

Supplementary Information

Simple Quantification of Zeolite Acid Site Density by Reactive Gas Chromatography

Omar A. Abdelrahman^{1,3†}, Katherine P. Vinter^{1†}, Limin Ren^{1,3}, Dandan Xu^{1,3},
Raymond J. Gorte^{2,3}, Michael Tsapatsis^{1,3}, Paul J. Dauenhauer^{1,3}

¹University of Minnesota, Department of Chemical Engineering and Materials Science. 421 Washington Ave. SE, Minneapolis, MN, 55455, U.S.A.

²University of Pennsylvania, Department of Chemical and Biomolecular Engineering. 220 South 33rd Street, Philadelphia, PA, 19104, U.S.A.

³Catalysis Center for Energy Innovation, University of Delaware. 150 Academy Street, Newark, DE, 19716, U.S.A.

†Authors Contributed Equally.

TABLE OF CONTENTS

1.0 Reactive Gas Chromatography Design and Setup.....	2
2.0 Procedure for Catalyst Pelletization & Inlet Packing.....	6
3.0 Software and Method.....	8
4.0 Flame Ionization Detector Calibration.....	10
5.0 Gas Chromatography Column and Cryogenic Conditions.....	11
6.0 Comparison of Pulsed and Flow Amine Saturation.....	12
7.0 Method of Acid Site Concentration Calculation.....	13

1.0 Reactive Gas Chromatography Design and Setup

Table S1. List of parts used for reactive gas chromatography with alkylamine titration

	Item	Manufacturer	Part Number	Description	Qty
1	Gas Chromatograph	Agilent	7890A	Gas chromatograph equipped with a split/splitless inlet, Automated liquid sampler and FID detector	1
2	Inlet liner	Agilent	5190-2295	Quartz, split liner	1
3	Glass wool	Restek	24324	Deactivated Glass wool	1
4	GC-Column	Agilent	19091P-Q04	HP-PLOT/Q column, 30 m long, 0.32 mm ID, 20 um film	1
5	Inlet Adapter	Restek	27184	1/16" capillary inlet adapter fitting	1
6	Tube adapter	Agilent	G1580-60060	1/16" x 1/32" adapter	2
8	FID adapter	Restek	20884	1/4" x 1/16" FID adapter fitting	1
9	Siltite Ferrule	Agilent	G3188-27502	Siltite Ferrules, pack of 10, for use with 0.32 mm ID column	1
10	Heated Valve Box kit	Agilent	G1581A	Heated valve enclosure, containing two pneumatically actuated valco valves	1
11	6 port valve	Vici Valco	DC6UWE	1/16", 0.70 mm bore 6 port valve, medium temperature	1
12	3 port valve	Vici Valco	DC3UWE	1/16", 0.70 mm bore 3 port valve, medium temperature	1
13	Pressure regulator	McMaster	3834T51	Miniature Pressure regulator, 1/16", 10-32 UNF	1

In a typical gas chromatography setup, a sample is injected into the inlet liner where it is first vaporized than sent to the chromatographic column. The various compounds in the sample are resolved by the column, exiting the column at different time intervals, and are finally sent to a detector for quantification. In the automated RGC setup, the direct connection between the GC inlet and the chromatographic column is replaced with a heated, pneumatically actuated 6-port gas valve, allowing for compounds exiting the GC inlet to be sent directly to the detector (Figure S1 A) or through the column and then to the detector (Figure S1 B). A pneumatically actuated 3-port valve is also installed prior to the inlet of the electronic pressure controller (EPC). This

valves adds the ability for the user to automatically switch between He and air as the gas sent to the inlet liner. During the catalyst pre-treatment step, the outlet of the GC inlet bypasses the column to avoid damaging it. Similarly, during the saturation of the catalyst surface with an alkylamine, the column is bypassed and the exiting alkylamine stream is sent directly to the detector. Finally, as the temperature of the inlet liner is ramped to reaction conditions, its outlet stream is directed through the column to trap any alkenes formed.

