TPAE run, was taken as equivalent with the ion exchange capacity of the sample.

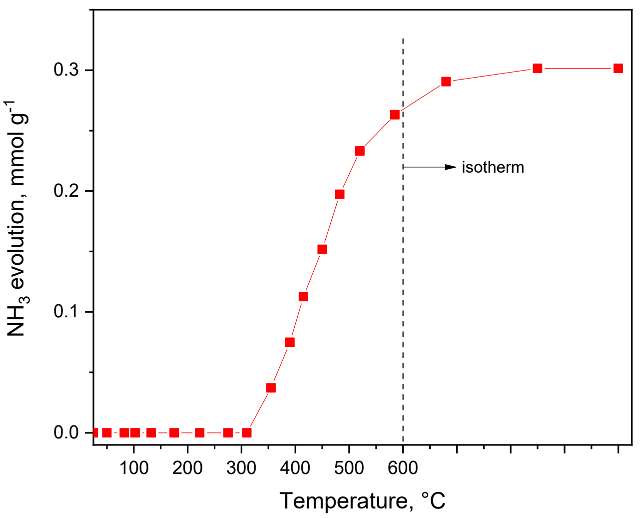

Figure S3. Temperature-programmed ammonia evolution (TPAE) curve for NH$_4$-Y.

11. Infrared analysis of zeolites

In order to determine the concentration of Brønsted (B) and Lewis (L) acid sites of the parent H-Y zeolite, FTIR spectra of self-supporting wafer were taken in transmission mode by a Nicolet 6700 FTIR spectrometer (Thermo Fisher). Prior to pyridine (Py) adsorption the sample was pretreated at 450 °C for 1 h under dynamic vacuum (10^{-6} mbar) then the temperature was lowered to 200 °C and the sample was contacted with 5 mbar vapor of pyridine for 30 min. After cooling the sample to 100 °C, the pyridine vapor was removed from the cell by 30 min successive evacuation at temperatures 100, 200, 300, 400, and 450 °C. A spectrum was recorded at room temperature after each evacuation. The integrated molar absorption coefficients for the absorption of Py-B and Py-L complexes at 1545 cm^{-1} and 1455 cm^{-1} (1.26 and 1.87 µmol^{-1} cm, respectively) were taken from [V. Zholobenko, J.Catal. 385 (2020) 52-60.].

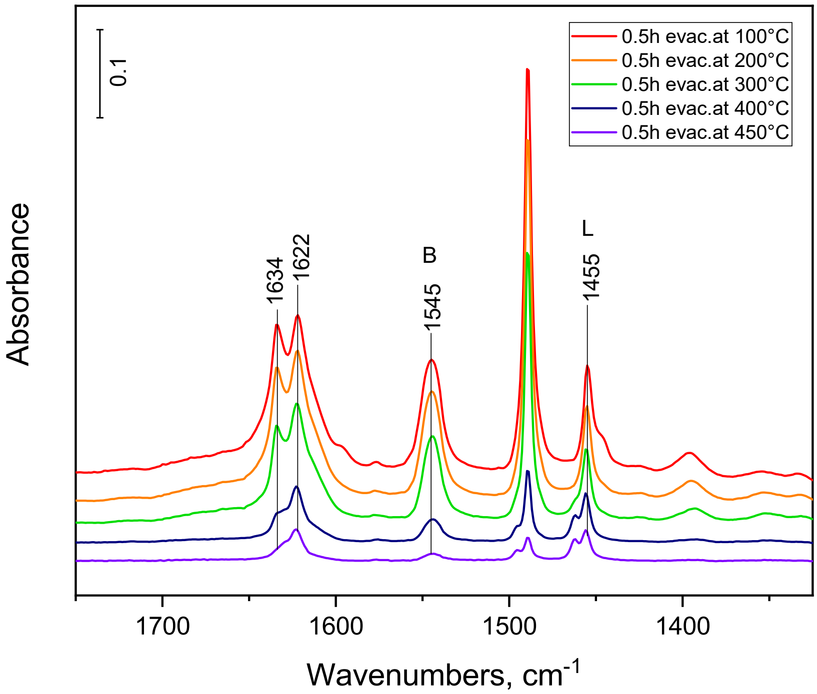

Figure S4. FT-IR spectra of surface species formed from adsorption of pyridine on the parent mesoporous H-Y. The sample was pretreated in situ in the IR cell at 450 °C under high vacuum for 1 h then were contacted with 5 mbar of Py vapor at 200 °C for 30 min. Spectra were taken at room temperature after evacuation at 100, 200, 300, 400 and 450 °C for 30 min. B and L represents Brønsted and Lewis sites, respectively.

