Real-time study on cumene formation based on RGA/MS analysis

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Abstract

Commonly, catalytic reactions are carried out in batch reactors and analyses are performed upon reaction completion yielding little information about time-resolved concentrations of reactants and products. Herein an in situ analysis by real-time mass spectroscopy provides time-resolved information about heterogeneous catalytic reactions, such as reaction completion time and product formation. This paper presents a novel application of real-time mass spectrometry to monitor the progress of an alkylation reaction of benzene with propylene to produce cumene, using an H^+ β-zeolite (Si/Al: 12/1) catalyst at 150 °C with a 7:1 benzene to propylene molar ratio. Quantitative analysis of products was performed by gas chromatography (GC). Mass spectroscopy (MS) was utilized to continuously monitor reactants being consumed and products being formed during the alkylation process in real-time, to identify side products formed during the reaction, and to determine reaction completion. The real-time monitoring indicated that propylene was quickly absorbed/consumed, while cumene had a delayed release back into the gas phase.
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Keywords: Alkylation of benzene; Gas chromatography; Mass spectroscopy; Real-time; Residual gas analysis

1. Introduction

Cumene is the top 28th largest bulk chemical produced in the United States [1]. The majority of this cumene is used to produce acetone and phenol [2]. Many of the current cumene plant production processes utilize either a phosphoric acid catalyst or an aluminum trichloride catalyst [3,4]. Both of these processes generate problems with equipment corrosion and environmental disposal issues and costs, leading to the exploration of a process using recyclable, environmentally friendly zeolite catalysts.

The use of large-pore zeolites for the alkylation of benzene has become preferred, as they do not form significant quantities of *n*-propyl benzene, as do the medium-pore zeolites. A number of catalytic alkylation studies have shown that using large-pore β-zeolite catalyst at medium temperatures (i.e. close to 200 °C) and higher acidities (lower Si/Al rations) favors higher cumene yield and selectivity [5,6]. Despite the amount of work that has been done towards optimization of the zeolites and their acidities (as well as experimental conditions of the reaction) there is a lack of data on production of cumene in real-time. Commonly,

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catalytic reactions are carried out in batch reactor and analysis is performed upon reaction completion yielding little information about time-resolved concentrations of reactants and products. However, in situ analysis by real-time mass spectroscopic monitoring of the reaction provides time-resolved information regarding the consumption of reactants and the evolution of products as a function of time. This time-resolved information will allow easier elucidation of the reaction mechanism [7–14]. Some other advantages to real-time monitoring includes the ability to monitor in situ the catalytic reaction, which allows for the determination of optimal reaction conditions while minimizing negative side reactions (e.g. optimized reactant concentration, temperature, time, catalyst degradation, impurity formation).

This paper presents a novel application of real-time mass spectroscopy to monitor the progress of an alkylation reaction of benzene with propylene over zeolite catalysts for producing cumene. This allows for the determination of both the optimal reaction time, e.g. when the cumene production has peaked and/or before the formation of impurities, as well as reaction completion. Additionally, gas chromatography (GC) was used to corroborate the residual gas analysis mass spectroscopy (RGA/MS) data and obtain quantitative information on the liquid-phase products and reactants. By combining GC and RGA/MS techniques a much more complete picture of the reaction is obtained. In addition, confirmation of compound identification was performed during a duplicate catalytic run where a complete mass spectrum was recorded periodically. Furthermore, this monitoring technique can be applied to any other heterogeneous catalytic reactions of interest where gas-phase reactants and products are involved.

2. Experimental

The catalyst β-zeolite (Si/Al: 12/1) in its protonated (H$^+$) form used in the reactions was kindly provided by Zeolyst International. Benzene (Aldrich, >99%) was used without further purification. The alkylating agent, propylene 14.5% in nitrogen, was purchased premixed from TriGas. A 7:1 benzene to propylene molar ratio was utilized. Benzene was added as an excess reactant in order to avoid successive alkylation

of cumene to diisopropylbenzenes (DIPB), given the high reactivity of propylene. Besides lowering the selectivity for cumene, lower benzene to propylene ratio would deactivate the zeolite due to formation of propene oligomers in the zeolite channels [15].