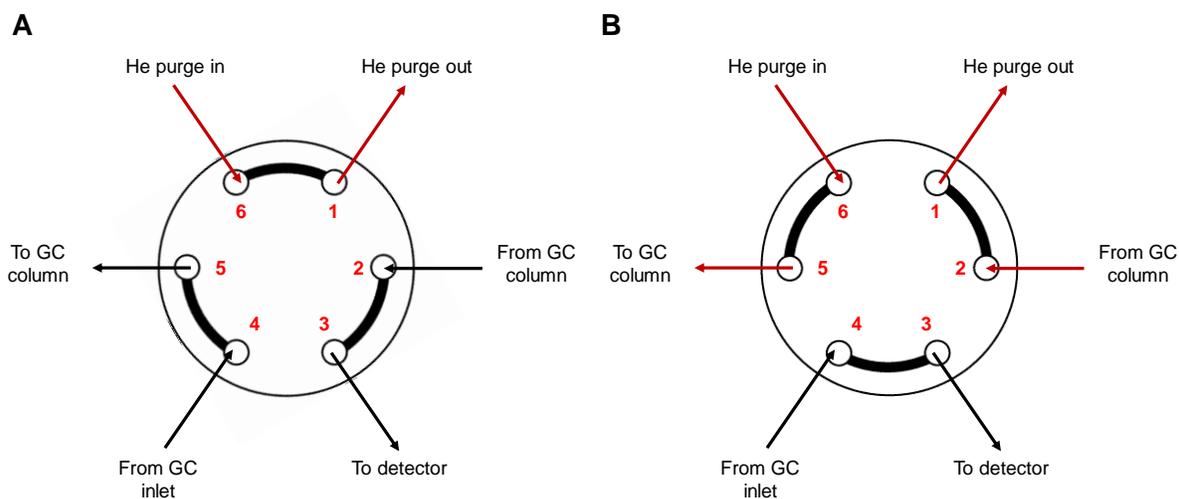


Figure S1. Distinct positions of pneumatically actuated 6 port valve **A.** Column bypass, used during catalyst pretreatment and surface saturation steps **B.** Sample trapping, used during reaction analysis step.