Table S1 Concentration of Brønsted and Lewis acid sites determined by pyridine adsorption

T of evacuation after pyridine adsorption	Brønsted acid site µmol/g	Lewis acid site µmol/g	Br.acid, %	Lewis acid, %
	1544 cm^{-1}	1455 cm^{-1}	1544 cm^{-1}	1455 cm^{-1}
100°C	290	97	100	100
200 °C	262	71	90	73
300 °C	194	53	67	54
400 °C	51	38	17	39
450 °C	14	23	5	24

DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectra of several samples were collected by a Nicolet iS10 FT-IR spectrometer, with a resolution of 2 cm^{-1}, collecting 512 scans,using COLLECTOR II diffuse reflectance mirror system and a flowthrough DRIFT spectroscopic reactor cell (Spectra-Tech). About 20 mg sample powder was placed in a porous ceramic sample holder, then dried helium flow (30 cm^{3} min^{-1}) was led through the sample and was kept at 70 °C for 90 min. Spectra were taken *in situ* at 70 °C.

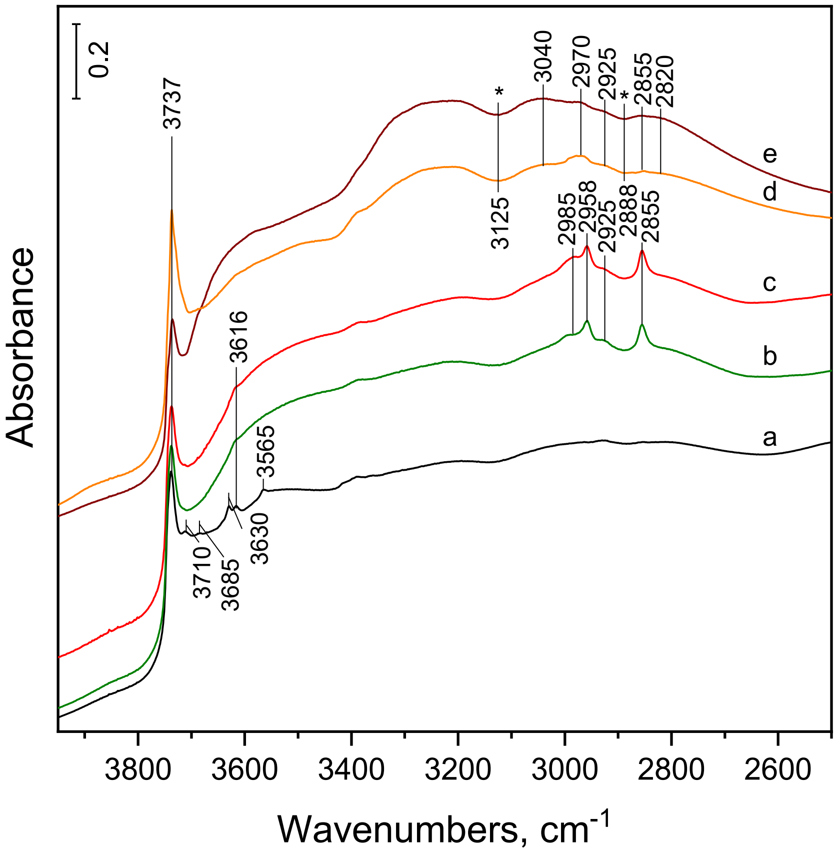

Figure S5. DRIFT spectra of (a) parent H-Y, (b) methanol-treated HY, (c) fresh catalyst **3**, (d) used but still active catalyst **3**, and (e) catalyst **3** fully deactivated in catalytic reaction. All spectra were taken in dry helium flow at 70 °C.

