Supplementary Materials: Ketone Formation via Decarboxylation Reactions of Fatty Acids Using Solid Hydroxide/Oxide Catalysts

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1. Catalyst Characterisation

a) Thermogravimetric Analysis of Catalyst Materials

The co-hydrated organo-LDH samples (**CoH-LDH**) were analysed by thermogravimetric analysis (TGA). The thermal decomposition of the co-hydrated samples is shown in Figure S1. The samples all show similar TGA profiles, with loss of water up to ~100 °C and then decomposition of interlayer adipate anions up to ~ 400 °C.

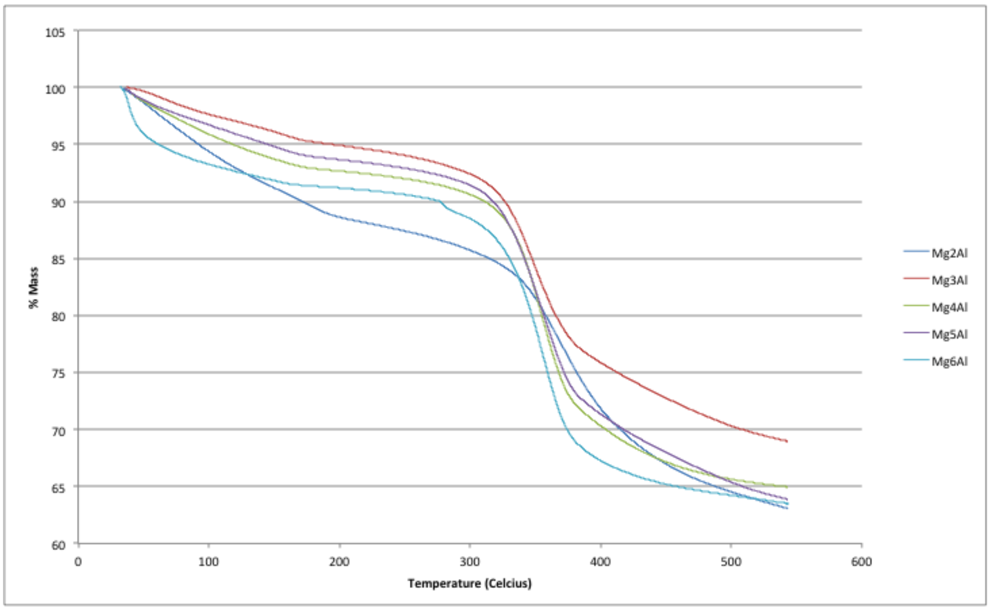


Figure S1. Thermogravimetric analyses of co-hydrated LDH (**CoH-LDH**) catalyst materials with different Mg/Al ratios.

2. Catalyst Material Synthesis Quantities

Table S1. Masses, moles and ratios of the reactants used for each R-value LDH co-precipitation preparation.

LDH	Mass per 100 ml solution / g			m Mol			Ratio	
	Mg $(NO_3)_2.6\ H_2O$	$Al(NO_3)_3.9H_2O$	$NaHCO_3$	Mg	Al	CO_3^{2-}	Mg:Al	CO_3^{2-}:Al
CoP-LDH-2	2.3120	1.6880	3.770	9.0	4.5	44.9	2	10
CoP-LDH-3	2.6884	1.3112	2.930	10.5	3.5	34.9	3	10
CoP-LDH-4	2.9290	1.0712	2.400	11.4	2.9	28.6	4	10
CoP-LDH-5	3.0944	0.9056	2.028	12.1	2.4	24.1	5	10
CoP-LDH-6	3.2152	0.7844	1.756	12.5	2.1	20.9	6	10

Table S2. Masses, moles and ratios of the reactants used for each R-value LDH co-hydration preparation.