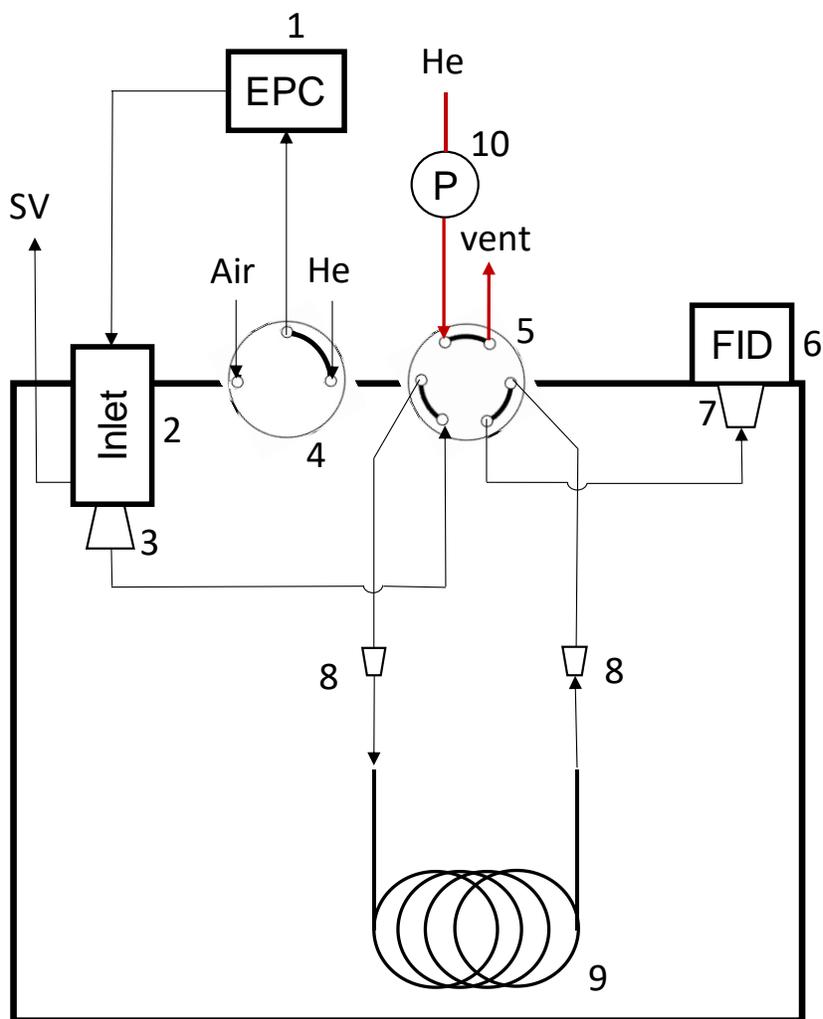


Figure S2. Detailed schematic of an automated reactive gas chromatograph. 1 – Electronic pressure control (EPC), 2- GC inlet liner, 3- 1/16” inlet adapter (27184), 4- 3-port valve (DC3UWE), 5 – 6-port valve (DC6UWE), 6- flame ionization detector 7- 1/16” FID adapter (20884), 8- 1/16” x 1/32” tube adapter (G1580-60060), 9- GC column (19091P-Q04), 10- Pressure regulator (3834T51).