The alkylation reaction was conducted in a standard 300 ml stainless steel Parr pressure reactor. The lid of the reactor vessel had an electric stirrer, a thermocouple, a pressure release, a gas valve, and a pressure gauge. A heat mantle maintained the reactor at the desired temperature. The temperature was monitored with the thermocouple placed in the headspace of the reactor, near the liquid. Two or more layers of aluminum foil were wrapped around the top of the reaction vessel to help evenly heat the top. Initially, 100 mg of zeolite catalyst were added to the well of the reactor, followed by 5 ml of benzene. After the reactor was assembled and reached 80 °C, propylene in N$_2$ was loaded to a pressure of 80 psig. Then the temperature was raised at 10 °C/min to the reaction temperature, 150 °C, which was held for the remainder of the run (2.5 h). After completion of the run, the reactor was quenched in an ice water bath until the reactor temperature reached approximately 7 °C or less. The vessel was vented, rinsed with solvent, and the liquid was extracted and filtered with a 0.22 μm filter. The reaction products were all quantitatively analyzed by gas chromatography (Hewlett-Packard 5890A Gas Chromatograph) with a Bentone 34/DNDP SCOT (0.02 in. × 50 ft, or 0.5 mm × 15.2 m) capillary column from Supelco, and a flame ionization detector (FID).

A residual gas analyzer mass spectrometer (RGA-300, Stanford Research Systems) monitored the catalytic reaction in real-time. A schematic diagram of this Parr reactor coupled to a mass spectrometer is presented in Fig. 1. This instrument generates ions by electron impact at 70 eV. The vacuum chamber of the quadrupole mass spectrometer was connected to the reactor vessel through a heated transfer line and a crimped-tube capillary leak. The leak rate of the capillary was small enough (∼10^{-6} atm cm^3/s) as to not significantly affect the pressure in the reactor over the reaction time. Immediately after the propylene/nitrogen gas was introduced into the system, mass spectrometer data collection started. Signal intensity versus time for the representative cation masses of interest was continuously recorded and the signal intensity was proportional to the relative
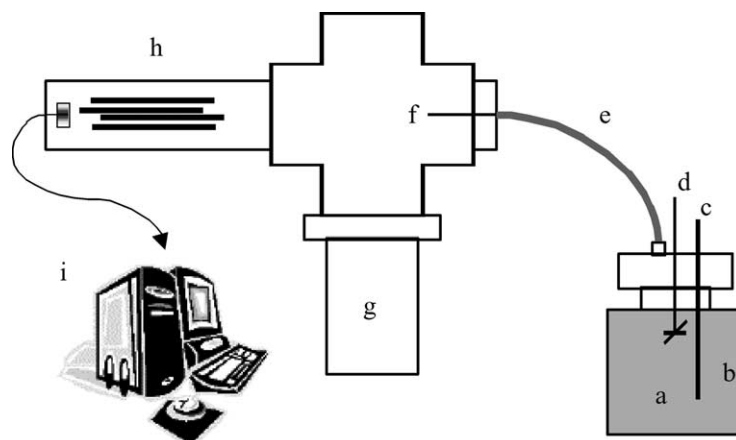
Fig. 1. Schematic diagram of the experimental apparatus: (a) 4561 Parr reactor 300 ml; (b) heating mantle, 4843 temperature controller unit; (c) thermocouple probe; (d) mechanical stirrer; (e) 1/4 in. flexible heated metal tubing; (f) crimped capillary leak tube; (g) balzer TPU 170 turbopump; (h) Stanford Research Systems RGA-300 quadrupole mass spectrometer; and (i) computer control and data acquisition.

concentrations of each reactant and product in the system. A representative mass/charge (m/z) fragment ion was selected for each molecular species of interest to represent its relative pressure. Each selected ion was then monitored as a function of time to record the progress of the reaction. The complete mass spectrum (10–150 Daltons (Da)) was also recorded at 30-min intervals in a duplicate run in order to verify the fragmentation pattern of the molecules of interest and to look for unexpected side products.