LDH	Mass per 100 ml solution / g			m Mol			Ratio	
	MgO	Al_2O_3	Adipic acid	Mg	Al	Adipic acid	Mg/Al	COO^-:Al
CoH-LDH-2	1.4900	1.0100	1.737	37.0	19.8	11.9	2	1.2
CoH-LDH-3	1.7220	0.7775	1.337	42.7	15.3	9.2	3	1.2
CoH-LDH-4	1.8993	0.6006	1.033	47.1	11.8	7.1	4	1.2
CoH-LDH-5	1.9952	0.5047	0.868	49.5	9.9	5.9	5	1.2
CoH-LDH-6	2.0647	0.4353	0.749	51.2	8.5	5.1	6	1.2

3. Ketonic Decarboxylation Reaction Product Analysis

a) Analysis of Liquid Phase Products

Standards of *n*-heptadecane, eicosane, stearic acid (including the silylating agents pyridine and BSFTA {N,O-Bis(trifluoroacetamide)}) and the solvent dodecane were purchased from commercial sources (see below). Quantitative measurements were performed using the internal standard (eicosane) to produce calibration curves for the reactants stearic acid and the possible decarboxylation product *n*-heptadecane. Samples were prepared in vials using the following quantities and made up to 5 ml with dodecane:

Solution S: 0.1 M Silylated Stearic acid in dodecane
0.1422 g Stearic acid
0.264 ml BSFTA (Acros Organics, 98+%) (100% wt excess)
0.0436ml pyridine (Acros Organics) (30% wt)
Made up to 5 ml with dodecane (Aldrich, 98+%).
The silylation reaction was left for a period of 12 hours.

Solution H: 0.1 M *n*-heptadecane in dodecane
0.155ml n-heptadecane (Acros, 99%)
Made up to 5 ml with dodecane.

Solution E: 0.1 M eicosane ($C_{20}H_{42}$) in dodecane
0.141 g eicosane (Acros, 99%)
Made up to 5 ml with dodecane.

Each of the individual reference solutions described above were made up into calibration standard mixtures as shown in Table S3, below.

Table S3. Reference samples prepared for calibration of stearic acid, and *n*-heptadecane**.**

Reference Name	Silylated Stearic Acid / µl	Heptadecane / µl	Eicosane / µl
9S1H5E	900	100	500
7S3H5E	700	300	500
5S5H5E	500	500	500
3S7H5E	300	700	500
1S9S5E	100	900	500
10S0H5E	1000	0	500
0S10H5E	0	1000	500

Each of the above calibration samples was analysed with a HP 5890 Series II gas chromatograph (GC), equipped with a non-polar column (VF-5MS, with dimensions 30 m x 0.25 mm x 0.25 µl) and a flame ionisation (FI) detector. Each sample was injected (5 µl) into the GC with helium as the carrier gas at pressure of 2.07 bar. The injector and detector temperatures were 250 and 275 °C, respectively. The GC was kept at 200 °C throughout the whole run. Data analyses and peak integrations were performed by using Clarity software [82].

GC analysis of each of the samples containing silylated stearic acid was undertaken 3 times; averages were obtained for peak integrations. A typical chromatogram is shown in Figure S2.