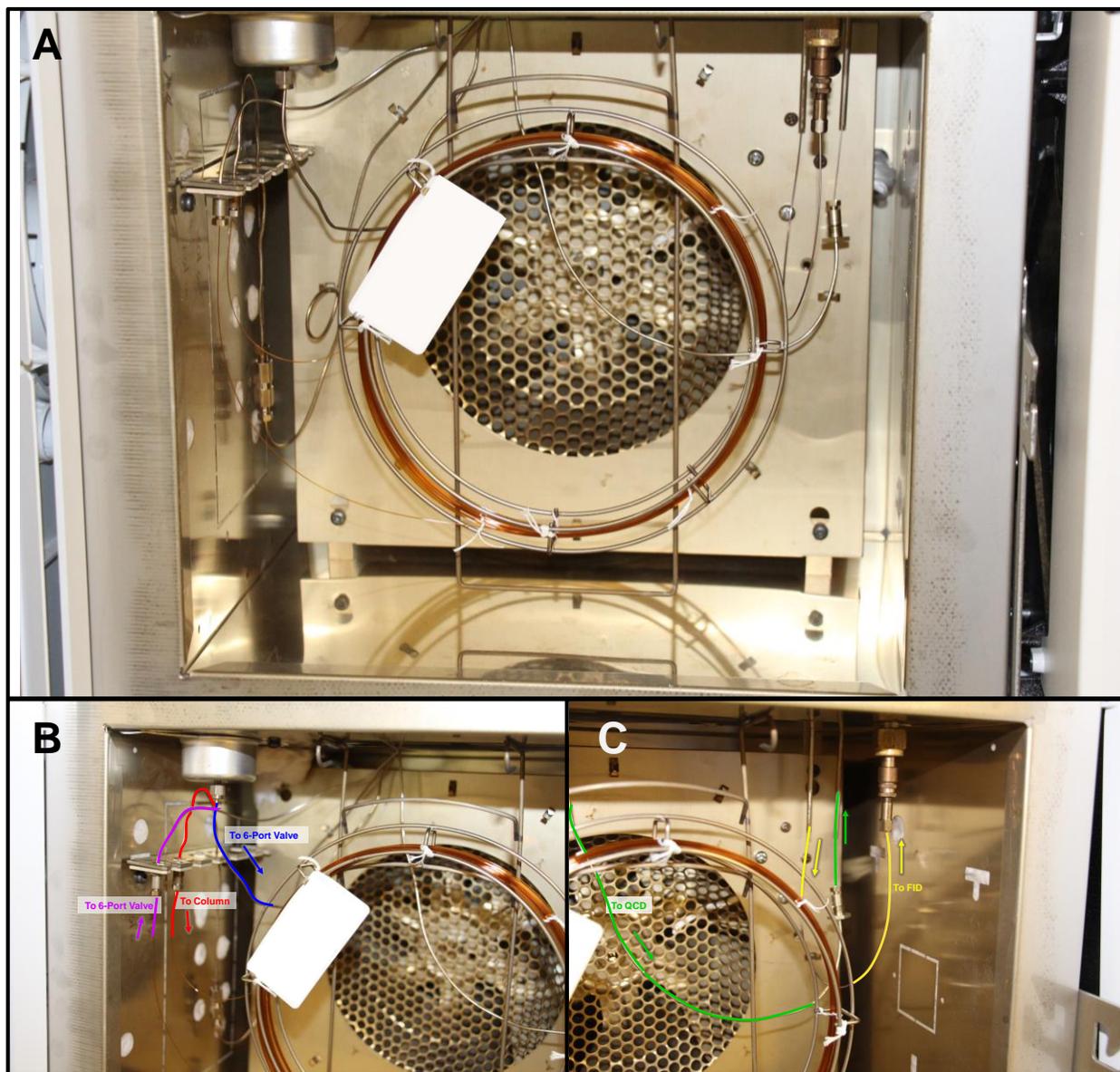


Figure S3. Picture of the GC oven of an automated reactive gas chromatograph. A. Overall setup of reactive gas chromatograph within GC oven **B.** Connections between inlet, column and 6-port valve assembly **C.** Connections between detector and 6-port valve assembly.

An alternative and simpler setup for RGC experiments is depicted in Figure S4. The main difference is the lack of pneumatically actuated valves. Here, an *ex-situ* calcination would be necessary, since an *in-situ* calcination cannot be performed without risking damaging the GC column. Additionally, in the surface saturation step, injected alkylamines will be sent directly to

the column and it is necessary to keep the oven temperature elevated for the alkylamines to rapidly elute. Care must be taken to ensure that the column of choice will not be damaged by overloading with alkylamines.

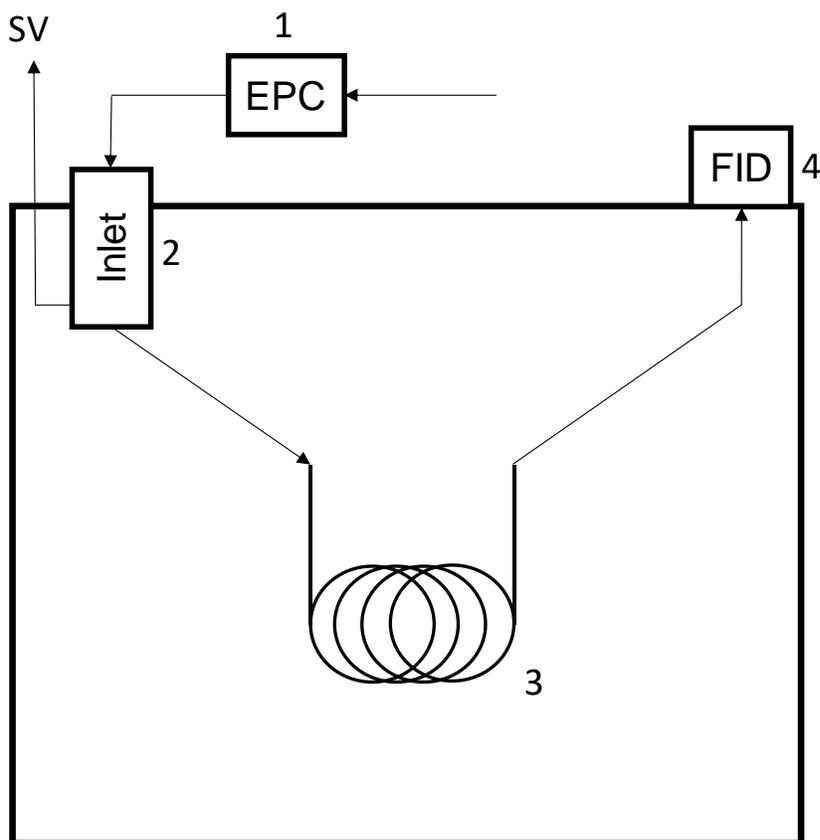


Figure S4. Detailed schematic of a reactive gas chromatograph without automated pneumatically actuated valves. 1 – Electronic pressure control (EPC), 2- GC inlet liner, 3- GC column (19091P-Q04), 4- Flame ionization detector (FID).

2.0 Procedure for Catalyst Pelletizing & Inlet Packing

Larger sized catalyst particles were specially used to ensure minimal pressure drop across the catalyst bed. Catalyst particles were formed by use of a pellet press (Pike Technologies, 13mm), and range of sieves. First, ~100 mg of catalyst is placed into the pellet press uniformly and pressed with a hydraulic press at ~2 tons for 10-15 minutes. Once pressed, the catalyst is

thrown away to ensure no contaminants from previously pressed catalysts were present. Next, the procedure was repeated for the same catalyst sample of no more than 150 mg and instead kept for sieving. The pellet was then lightly broken up with a metal spatula to smaller particles and finally sieved. Only particles in the size range of 500 – 1000 μm were used for the RGC experiments.

