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Propane dehydrogenation on single site gallium on silica catalyst

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PROPANE DEHYDROGENATION ON SINGLE SITE GALLIUM ON SILICA
CATALYST

A Thesis

Submitted to the Faculty

of

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by

Shankali U. Pradhan

In Partial Fulfillment of the

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of

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For my father who inspires me always

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My journey so far in Purdue has been an amazing one, full of adventures and has been possible due to the support and guidance of many people.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BET	Brunauer - Emmett - Teller
Cp	Specific heat capacity at constant pressure
EXAFS	Extended X-ray absorption fine structure
FID	Flame ionization detector
FTIR	Fourier transformed infrared
GaAcAc	Gallium acetylacetonate
GC	Gas chromatograph
IR	Infrared
NIST	National Institute of Standards and Technology
TCD	Thermal conductivity detector
TGA	Thermo gravimetric analysis
TPR	Temperature programmed reduction
WHSV	Weight hourly space velocity
XANES	X-ray absorption near edge spectroscopy
XAS	X-ray absorption spectroscopy

ABSTRACT

Pradhan, Shankali U. M.S.Ch.E., Purdue University, May 2015. Propane Dehydrogenation on Single Site Gallium on Silica Catalyst. Major Professors: Fabio H. Ribeiro and W. Nicholas Delgass.

Light alkane dehydrogenation is gaining increasing importance due to the discovery of shale gas. Gallium based catalysts such as Ga/HZSM-3 and Ga_2O_3 have been used to dehydrogenate propane to propylene. However, the exact nature of the active site for propane dehydrogenation on Gallium based catalysts is still debated in literature. This work is aimed at understanding the nature of active site in Ga/SiO_2 catalyst for propane dehydrogenation. The Ga/SiO_2 catalyst is active and selective for propane dehydrogenation reaction. It is shown that Ga^{+3} site co-ordinated with four O atoms is the most active form of Gallium during the propane dehydrogenation reaction. The catalyst is subjected to different pretreatment conditions and it is observed that the pretreatment with H_2 at 650^oC results in lower initial rates for propane dehydrogenation. The Ga/SiO_2 catalyst is studied using *operando* X-Ray Absorption Spectroscopy, *in-situ* Fourier Transform Infrared Spectroscopy and X-Ray Photoelectron Spectroscopy. Reduction of the catalyst at 650^oC resulted in the formation of a reduced Gallium species which results in lower rates of propane dehydrogenation. These reduced Gallium species were found to be unstable under conditions of propane dehydrogenation

and get reoxidized to Ga^{+3}. It is proposed that the reduced Gallium species has the form of Gallium hydride which is less active for propane dehydrogenation.

CHAPTER 1. INTRODUCTION

The recent exploration and discovery of shale formations has resulted in the production

of surplus oil in the US. The import of oil in the US has significantly dropped and has

resulted in a 25-year low which is reflected in the current oil prices[1]. The natural gas and

light alkanes production has also significantly boosted along with the increased

production of oil in the US due to the high natural gas content of shale. This has led to

cheap excess of light alkanes like ethane and propane. Figure 1. 1 shows the average

wholesale price of propane during the heating months (Oct- Apr) in the last two years. It

can be seen that the price of propane has significantly decreased due to the discovery of