Figure S5 shows the DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectra of five zeolytic samples. Compared to the spectrum of the parent H-Y (spectrum a), new bands are discernible in the spectrum of catalyst **3** (spectrum c) in the ν(CH) region, between 3100 and 2800 cm^{-1}, and most of the bands in the ν(OH) region, between 3750 and 3500 cm^{-1}, disappeared. These spectral changes are not assignable to the presence of complex **1** on the zeolite, but to the formation of methoxy groups on H-Y when treated with methanol at room temperature. Spectrum b belongs to a sample that was obtained by treating the parent H-Y zeolite with methanol under the same conditions like by the preparation of catalyst **3**, except the addition of complex **1** to the methanol. Between spectrum b and c, hardly any differences can be observed. It infers that due to the low concentration, neither the bands of complex **1** nor the bands of its cation were detectable in the spectrum of the zeolite supported complex, i.e. catalyst **3**. The most intense bands at 2958 and 2855 cm^{-1} belong to the asymmetric and symmetric ν(CH) vibrations of methoxy groups bound to external silanol groups, while 2985 cm^{-1} can be assigned to ν_{as}(CH) vibration of Brønsted acid bound methoxy groups[1]. The disappearance or intensity decrease of the different ν(OH) bands after methanol treatment (c.f. spectrum a and b) shows that all types of hydroxyl groups of the parent Y zeolite were involved in the interaction with methanol, namely, the silanol groups on the external zeolite surface (band at 3737 cm^{-1}), the silanol groups inside the zeolite crystals (band at 3710 cm^{-1}), framework Si-OH groups at defect sites (band at 3685 cm^{-1}), acidic Brønsted sites pointing inside the supercage (band at 3630 cm^{-1}), extra-framework Al-OH group located in the zeolitic sodalite cages (band at 3616 cm^{-1}) and Brønsted acid sites oriented inwards the β-cage (sodalite cage, band at 3565 cm^{-1}). These methoxy species are readily exchanged to NH_4^+ cations during catalytic application. Spectrum d belongs to catalyst **3**, used only for 1 hour at 100 ppm **Ru-CAAC**/**AB** ratio, i.e. used but still active, while spectrum e belongs to catalyst **3** used until full deactivation. In both spectra (Fig. S5 d and e) three broad N-H stretching vibration bands of H-bonded NH groups appear at about 3250, 3040, and 2820 cm^{-1}, with Evans windows at 3125 and 2888 cm^{-1}. All these features are characteristic for ammonium zeolites.[2] The asymmetric band at 1470 cm^{-1} is attributed to the ν_4 component bands of ammonium ions.[3] It confirms that during catalytic run, NH_4^+ ions occupy most of the cation positions of the zeolite. Bands with low intensity at 2970 and 2855 cm^{-1} show that methoxy groups are present only in a low concentration.

12. ESI – TOF MS analysis of the impregnated complexes

Electrospray Time-of-Flight measurements ESI(+)-TOF measurements

ESI-TOF MS measurements were performed using a Bruker MicroTOF Q instrument (Bruker Daltonik, Bremen, Germany) equipped with an ESI source operated in the positive ion mode. The spay voltage was 3.5 kV, nitrogen was used as nebulizer and drying gas (180 °C, 4 L/min). The mass spectra were recorded by means of a digitalizer at a sampling rate of 2 GHz. The calibration was carried out with the exact masses of sodium trifluoroacetate (NaTFA) clusters. The mass spectra were evaluated with the DataAnalysis 3.4 software from Bruker.

Sample preparation for ESI-TOF MS

101.9 mg of zeolite (**3**) was added to 1 mL MeOH and placed in an ultrasound bath, where it was stirred for 1 hour, and centrifuged at 2500 rpm for 5 minutes.

Filtered sample from the generated supernatant was injected into the ESI-TOF MS and the MS spectrum was recorded (Fig. S6.).

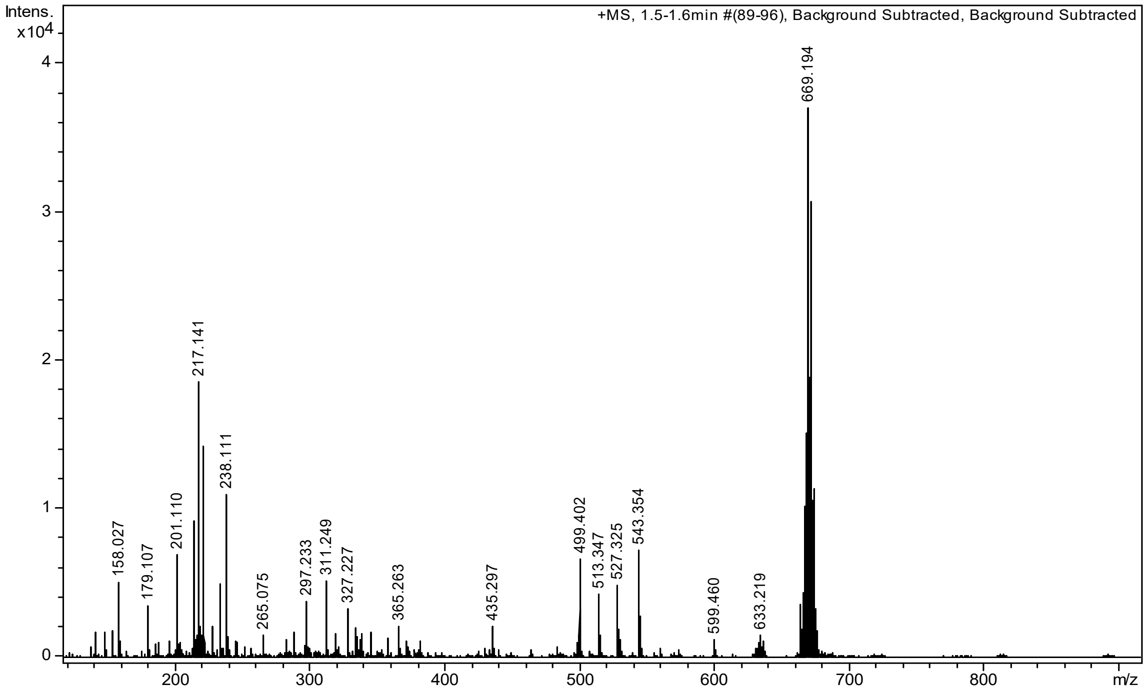

Figure S6. ESI-TOF MS spectrum of the supernatant generated from **3**.