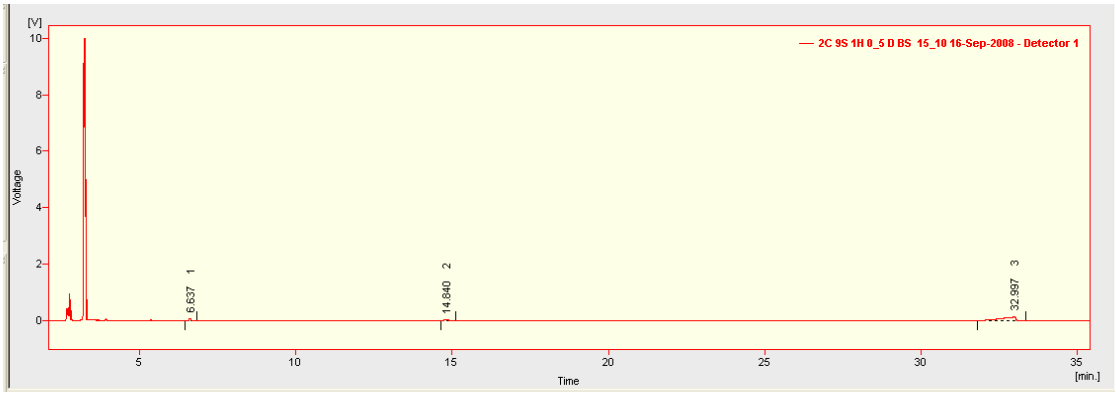
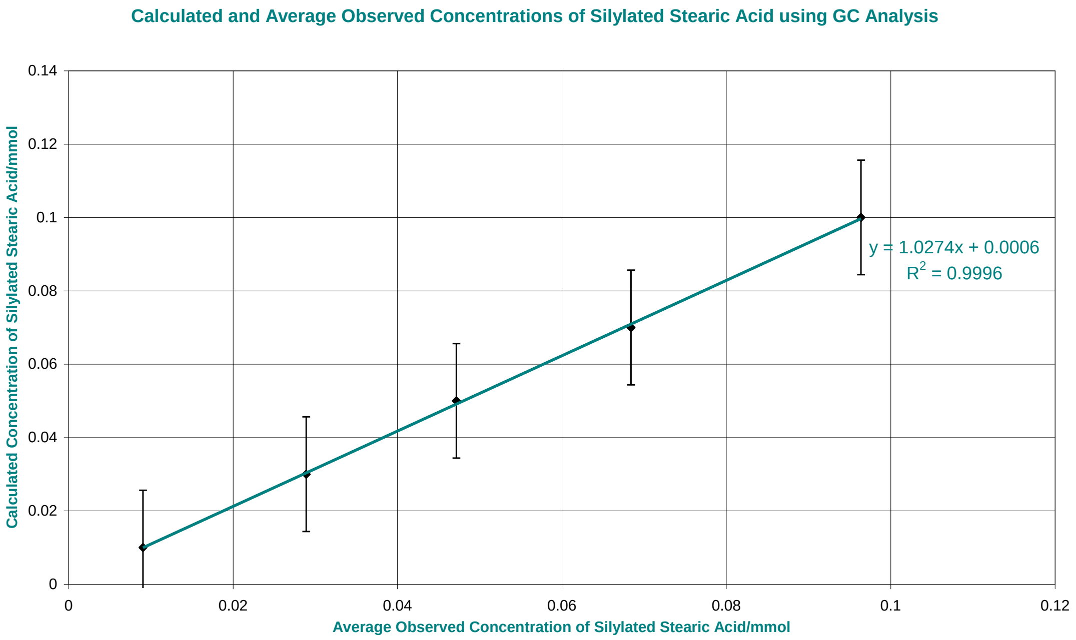