shale reserves.
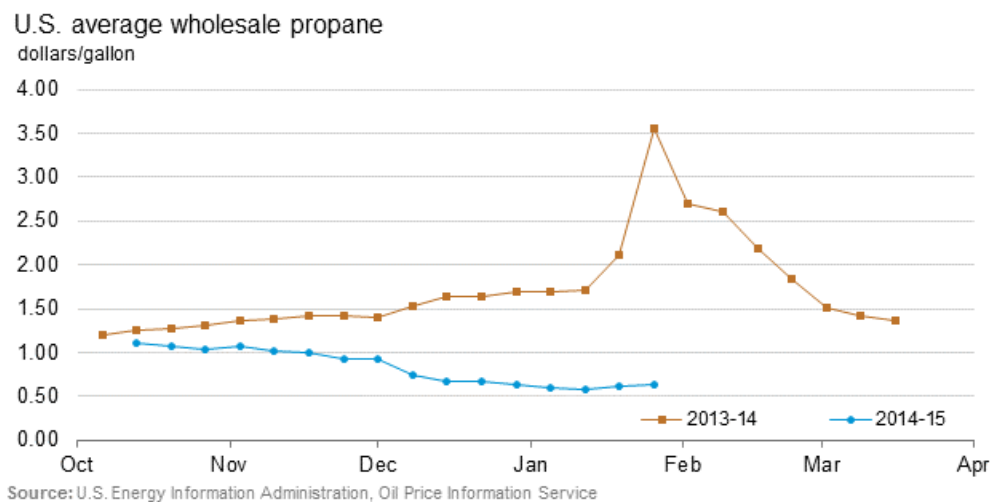
Figure 1. 1: Average wholesale price of propane in 2013-2014 and 2014-2015

The US chemical prices currently track oil and not natural gas. Hence, there is a vast interest in utilizing this cheap raw material of propane to manufacture valuable chemicals such as propylene. Propylene is an important building block of the chemical industry in that, it is the raw material for the manufacture of various products such as polypropylene, acrylonitrile, cumene, propylene oxide etc. A lot of emphasis has been put on the expansion of propane dehydrogenation to manufacture propylene. It is important to note that 8 new propane dehydrogenation plants have been announced to be set up in the US in the near future[2]. Most of the projects are based on either of the two existing processes for propane dehydrogenation – the OLEFLEX process which uses $Pt-Sn/Al_2O_3$ introduced by UOP and the CATOFIN process which uses Cr/Al_2O_3 introduced by CB&I[3]. There is, however, a need for improving the processes in terms of the rates, selectivity and the stability of the catalysts.

Propane dehydrogenation is an endothermic reaction giving propylene and H_2 as the products. The reaction can be represented as:

$$C_3H_8 \leftrightarrow C_3H_6 + H_2$$
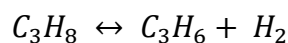
Propane dehydrogenation is an equilibrium limited reaction[3]. The thermodynamics of the reaction as well as equilibrium conversion for 5% propane concentration are given in Appendix A. This reaction is often associated with side reactions which results in loss of carbon atoms to cracking and coking. The cracking reaction gives ethylene and methane as the products and can be represented as:

$$C_3H_8 \leftrightarrow C_2H_4 + CH_4$$
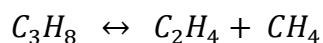
Hence, there is a need to selectively break the C-H bond vs the C-C bond of propane to minimize the loss of carbon to cracking reaction.

The propane dehydrogenation activity of bulk and supported Ga_2O_3 has been reported in the late 1980s particularly pertaining to the conversion of propane to aromatics. It has been reported that Ga_2O_3 has selectivity higher than 85% towards the C-H bond scission of propane vs the C-C bond scission[3]. The exact nature of the active site of Ga in supported Ga catalysts has been widely debated in the literature. Meitzner et al have studied the Ga/HZSM-5 catalyst and shown that the Ga is present in the reduced state under propane dehydrogenation conditions. They have shown that the reduced Ga in their catalyst is unstable and readily reoxidizes to Ga^{+3} on cooling in H_2 atmosphere[4]. Xu et al have shown that in the absence of oxidizing agent, the Ga/SiO_2 had low activity to propane dehydrogenation[5]. Biscardi et al have shown from their experiments that the C-H bond activation of propane occurs at similar rates on Ga/HZSM-5 and HZSM-5. However, the higher propane conversion observed for Ga/HZSM-5 occurs on the account of recombinative H_2 desorption aided by the Ga sites[6]. Hensen and co-workers have also studied the Ga/HZSM-5 catalyst for propane dehydrogenation and suggest that the propane is selectively converted over the monovalent Ga^+ cations as against the $[GaH_2]^+$ species[7]. This study aims to study and understand the active site for propane dehydrogenation reaction in a simplified heterogeneous catalytic system with only single site Ga atoms dispersed over an amorphous SiO_2 support without the presence of Bronsted   acid   sites.