Several m/z values that are characteristic of the complex appear in the ESI-TOF MS spectra. The most intensive peak occurs at m/z 669 ($C_{34}H_{45}ON_2Cl_2Ru^+$) with an isotopic distribution that is characteristic of the complex containing ruthenium (**1**). The measured and the calculated masses for the most intensive isotope peak of $C_{34}H_{45}ON_2Cl_2Ru^+$ are 669.194 and 669.195, respectively. The measured isotopic distribution of this peak match exactly the calculated one as it can be seen in Fig. S7.

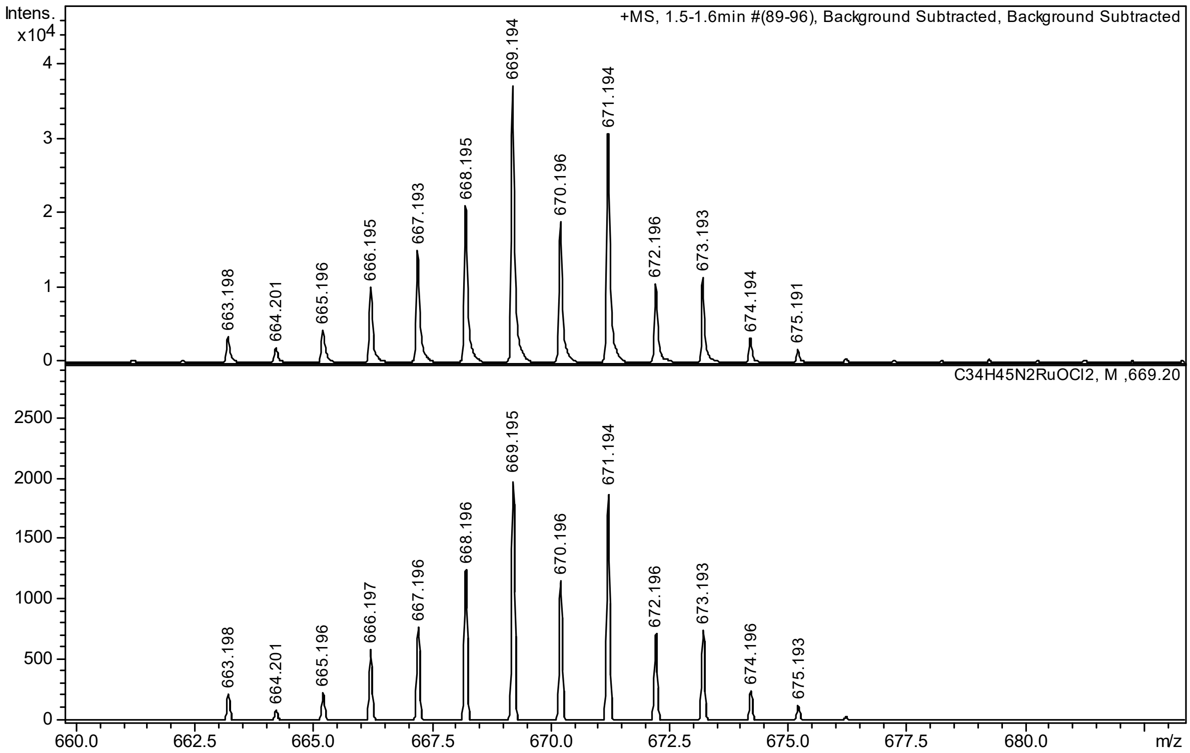

Figure S7. The measured (top) and the calculated isotopic (bottom) distribution for the peak at m/z 669.

Based on the isotopic distribution and the composition it can be concluded that the intact complex was detached from surface of the zeolite.

The same sample preparation was applied for catalyst **4**, however, neither the intact complex nor its fragments could be detected. Prolonging the ultrasonic tereatment did not yield characteristic fragment ions either. To facilate the detachment of the complex from the catalyst surface, **4** was suspended in hydrochloric acid of 0.5 mol/L and prolonged ultrasonic treatment was also applied (1 hours). After centrifugation at 2500 rpm for 5 minutes, 50 µL of supernatant was dried under vacuum and dissolved in 50 µL water: methanol mixture (1:1 V/V),. then this solution was injected into the ESI-TOF MS (Fig. S8.).