Once the appropriate catalyst particle sizes are obtained, they can be loaded into a GC inlet liner sandwiched between two plugs of quartz wool Figure S5. The packed inlet liner can then be placed within the GC inlet, to perform a RGC experiment Figure S6.

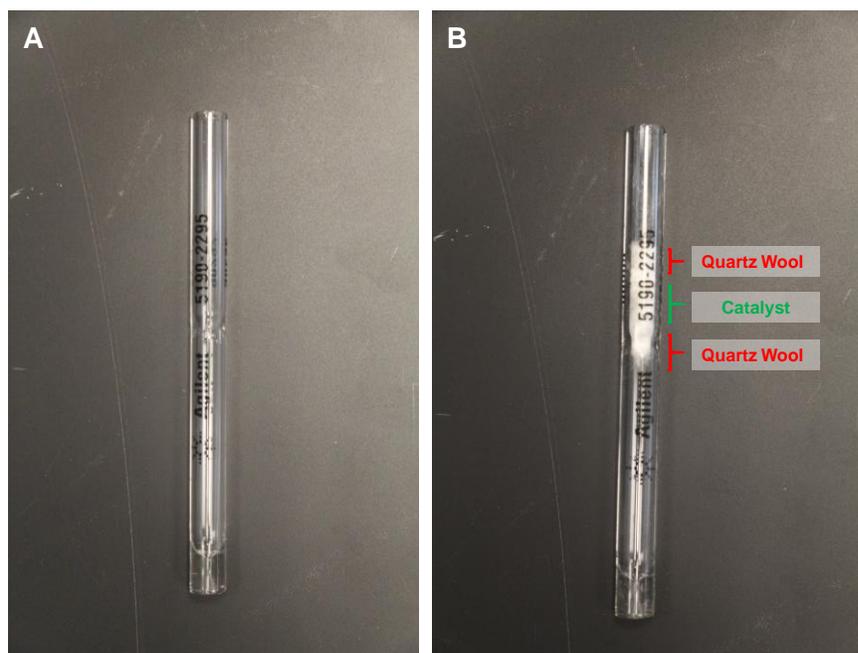


Figure S5. Inlet liner microcatalytic reactor A. Quartz split liner (5190-2295, Agilent) before packing **B.** Catalyst sample sandwiched between two plugs of quartz wool in liner.

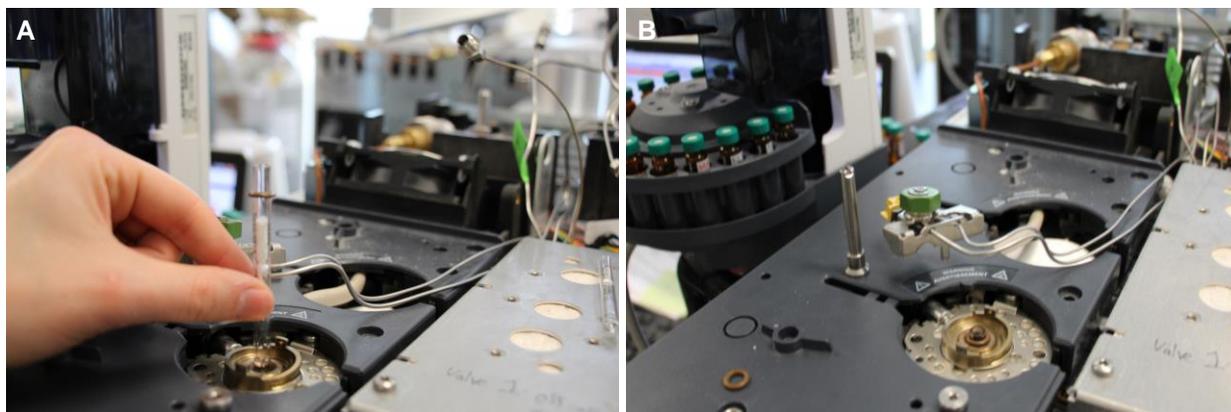


Figure S6. Installation of inlet liner microcatalytic reactor into RGC **A.** liner is placed into GC inlet **B.** liner is shown fully inserted into the inlet.