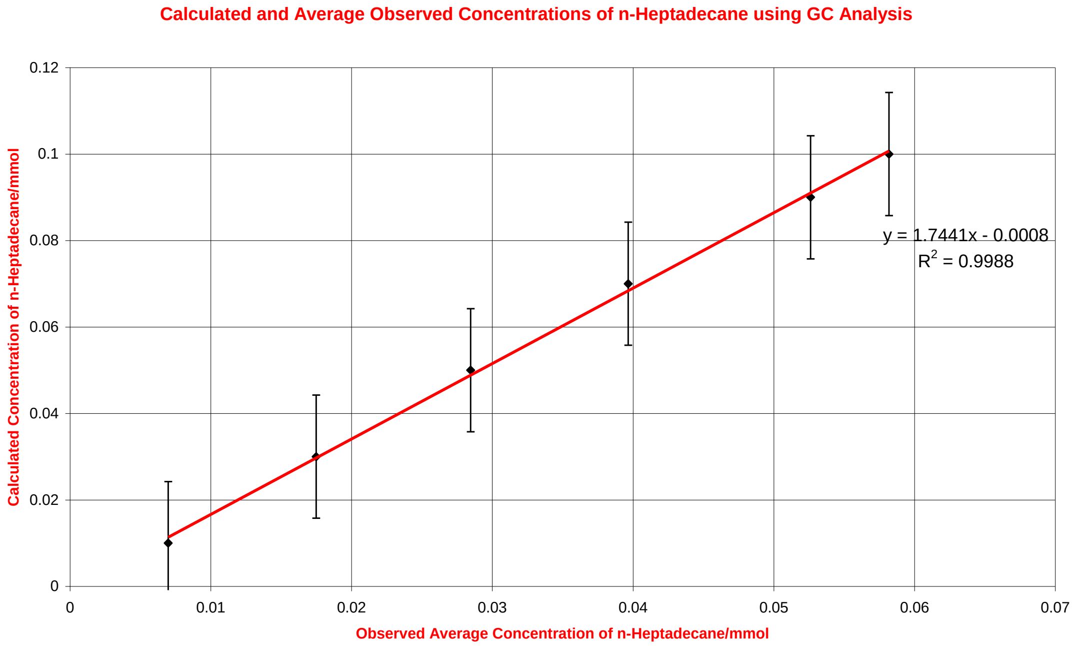
Figure S2. A typical GC chromatogram for silylated stearic acid (~33.0 min.) and n-heptadecane (~6.6 min.) with the internal standard eicosane (~14.8 min.) in the solvent dodecane (~2min).

Using the internal standard eicosane ($C_{20}H_{42}$), the observed and expected numbers of moles were calculated and calibration curves were derived for stearic acid and *n*-heptadecane (Figure S3).

Using these calibration curves quantitative experiments were performed on the liquid portions of reaction mixtures from each of the catalytic tests enabling percentage conversions and percentage yields for the reactions to be calculated.



(a)



(b)

Figure S3. Calibration curves obtained by gas chromatography for: (a) silylated stearic acid and (b) *n*-heptadecane in dodecane.

b) Analysis of Solid Reaction Products

Analysis Method

The reaction mixture, containing the solid oxide and wax residues was filtered through a sintered glass frit. The filtrate was retained for analysis and the solid/wax fraction subjected to Soxhlet extraction using ethanol (250 mL) at reflux for a period of 12 hours in order to remove any reactants or wax products from the oxide materials.

Solid product calibration samples were analysed in ethanol solvent with a gas chromatograph (GC, HP 5890 Series II) equipped with a TR-SD capillary column (length 10 m, ID 0.53 mm and film thickness 2.65 µm) and a flame ionisation (FI). The injector and detector temperatures were set to 250 and 350 °C respectively. Each sample was injected (5 µl) into the GC with helium as the carrier gas at pressure of 2.07 bar. The GC temperature program was based on ASTM D6584 10ae1 Standard Test Method for Determination of Total Monoglyceride, Total Diglyceride, Total Triglyceride, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography [83]. The GC was held at 50 °C for 1 min then heated at 15 °C /min up to 180 °C, followed by further heating at 7 °C /min up to 230 °C then increasing up to 350 °C at 10 °C /min where it was held for 5 mins. Data analysis and peak integration were performed by Clarity software [82].

Standard Solution Preparation

Chemical standards of eicosane, stearic acid (including the silylating agents pyridine and BSFTA), stearone and the solvent THF were purchased. Quantitative calibrations to produce calibration curves were performed using the methods described below.

Stearic acid

Samples were prepared in vials with the following quantities and made up to 10 ml with THF:

Solution Sc: 0.1 M Silylated Stearic acid in THF
0.2845 g Stearic acid
0.528 ml N,O-Bis(trimethylsilyl)trifluoroacetamide, BSFTA (Acros Organics, 98+%) (100% wt excess)
0.0872 ml pyridine (Acros Organics) (30% wt)
Made up to 10ml with THF (Fischer Scientific, 98+%).

The solution was left to silylate for 12 hours.

Solution E: 0.1 M eicosane in THF
0.2820 g eicosane (Acros, 99%)
Made up to 10 ml with THF.

These solutions were made up into calibration standard mixtures as shown in Table S4.