CHAPTER 2. EXPERIMENTAL METHODS

2.1. Kinetics

Kinetics of propane dehydrogenation was measured using a plug flow quartz reactor of diameter 10 mm at atmospheric pressure. Appendix B shows the process flow diagram of the reactor system used for measurement. In order to measure blank reaction rates in empty reactor, a clean reactor was mounted in the furnace (ATS furnace 3210, 870 W, maximum temperature 1000°C) and connected to the feed gas inlet. The temperature was ramped to the reaction temperature using a Eurotherm 2408 temperature controller at the ramp rate of 10°C/min. The reaction mixture consisted of 5% propane (Matheson purity > 99.5%), 10% argon (Ultra High Purity, 99.999%) used as internal standard for gas chromatograph and balance helium (Ultra High Purity, 99.999%) to make up a total flow rate of 60 ml/min. The products were analyzed by a gas chromatograph Agilent GC 6890 equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Gaseous products detected from the reaction include propylene (C_3H_6), hydrogen (H_2), methane (CH_4) and ethylene (C_2H_4). Helium (He) was used as a carrier gas in the gas chromatograph instrument. The permanent gases such as hydrogen and argon were separated using a 2 ft Carboxen 1000 column connected to the TCD. The hydrocarbon gases were separated using 60 ft GS-GASPRO column connected to the FID.

300 mg of sieved catalyst (150 µm < dp < 250 µm) was loaded over a bed of quartz wool and quartz chips to measure the rate of propane dehydrogenation on the SiO_2 support and on the Ga/SiO_2 catalyst. The catalyst was pretreated by flowing 75 ml/min of helium over the catalyst bed for 15 minutes at room temperature. The temperature was then ramped to 100^oC and maintained for 15 minutes under helium flow. Following this, the temperature was ramped to 550^oC and maintained at 550^oC for 2 hours under helium flow. The temperature ramp rate used was 10^oC/min. After the completion of the catalyst pretreatment, the reaction mixture was fed into the fixed bed reactor at 550^oC. The conversion of the catalyst was kept below 10% to maintain differential conditions inside the reactor. The catalyst was allowed to stabilize under the reaction mixture for a period of 13 hours on stream at 550^oC after which the catalyst had achieved steady rates for propane dehydrogenation.

2.2. Catalyst pretreatment:

Three different pretreatment conditions were performed on the fresh catalyst before testing:

For the helium pretreatment, 75 ml/min helium was passed over the catalyst bed at room temperature for 15 minutes. The temperature was then ramped to 100^oC and maintained at 100^oC under helium flow for 15 minutes. Following this, the temperature was ramped to 550^oC and maintained under helium flow for 2 hours. The temperature ramp rate used was 10^oC/min.

For 1 hour H_2 pretreatment of the catalyst at 550^oC, 25 ml/min of H_2 was passed over the catalyst bed at room temperature for 15 minutes. The temperature was then ramped to

550°C at the ramp rate of 10°C/min and maintained at 550°C under H_2 flow for 1 hour. Following this, the H_2 flow was cut off and the reactor was flushed with 50 ml/min of helium for 15 minutes to remove residual H_2 gas.

For 1 hour H_2 pretreatment of the catalyst at 650°C, 25 ml/min of H_2 gas was introduced into the reactor at room temperature for 15 minutes. The temperature was then ramped to 650°C at the ramp rate of 10°C/min and maintained at 650°C for 1 hour. Following this, the H_2 flow was shut off and the reactor was flushed with 50 ml/min of helium for 15 minutes to remove residual H_2 gas. The reactor was then cooled to 550°C under the flow of helium.