3.0 Software and Method

Automation of the RGC experiments was achieved via OEM software typically used to control a gas chromatograph (Chemstation rev B.04.02), where various method files were loaded in the appropriate sequence. Six steps were typically run as a sequence in the following order:

1. Calcination

In the first calcination step, the 3-port valve is actuated at the start to feed air through the inlet liner. The pressure regulator controlling the flow of the purge gas is set at 15 psi, to provide sufficient He flow through the column when not in use. It is kept at this setting for all the remaining steps. The temperature of the inlet liner is ramped to 673 K at a rate of 10 K min⁻¹, where it is then held there for one hour. Once completed, the 3-port valve is returned to its original position to send He through the inlet liner. Throughout this step, the GC column is bypassed by appropriately directing the 6-port valve (Figure S1 A).

2. Post-calcination

In the post-calcination step, the inlet liner is simply allowed 30 mins for its temperature to equilibrate at 423 K under a flow of He.

3. Dosing

To saturate the catalyst surface with alkylamines, a dosing method is applied. Here the automated liquid sampler (ALS) is instructed to withdraw a known volume of alkylamine from a GC vial placed within the instrument and inject it into the liner. Typically, 0.2 μl of alkylamine are injected at a time and the method was allowed to run for 4 minutes per single injection. This was typically performed 15 times consecutively, to ensure a saturated catalyst surface.

Alternatively, the dosing section could be performed through a continuous flow method. Here, the ALS is instructed to withdraw the maximum allowable volume from the desired alkylamine vial, followed by an injection with a controlled dispensing rate (typically 1 $\mu\text{l min}^{-1}$). This procedure is performed until at least 300 $\mu\text{l g catalyst}^{-1}$ has been dispensed, to ensure a saturated catalyst surface.

4. Inlet Purge

Once the catalyst surface is saturated, a purge method file is used to ensure that no excess alkylamine is present in the catalyst pores prior to ramping the temperature of the inlet liner. The GC is instructed to hold the catalyst temperature at the same temperature of 423 K under a continuous flow of He for two hours, which was found to be sufficient to remove any excess alkylamine by tracking the FID signal throughout the method.

5. Column Purge

Before performing the reaction, it is necessary to ensure that no residual compounds are present in the GC column. An oven purge method is used in which the temperature of the GC oven is raised to the maximum temperature and held for 10 minutes.

6. Reaction analysis

In the final method, the GC oven temperature is reduced to 30 °C to trap any evolving alkenes. The 6-port valve is actuated at the start of the method to send the effluent stream from the inlet liner through the column, before reaching the FID. The temperature of the inlet liner is ramped from 423 to 673 K at 10 K min⁻¹ and held there for 30 minutes, all while holding the GC oven at 30 °C. The GC oven is then ramped to the maximum allowable temperature of the column at 10 K min⁻¹, allowing the alkene to elute from the column.

4.0 Flame Ionization Detector Calibration

Due to the use of a quantitative carbon detector (QCD, POLYARC, Activated Research Company) calibrations for these reactions were performed using a gas blend of methane and Argon (10.01 % Methane in balance Ar, Matheson). However, if these experiments were performed without a QCD, a set of calibrations would be required for each of the alkenes analyzed.

Calibrations were performed through manual injections of the methane blend. A Tedlar gas sampling bag (SKC, 232-01) was first filled with the methane blend, from which known volumes were withdrawn using a gas tight syringe (Scientific Gas Engineering, 100 uL gas tight syringe, 100R-GT). The contents of the syringe were then injected into the GC inlet housed with a blank liner. The resultant calibration curve is depicted in Figure S7, where the slope of the line is used as a calibration curve for all the RGC experiments. The calibration curve was produced

using the same chromatographic method as is employed in the reaction analysis step of the RGC method described in the main text.