Table S4. Reference samples prepared for calibration of stearic acid in THF.

Reference Name	Silylated Stearic Acid / µl	Eicosane / µl	THF / µl
9Sc5E1T	900	500	100
7S5E3T	700	500	300
5S5E5T	500	500	500
3S5E7T	300	500	700
1S5E9T	100	500	900
10S5E0T	1000	500	0
0S5E10T	0	500	1000

Using the internal standard eicosane ($C_{20}H_{42}$), the observed and expected number of mols were calculated and calibration curves were obtained for stearic acid using the GC method described above.

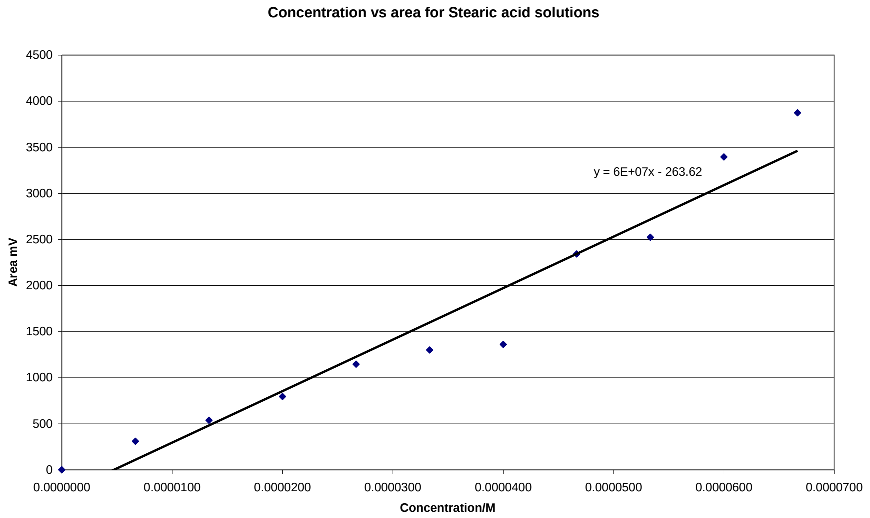


Figure S4. Calibration curve obtained by GC for silylated stearic acid analysed as a THF solution.

Stearone

Samples were prepared in vials with the following quantities and made up to 10 ml with THF:

Solution Se: 0.1M Stearone in THF
0.0046 g Stearone
Made up to 10 ml with THF.

Solution E: 0.1 M eicosane in THF
0.282 g eicosane (Acros, 99%)
Made up to 10 ml with THF.

1000 µl solution Se was then added to 100 µl solution E, to produce a standard stock solution denoted SeE. The GC calibration for stearone was then performed by diluting this standard stock solution according to the values in Table S5 to produce the calibration curve for stearone shown in Figure S5 using the GC method described above.

Table S5. Dilutions of the stock solution SeE used in stearone GC calibration.

Reference Name	SeE / µl	THF / µl
100 % SeE	1000	0
90 % SeE	900	100
80 % SeE	800	200
70 % SeE	700	300
60 % SeE	600	400
50 % SeE	500	500
25 % SeE	250	750
12.5 % SeE	125	875