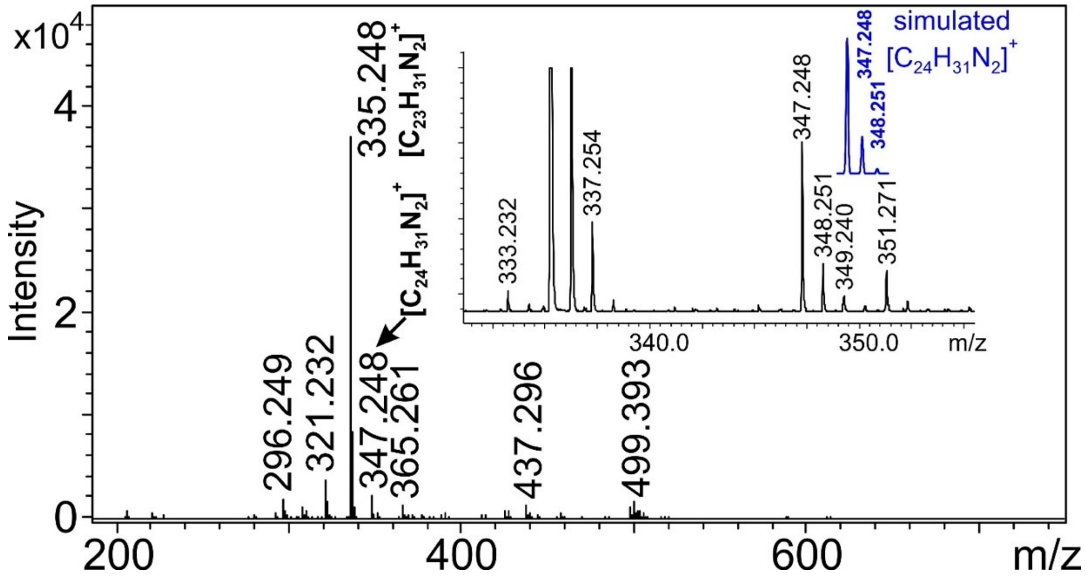

Figure S8. ESI-TOF MS spectrum of the supernatant generated from catalyst **4**.

As seen in Fig. S8. no intact complex can be detected, however, fragment ions, originated from the ligand, with compositions of $C_{23}H_{31}N_2$ and $C_{24}H_{31}N_2$ appeared at m/z 335 (the measured accurate mass/calculated mass: 335.248/335.248) and m/z 347 (the measured accurate mass/calculated mass: 347.248/ 347.248), respectively.

13. MALDI – TOF MS analysis of the impregnated complexes

Matrix-Assisted Laser Desorption/Ionization, Laser Desorption/Ionization Time of Flight (MALDI, LDI-TOF) measurements

The MALDI/LDI-TOF measurements were carried out with a Bruker Autoflex Speed mass spectrometer (Bruker Daltonik, Bremen, Germany). Reflectron mode was applied, where the ion source1, ion source 2, reflector 1 and reflectron 2 voltages were 19 kV, 16.65 kV, 21 kV and 9.55 kV, respectively. The instrument was equipped by a solid phase laser (355 nm), which was operated at 200 Hz and 5000 shots were summed. The spectra were calibrated externally with polyethylene glycol. The mass spectra were evaluated with the FlexAnalysis 3.4 software.

Sample preaparation

For MALDI-TOF MS measurements, 1.4 mg of impregnated zeolite sample (**3** and **4**) was suspended in 14 µl of DHB solution (2,5-dihydroxybenzoic acid, 20 mg/mL, methanol) matrix. For the LDI-TOF MS measurements, the samples were prepared in the same way as it was done for the MALDI-TOF MS but in the absence of matrix.