3. Results and discussion

The real-time mass spectral monitoring of the reactor gives added insight into the heterogeneous catalysis process. The fragmentation of benzene and propylene needed to be considered when selecting their most unique, representative ions. A mass/charge ion of 78 Da was easily selected to represent benzene. This parent mass ion is quite strong, and ensures little direct overlap from heavier hydrocarbons due to it being a radical–cation species. Standard spectra from the *Registry of Mass Spectral Data* [16] shows propylene with very prominent ion peaks at $m/z = 39$ and 41 Da. Benzene, however, is known to have a notable peak at $m/z = 39$ Da (~10%). This was confirmed experimentally by analog mass spectra taken from the

pot reactor containing only benzene as compared to a propylene/nitrogen mixture. These two spectra are compared in Fig. 2, confirming that $m/z = 41$ Da is indeed the best mass for monitoring propylene. The high amount of $m/z = 32$ Da signal, is likely from the initial oxygen (from air) present in the system. Standard spectra confirmed m/z of 105 Da as the major ion generated from cumene, as opposed to its parent ion mass of 120 Da. The side product DIPB has a
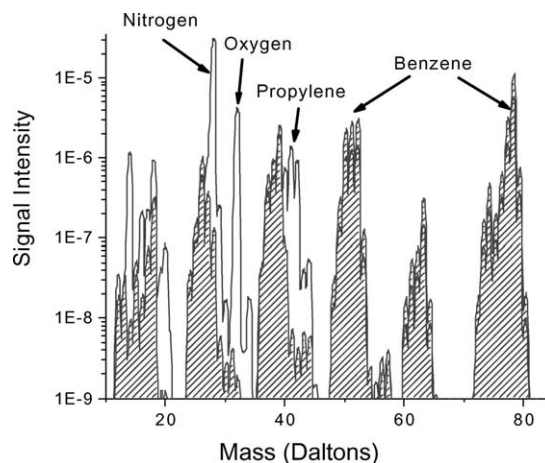

Fig. 2. Mass spectra of the headspace gases in the pot reactor filled with benzene and residual air only (filled with diagonal lines) as compared to after pressurizing with 14.5% propylene in N_2 (in solid lines).
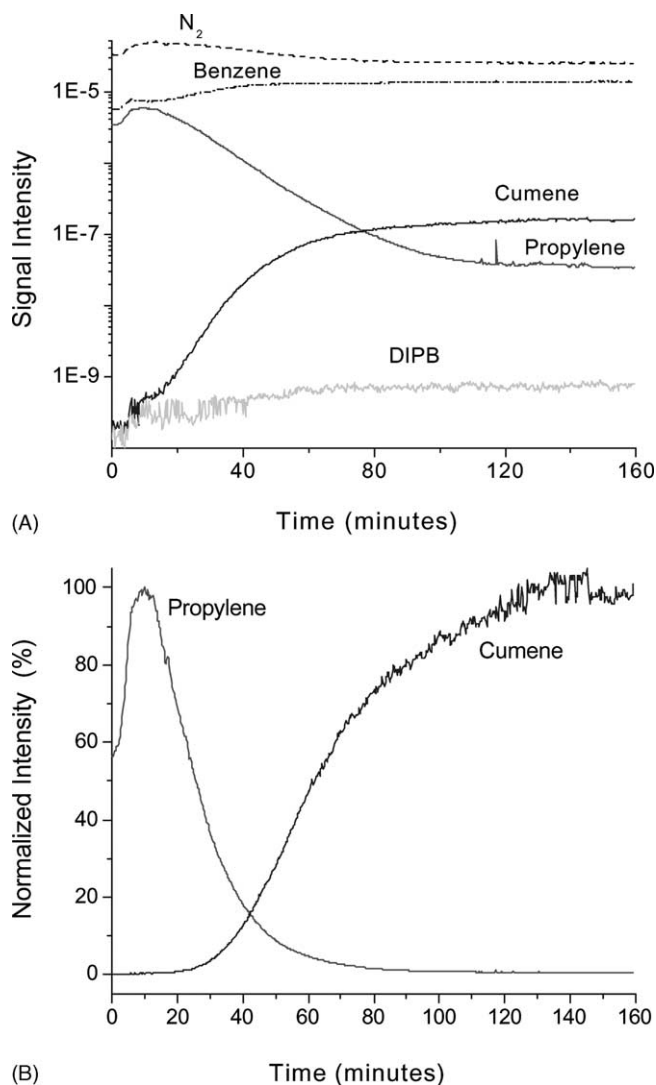
Fig. 3. Real-time ion-monitoring plot of pressure vs. time illustrating the conversion of benzene and propylene into cumene and DIPB: (A) full log scale, and (B) propylene and cumene each normalized to their maximum signals observed.

small overlap with this cumene signal; standard spectra show all the DIPB isomers have $m/z = 147$ Da as the highest ion population.