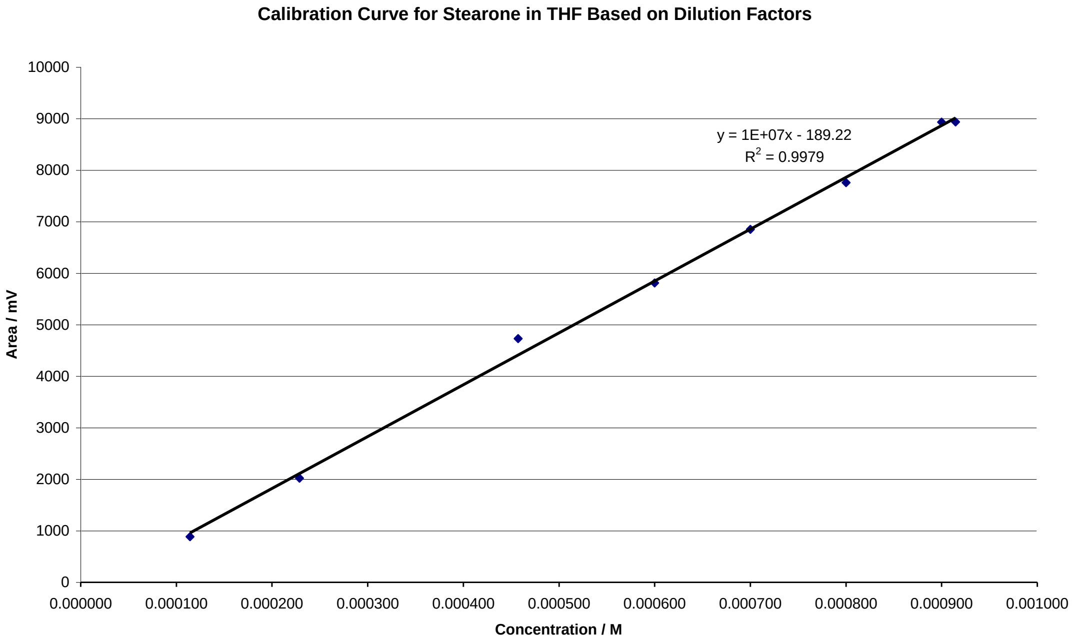


Figure S5. Calibration curve obtained for Stearone based on dilution factors of the stock solution SeE.

Attempted Alternative Method for Determination of the Basicity of Selected MMO Materials

The characterisation of active sites in basic catalysts can be performed, often with limited success, using a number of approaches, such as adsorption of probe molecules monitored by FTIR spectroscopy, XPS measurements and temperature programmed desorption of carbon dioxide (CO_2-TPD) [84–86]. For instance, FTIR spectra of test-molecules adsorbed on the cationic forms of zeolites have been reported in the literature [84,85], however, to the best of our knowledge this approach has not been applied to LDH-type materials, and in general, only qualitative comparison of zeolites with similar structures, *e.g.* faujasites, has been successfully undertaken. Hence, the results should be considered at best as semi-quantitative. Furthermore, pyrrole is too large a test molecule to penetrate into the micropores smaller than 0.5 nm, and no meaningful FTIR data would be obtained for such materials.

FTIR spectra of pyrrole adsorbed on reference materials, the Na- and K-forms of faujasites (Figure S6), show a clear trend: the broad band of N-H vibration is shifting to low frequency with the decreasing Si/Al ratio and Na substitution by K, thus confirming the greater basic character of framework oxygen in zeolite X as compared to Y, and in K-faujasites as compared to their Na-form. The data obtained for the CoH-MMO-3 and CoP-MMO-3 samples (Table S6) indicate that the basic strength of the active sites in these materials is similar to that of zeolite KY, a rather weak base. It should be noted that the number of active sites cannot be estimated using this approach. The application of the acetylene-based probe-molecules has not been successful for the LDH catalysts as the interaction between the probe and the catalyst surface is very weak.

Table S6. Pyrrole adsorption on FAU type zeolites and LDH catalysts

Sample	**N-H frequency of H-bonded pyrrole, cm^{-1}**
Na-Y	3420
K-Y	3350
Na-X	3255
K-X	3215
CoH-MMO-3	3340
CoP-MMO-3	3370