2.3. 4-hour H_2 reduction:

After the catalyst was allowed to stabilize under the propane dehydrogenation reaction mixture and achieve steady rates, the feed mixture was cut off and the reactor was flushed with helium for 15 minutes to remove the residual gases. H_2 was then introduced into the reactor at 550°C at a flow rate of 25 ml/min. The temperature was ramped to 650°C at the ramp rate of 10°C/min and maintained at 650°C for 4 hours under the flow of H_2 gas. After the 4 hour reduction treatment was completed, the H_2 flow was shut off and the reactor was flushed with helium and cooled to 550°C under the flow of helium. The propane dehydrogenation mixture was then introduced for further testing of the catalyst.

2.4. Catalyst regeneration:

The catalyst was subjected to a room temperature reoxidation treatment following the 4 hour reduction treatment. For the room temperature reoxidation, the catalyst was cooled from the reaction temperature to room temperature under helium environment (50

ml/min) and was flushed with helium at room temperature for 15 minutes. The helium flow was then cut off and the catalyst was flushed with air (Commercial Grade) for 20 minutes. Following this, the air flow was stopped and the reactor was flushed with helium at room temperature for 15 minutes to remove residual air. The temperature was then ramped to $550^{o}C$ in the presence of the flow of helium through the reactor. The reaction mixture was then introduced into the reactor to test the catalyst performance after the room temperature reoxidation treatment.

2.5. Catalyst Characterization:

2.5.1. Surface Area measurement:

The BET surface area of the catalyst was measured by ASAP 2020 unit using nitrogen adsorption isotherms. The sample heated to $150^{o}C$ was degassed for 5 to 6 hours to remove any adsorbed contamination on the catalyst before measuring the BET surface area using N_2 adsorption.

2.5.2. Thermogravimetric Analysis:

The Thermo Gravimetric Analysis (TGA) of the used sample was performed on the Thermo Gravimetric Analysis unit SDT Q600 (TA instruments) capable of analyzing two samples simultaneously. 20 mg of the used sample was placed in an Al_2O_3 cup on the sample balance. 20 mg of fresh catalyst sample was placed in an Al_2O_3 cup on the reference balance. The sample was flushed with 100 ml/min helium heated upto a temperature of $150^{o}C$ under helium and maintained at that temperature for 15 minutes. This is to remove any moisture adsorbed on the catalyst. The catalyst is then cooled to $30^{o}C$ and the flow is switched to air. The temperature is ramped under the flow of air

from 30^oC to 700^oC at the rate of 10^oC/min. After the temperature equilibrated to 700^oC, it was maintained at 700^oC for 3 hours. The catalyst was then cooled to room temperature.

2.5.3. X-Ray Absorption Spectroscopy (XAS):

Operando XAS measurements were performed at the beamline of the Materials Research Collaborative Access Team (MRCAT, 10-ID) at the Advanced Photon Source at Argonne National Laboratory. The Ga K-edge was used to collect the spectra in transmission mode. The catalyst (~150 mg) was loaded in a quartz reactor (5 mm ID, 1 mm wall thickness) over a bed of quartz wool. Since the SiO_2 support and the quartz absorbs X-rays, it was essential to use a reactor with small diameter and wall thickness to minimize the attenuation of the X-Rays to the detector in order to obtain data with good signal to noise ratio. The sample was pretreated under the flow of pure H_2 at 550^oC and 650^oC for 1 hour, cooled to room temperature under He and then heated to 550^oC under the propane dehydrogenation reaction mixture (5% propane, 10% Ar, bal He). The WHSV was maintained identical to that of the reaction studies. The products were analyzed using gas chromatograph Agilent GC 6890 equipped with a TCD and FID. The temperature dependent Debye-Waller factor was estimated by the difference of the XAS spectra collected at the reaction temperature (550^oC) and room temperature. The co-ordination number was assumed to be the same at both the temperatures. The Ga_2O_3 and GaAcAc were used as reference compounds for the XAS data. The reference data was collected simultaneously as the transmission data.