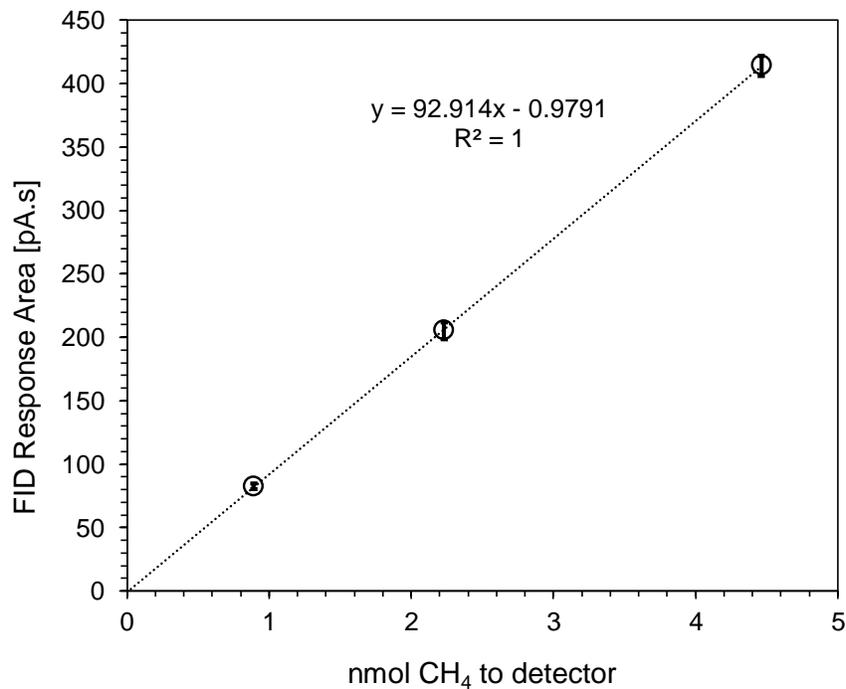


Figure S7. Calibration of methane and Argon calibration gas mixture (Matheson, 10.01 % methane in balance Ar). Depicts FID response area of methane versus moles of methane to detector.

5.0 Gas Chromatography Column and Cryogenic Conditions

The choice of chromatographic column for Reactive Gas Chromatography (RGC) experiments depends almost completely on the column's ability to retain the product species to be quantified; in the case of amine decomposition this is the alkene. Unlike a traditional gas chromatography procedure, the column is tasked with retaining the species for an extended period of time as the catalyst heats and the reaction occurs. The HP-PLOT/Q column used can trap alkenes at near ambient temperatures, resulting in a clean chromatogram with one clearly defined peak associated with the alkene. The ammonia produced is not observed due to the use

of a Flame Ionization Detector (FID) while the unreacted alkylamines do not elute well as a single clear peak, likely due to unfavorable interactions with the column.

Other chromatographic columns can be used to perform RGC experiments, however, lower temperatures may be necessary to trap the alkene products within the column for extended periods of time. This can be achieved through cryogenic cooling to reach lower temperatures, where cryogenic fluids such as LN₂ and CO₂ can be introduced by installing a GC oven cryogenic cooling attachment.

6.0 Comparison of Pulsed and Flow Amine Saturation

The effect of the saturation method was examined through a direct comparison of the measured BAS density for a given material using both methods. Two methods of catalyst saturation were examined, pulse and flow. The alkylamine can either be added through discrete pulses or a continuous flow, using the automatic liquid sampler as a syringe pump. Summarized in Table S2 are the measured BAS densities for a ZSM-5 (Si/Al 40, CBV8014), with an isopropylamine titrant and pulse and flow catalyst saturation methods. The method in which the alkylamine titrant is introduced appears to have no observable effect on the measured BAS density.

Table S2. Summary of the measured Brønsted acid site density for a ZSM-5 sample (Si/Al 40, CBV 8014) using isopropylamine that was introduced via pulse and flow methods

Saturation Method	Carrier flow (sccm)	Catalyst mass (mg)	Titrant	BAS density (umol/g)
Pulse	205	31.3	Isopropylamine	339
Flow	205	31.3	Isopropylamine	337
Flow	205	54.0	Isopropylamine	342

7.0 Method of Acid Site Concentration Calculation

The method of calculating Brønsted acid site (BAS) density from the alkene peak area is described using the following equation:

$$BAS\ Density = \frac{A_{alkene} * CF * (Split\ Ratio + 1)}{Catalyst\ Mass} \quad (1)$$

Where A_{alkene} is the integrated area of the alkene peak in the chromatogram and CF the calibration factor. Determining the calibration factor has been discussed in detail in Section S4. It is important to note that the calibration factor is described as moles to *detector* not moles *injected*; this is the reason for the split ratio as part of the equation. The catalyst mass refers to the sample loaded into the GC liner.