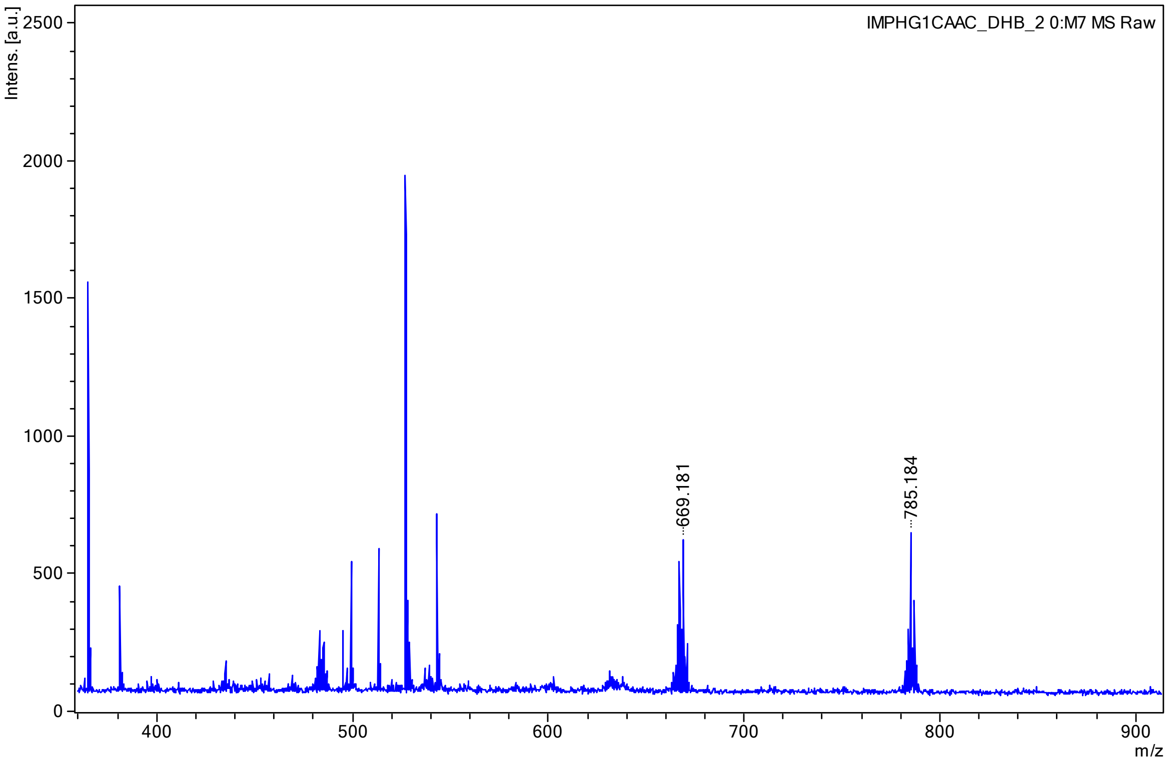

Figure S9. MALDI – TOF MS spectrum of the sample made with catalyst **3**.

As seen in Fig. S9., similarly to the results of ESI-TOF MS, the intact complex containing ruthenium can be detected at m/z 669.

In the case of sample made with catalyst **4**, no presence of intact complex, similary to ESI-TOF MS, was observed. However, in the LDI-TOF MS spectrum of **4** (Fig. S10) only the characteristic fragment ion at m/z 335 appeared.

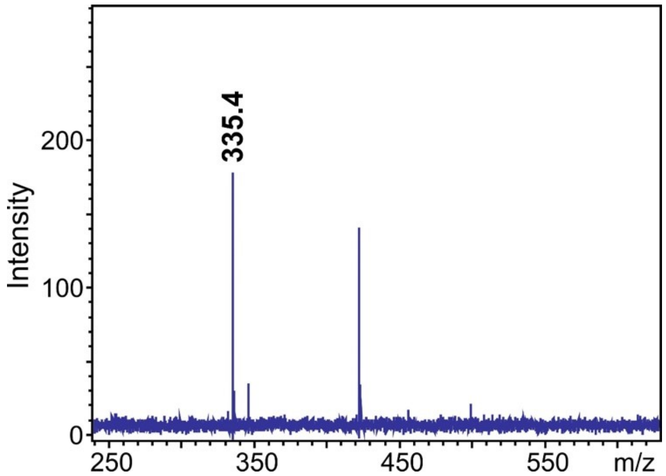

Figure S10. LDI – TOF MS spectrum of the sample made with catalyst **4**.

14. XRD Analysis

X-ray powder diffraction patterns of the impregnated zeolites, along with the y-zeolite itself were recorded by a Philips PW 1810/3710 diffractometer, equipped with a graphite monochromator. The CuKα radiation (λ = 0.1541 nm) was used. The X-ray tube was set at 40 kV and 35 mA current. The scan step size was 0.02 degrees 2-theta, whereas the scan time was five seconds in each step.