2.5.4. X-Ray Photoelectron Spectroscopy (XPS):

The X-Ray Photoelectron Spectroscopy measurements were performed in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K-alpha source (1486.6 eV), magnetic immersion lens, hemispherical electron analyzer and a charge neutralization system. These provided high energy resolution and high sensitivity spectroscopic performance, allowing to achieve small surface areas of XPS analysis (diameter < 15µm). The system was operated at 75 W and 14.7 kV was applied across the anode. The high resolution XPS spectra were collected in a constant pass energy mode of 20 eV. The base pressure used for the collection of all the spectra was ~ 10^{-12} bar.

The XPS spectra were obtained for Ga/SiO_2 catalyst after different experimental conditions. First, the fresh catalyst was scanned at room temperature. The catalyst was then treated at 550^oC in H_2 flow under atmospheric pressure for 1 hour in an ex-situ reactor and then transferred to the XPS chamber for scans without exposure to air. The catalyst was then transferred back to the ex-situ reactor, treated in H_2 at 650^oC for 1 hour and scanned in XPS chamber. A second batch of fresh catalyst was crushed and pressed into the well and similar scans and treatment was performed for the pressed sample. XPS spectra for survey scans as well as high resolution scans for Ga3d, Ga2p, Si2p, O1s, O2s and C1s peaks were recorded.

The CasaXPS 2.3.14 software was used to deconvolute the spectra and perform quantification. The binding energy correction on all the spectra was calibrated to the Si2p

peak at 103.4 eV. The Shirley type background was used for all the peaks and the peaks were assumed to have a Gaussian-Lorentzian line shape.

The high resolution XPS scan for Ga3d peak showed two peaks at 21.03 eV and 19.65 eV binding energy. A sum Gaussian-Lorentzian line shape with m=30 was used to fit both the peaks. However, due to the poor signal to noise ratio of the peak, the Ga3d peaks were not used for quantification of the gallium content in the sample.

The Ga2p peaks are observed at around 1119 eV and 1117.5 eV. However, the low binding energy component for room temperature and $550^{\circ}C$ H_2 treatment samples appeared to be completely inside the high binding energy component and thus can be treated as an attribute of the XPS fitting procedure being consistent for all scans and not a real peak. The binding energy of both the high and low binding energy components for all the samples has been reported. A sum Gaussian-Lorentzian line shape with m=30 was used to fit both the peaks. The relative sensitivity factors for both the peaks were taken to be 21.4 which is the standard value for Ga^{+3}. The position of the two peaks is constrained to be at a binding energy distance of 1.38 eV which is the same as the binding energy distance between the 3d peaks. The Ga2p peaks were used for quantification of Ga due to the better signal to noise ratio. The O1s peak was also fitted with two component peaks. The Si2p peak was fitted with one peak component. The C1s peak has poor signal to noise ratio and was not used as reference as well as for quantification of the other elements.

2.5.5. *In-situ* Fourier Transform Infrared Spectroscopy:

The sample was studied using *in-situ* Fourier Transform Infrared Spectroscopy under conditions of H_2 reduction and propane dehydrogenation reaction to understand the nature of the adsorbed species on the surface of the catalyst. About 80 mg of sample was ground and pressed into a self-supporting wafer of diameter 20 mm and mounted inside a 1" quartz cell sealed with CaF_2 windows. The cell is housed inside a coiled heating rod (Ari heating cable, 20" long, 0.125" diameter, 1500W) surrounded by a ceramic block which is well insulated from the outside. The temperature of the cell was controlled by Eurotherm 2408 temperature controller and two thermocouples on either side of the wafer were used to read the temperature. The infrared spectra were recorded by Nicolet 4700 FTIR instrument and OMNIC software was used to save, view and process the spectra. All spectra were collected at $100^{o}C$, $200^{o}C$, $300^{o}C$, $400^{o}C$, $500^{o}C$, $550^{o}C$, $600^{o}C$ and $650^{o}C$ to observe variations in the sample with respect to temperature.