Fig. 3(A) contains the ion-monitoring mode plot beginning immediately after filling the reactor with propylene/nitrogen mixture. As the pot reactor was initially heated the signals for nitrogen, propylene and benzene all increased as the internal pressure increased. The reaction clearly started soon after the system was heated, with propylene being quickly

consumed and cumene being produced. Little DIPB isomers, identified as side products, were observed, as shown by the DIPB signal. The DIPB signal eventually appeared barely rising above the level of noise. Production of both cumene and DIPB then ceased due to a lack of propylene. Propylene was nearly totally consumed and the bulk of the remaining signal at $m/z = 41$ Da was due to a cumene ion fragment (∼3% as compared to main $m/z = 105$ Da fragment) [16]. In Fig. 3(A) no appreciable decrease in the

benzene signal is observed because benzene was the excess reagent and the plot is on a log scale. Also, there may be some amount of liquid benzene remaining in the pot reactor, or saturated on the zeolite, that fixes the benzene at its vapor pressure point for this constant temperature. Nitrogen is seen to decrease slightly as the gas pressure in the reactor was lowered by the sampling leak, lending credence to the presence of benzene liquid.

As seen in Fig. 3(B), at 1-h reaction time more than 95% of the propylene mass spectral signature was gone, indicating the reaction is nearing completion at that time. When analyzing these data it is important to note that the intensities of the different species cannot be directly compared as they are affected not only by ionization efficiency but also by their vapor pressures. Propylene, having the largest vapor pressure of the organics here, will result in the
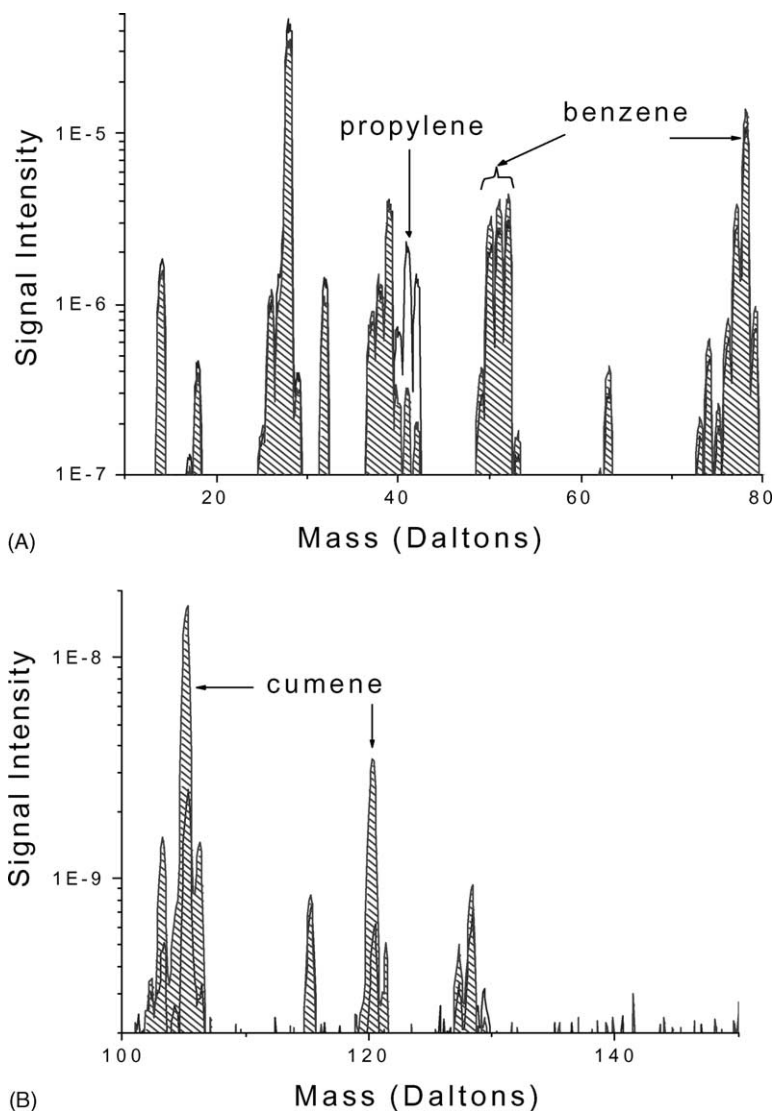