Supplementary FTIR data

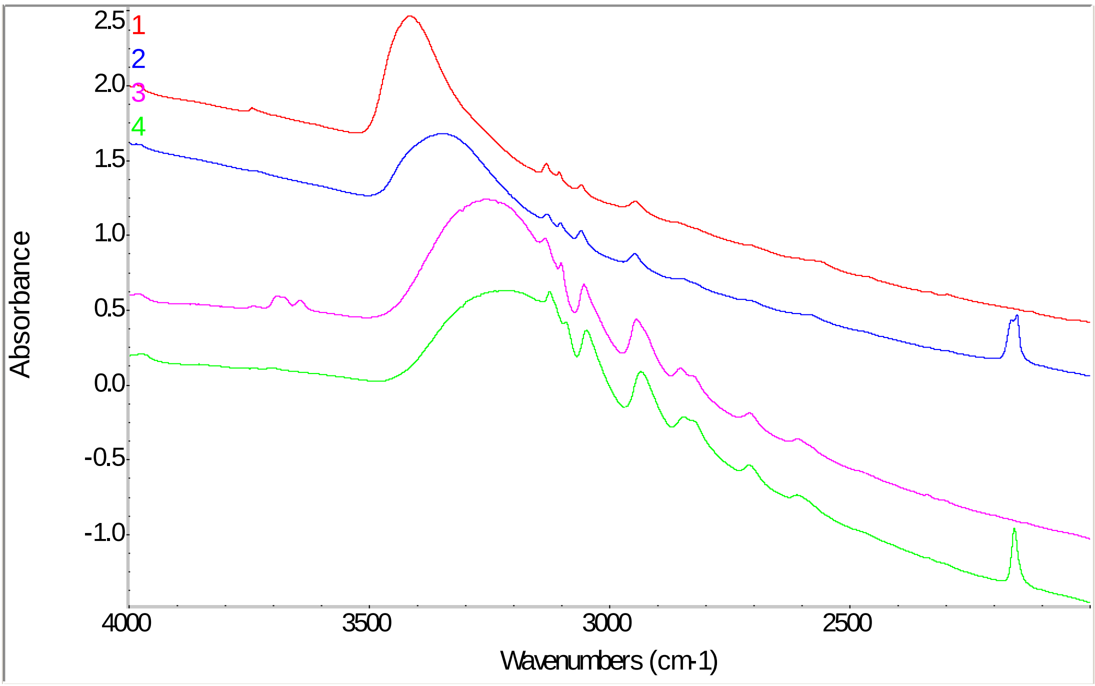


Figure S6. FTIR spectra of pyrrole adsorbed on ion-exchanged faujasites. 1 - NaY, 2 - KY, 3 - NaX, 4 – KX. The broad band of N-H vibration is shifting to low frequency with the decreasing Si/Al ratio and Na substitution by K.