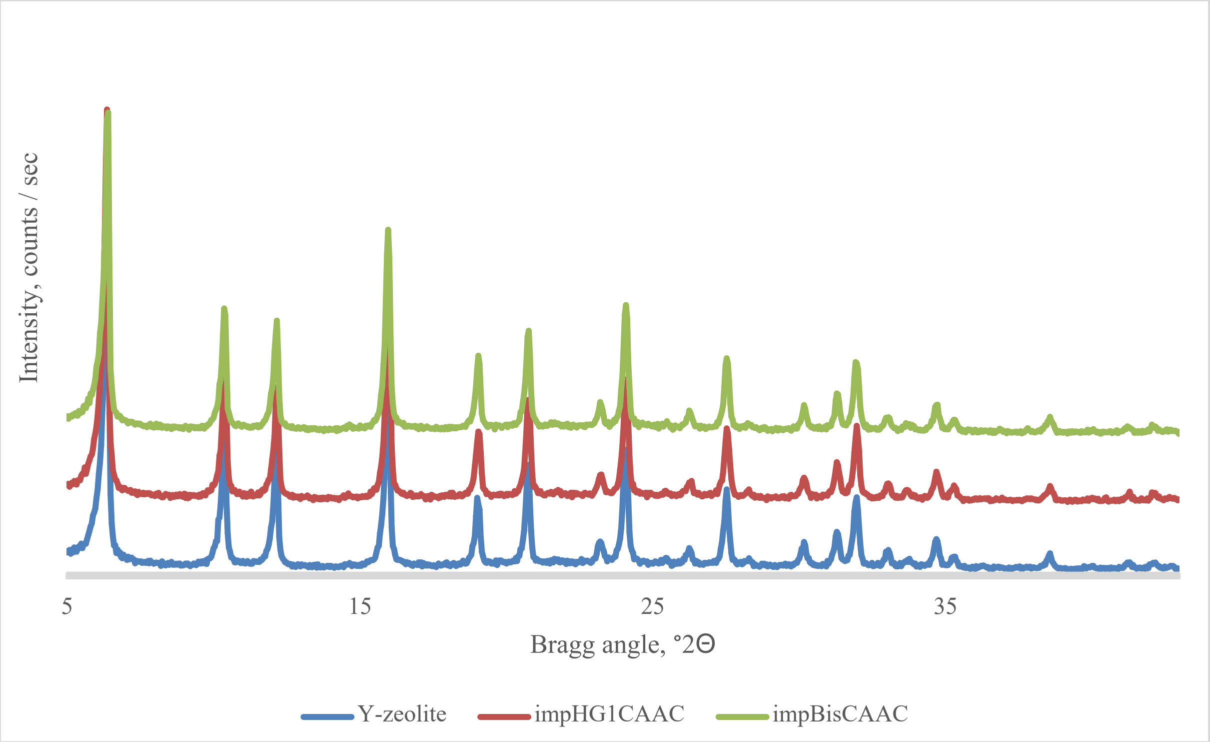

Figure S11. XRD patterns of catalyst **3**, **4** and zeolite Y.

The three samples showed no difference which means that the impregnation did not make any change to the structure of the zeolite.

15. X-ray Fluorescence (XRF)

XRF analyses of impregnated zeolites were performed with an Olympus Delta Premium XRF instrument (Olympus, Hamburg, Germany) equipped with Teflon sample holder and rhodium anode. The X-ray tube was at 40 kV.

Sample of 18 mg was placed in the PTFE sample holder and closed with PET foil. The measurement time was set to 10 min for each sample (Fig. S12. and Fig. S13.).