Fig. 4. Scanning mass spectra taken at 30 min (solid lines) and 60 min (filled with diagonal lines) from a 150 °C reaction of H$^+$-form β-zeolite (25:1) in the pot reactor: (A) the low mass end of spectrum showing propylene and benzene signals, and (B) the high mass spectrum where cumene is detected.

largest signals followed in descending order by benzene, cumene, and DIPB. In addition to the RGA information, gas chromatography data of the resulting liquid provides a good quantification of each component, either left over reactants or synthesized products. For the reaction conditions studied here, 70% cumene yield (i.e. conversion of propylene to cumene in wt.%) and 80% selectivity for cumene were obtained. All reactant and product peaks were fully separated in the GC spectra. The mass spectral results show selectivity greater than 99% when the raw signal intensities are compared.

Fig. 3(B) is the data of Fig. 3(A) plotted with only propylene and cumene, each normalized to their maximum signal intensities on a linear scale. It shows a delay in the cumene formation, initially due to the warm-up period during the first 10 min of reaction; time zero begins immediately after addition of the propylene/nitrogen mixture at 80 °C. After the warm-up period, there is a delayed release of cumene back into the gas phase. As a matter of fact, it takes 37 min for 10% of cumene to be seen in the gas phase, by which time 80% of the propylene has been removed. It seems that propylene is quickly absorbed and/or consumed, and that it takes less than 50 min to deplete 90% of propylene, while it takes about 100 min for 90% of the cumene formed to be observed in the gas phase. This indicates that cumene desorption from the zeolite may be slow at this temperature. This delayed cumene release must be taken in account during analysis of the experimental data. In the literature, higher yields have been reported at temperatures between 150 and 200 °C, where the main side products were DIPB isomers with small amounts of n-propylbenzene [6,17]. At this time, a definitive explanation for the higher yield at the higher temperature is unknown; however, the slower release of cumene into the headspace at the lower temperature may be a contributing factor. The residence time of the molecules on the zeolite influences side reactions, but the appearance of these compounds in the headspace gases is complicated by factors like vapor pressure and solubility in the liquid phase. More work over a wide temperature range is needed to explain the results. Further research is also needed to examine the reaction products early in the reaction to improve our understanding of the sensitivity of cumene yield to reactor variables.

Confirmation of the molecular identities attributed to the signals recorded in the ion-monitoring mode was performed by re-running the same reaction and acquiring a complete mass spectrum at 30 and 60 min into the reaction. Fig. 4 shows the resulting spectral areas of interest at two time periods, 30 (solid line) and 60 min (diagonal filled). The low mass range spectrum of Fig. 4(A) ($m/z = 10$–80 Da) shows a marked reduction in the $m/z = 41$ Da signal at 60 min when compared to the 30 min peak height demonstrating the consumption of propylene. The high mass part of the spectrum in Fig. 4(B) ($m/z = 100$–150 Da) shows formation of cumene, with an increase in the $m/z = 105$ and 120 Da signals. DIPB is not visible in the plots at either time since it lies a little more than two orders of magnitude below the cumene peak and in the noise of these scans. Note that the intensity scales in Figs. 3 and 4 are not the same due to experimental variations. The complete mass spectra did not show any detectable propylene oligomerization, i.e. no increase in C_4–C_6 products, of which hexenes are preferred oligomer products formed from 0.15 to 0.41% [15]. These and other coke products generated from propylene can be readily adsorbed into the zeolite, thereby avoiding detection but decreasing the catalytic efficiency [6,18], as indicated by the change in color of the catalyst from white to light yellow after the reaction.

4. Conclusions

Real-time RGA/MS was used to monitor the production of cumene by benzene alkylation with propylene at 150 °C using the H^+-form β-zeolite with a Si to Al ratio of 12 and a 7:1 benzene to propylene molar ratio in a pot reactor. The real-time mass spectral data provides time-resolved information about the heterogeneous catalysis process and can be easily applied to other catalytic reactions. RGA/MS allowed for the continuous monitoring of reactant consumption and product formation, provided reaction rate information, and indicated that the reaction was completed after 1 h, as judged by the propylene depletion. The mass spectral monitoring also showed a delayed appearance of cumene in the reactor headspace. This technique and information will be used for optimizing the catalytic reaction for production of cumene.

Acknowledgements

The authors would like to thank Stacia Barrow for her contributions in performing these experiments. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE–AC04–94–AL85000.

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