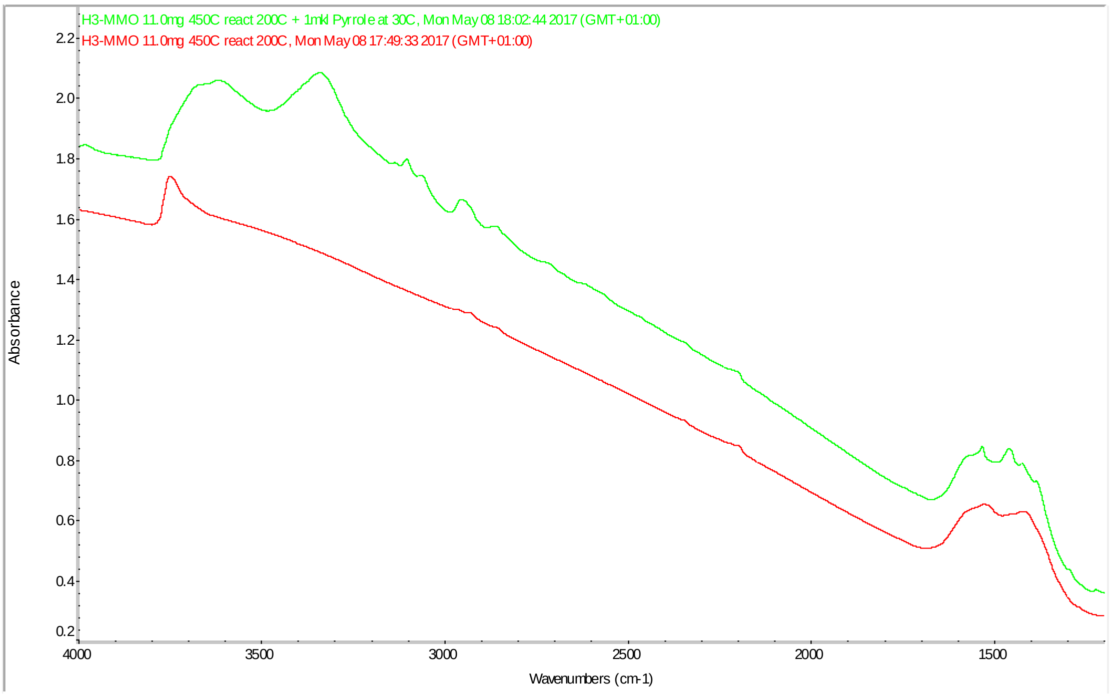


Figure S7. FTIR spectra of pyrrole adsorbed on CoH-MMO-3.

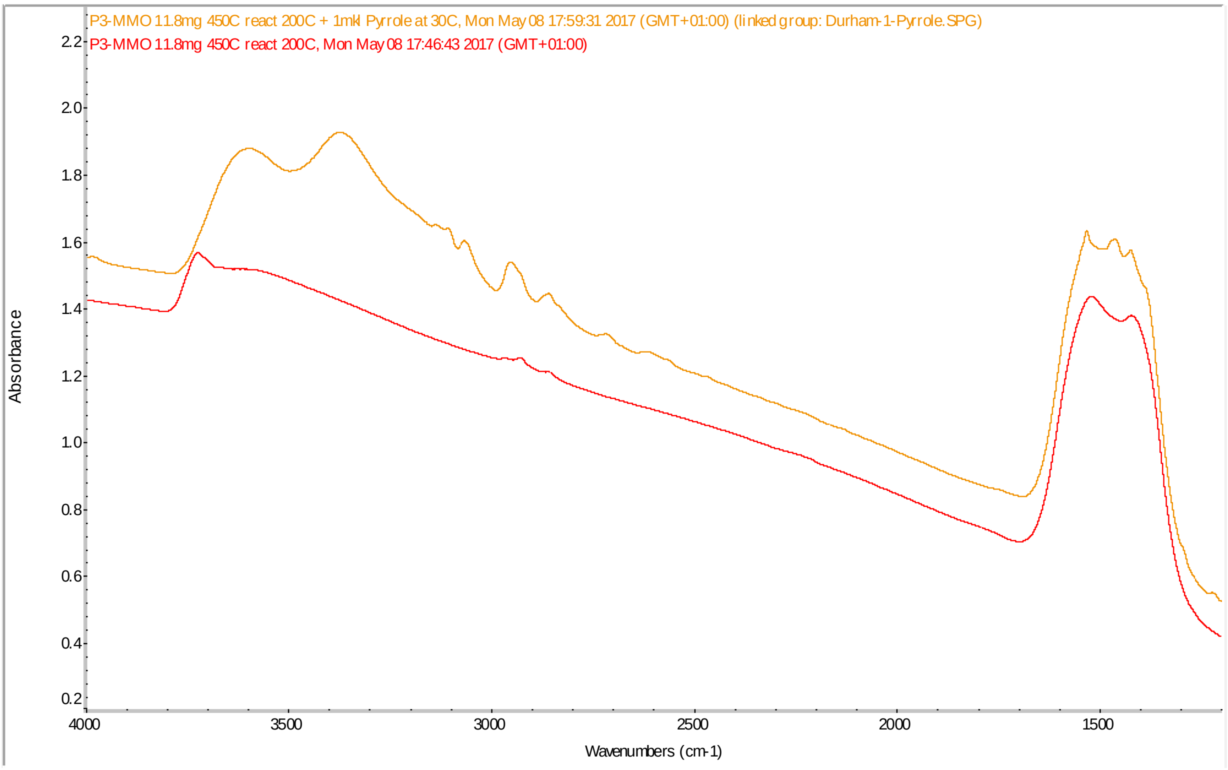


Figure S8. FTIR spectra of pyrrole adsorbed on CoP-MMO-3.