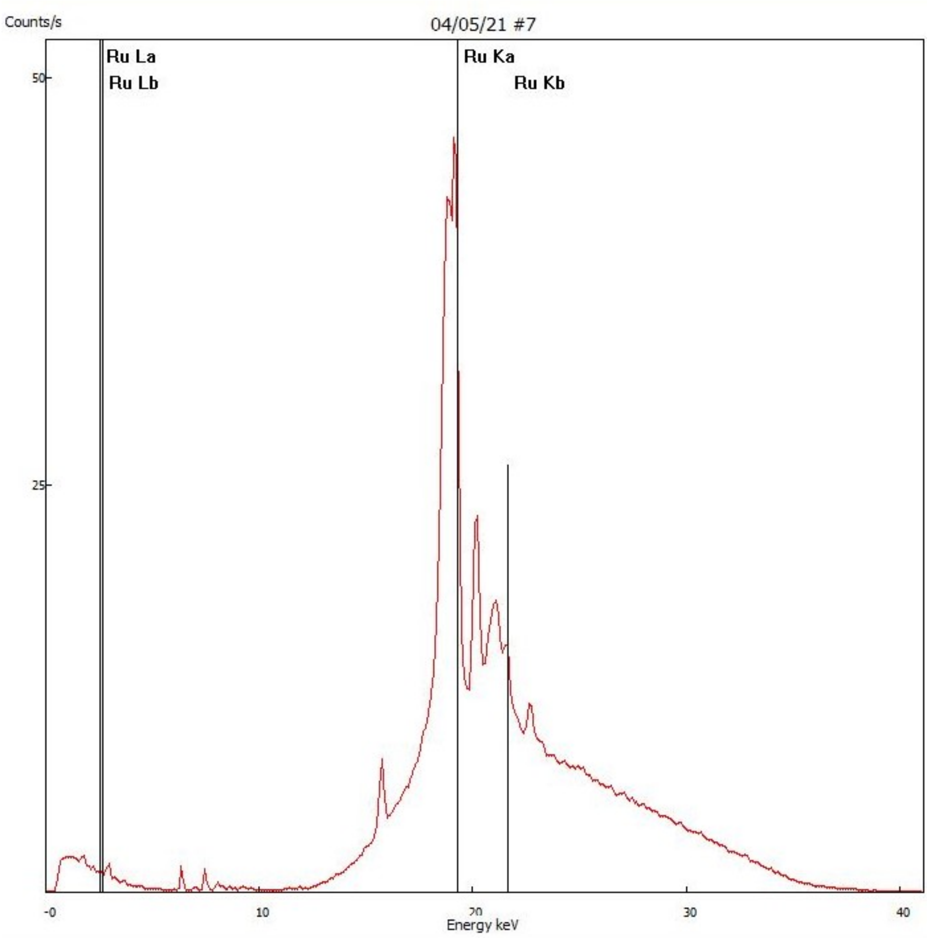

Figure S12. X-ray fluorescence spectrum of the zeolite impregnated with catalyst **3**.

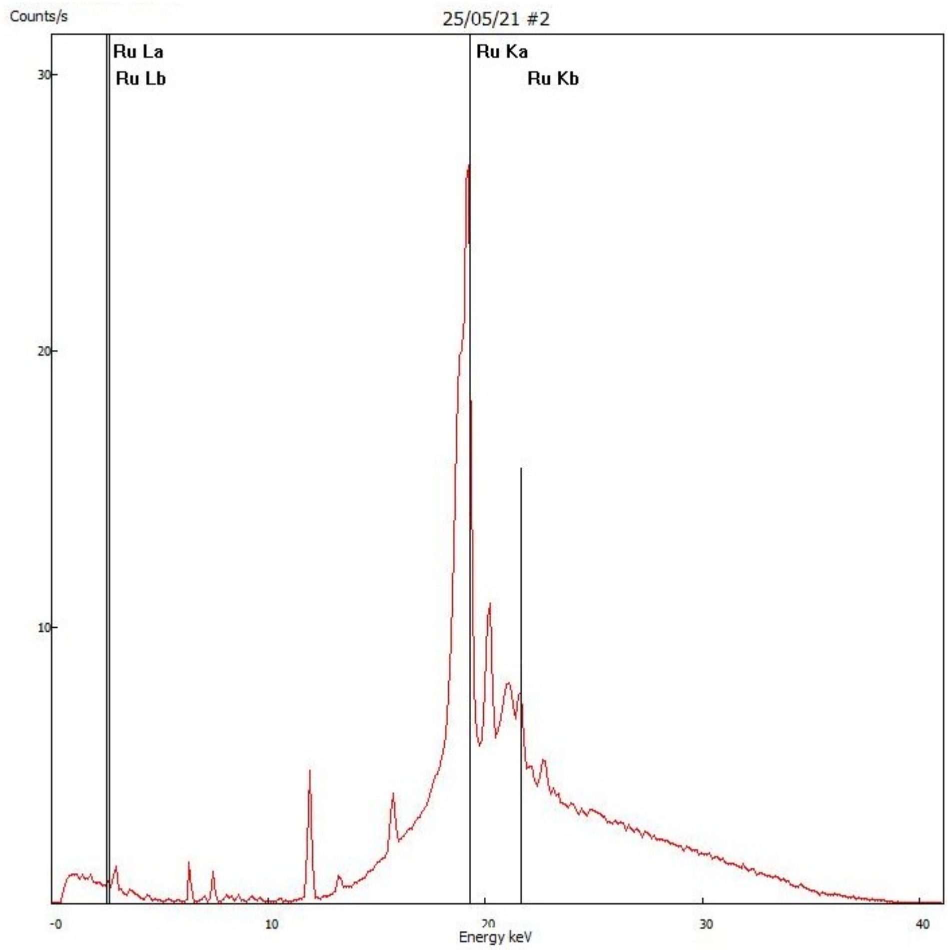

Figure S13. X-ray fluorescence spectrum of the zeolite impregnated with catalyst **4**.

As seen in Fig. S13. no intact complex can be detected. XRF peak of ruthenium can be observed, which confirms the successful impregnation of zeolite.

16. Refrences

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(3) Valyon, J.; Lo, F. A TPD and IR Study of the Surface Species Formed from Ammonia on Zeolite H-ZSM-5 , H-Mordenite and H-Beta. *Thermochim. Acta* **2001**, *373*, 53–57.