Empty cell backgrounds with inert and 5% propane in inert mixture were recorded. The sample wafer was then mounted inside the cell and sample spectra in inert gas flow (10% argon, balance helium) were recorded at the same temperatures as mentioned above. The sample was then exposed to H_2 at room temperature and the temperature was ramped to $550^{o}C$. The sample was treated at $550^{o}C$ with H_2 for 1 hour and spectra were collected every 15 minutes. The sample was then heated to $650^{o}C$ in H_2 and treated at $650^{o}C$ for 4 hours. The spectra were recorded every 15 minutes for 1 hour and then every 30 minutes. After the reduction treatment, the sample was cooled to room temperature in inert flow.

The sample was then exposed to the propane dehydrogenation reaction mixture (5% propane, 10% argon, balance helium) at room temperature and the temperature was ramped to 550°C and the spectra were collected every 30 minutes for 2 hours. Following this, the sample was cooled to room temperature in inert and reheated to 650°C in H_2 and the reduction treatment at 650°C was performed for 4 hours. The sample was then cooled to 550°C in inert and exposed to the propane dehydrogenation reaction mixture for 1 hour.

CHAPTER 3. RESULTS

3.1. Kinetics:

3.1.1. Catalyst stabilization:

The catalysts used for propane dehydrogenation are known to deactivate over time on stream[8]. A typical catalyst deactivation curve is shown in Figure 3. 1
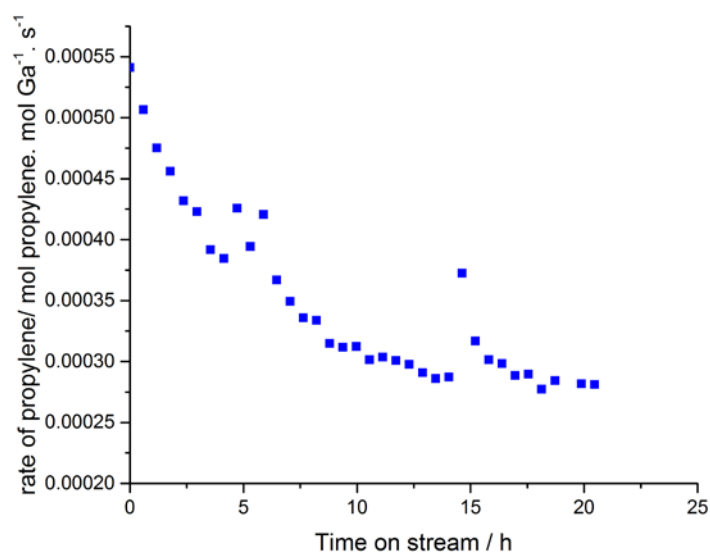
Figure 3. 1: Catalyst stabilization studies over 3% Ga/SiO$_2$ catalyst at 5% propane concentration and temperature of 550°C

It can be seen that the catalyst achieves stabilized rate after 13 hours on stream under propane dehydrogenation at 550°C. The Table 3. 1 summarizes the initial and stabilized rate of propane dehydrogenation, ratio of the dehydrogenation rate to cracking rate and the products selectivities.

Table 3. 1: Summary of results of propane dehydrogenation on 3% Ga/SiO_2 catalyst at 550°C, 5% propane in inert

Initial Rate/ 10^{-4} mol propylene. mol Ga^{-1}. s^{-1}	5.4 ± 0.3
Stabilized Rate/ 10^{-4} mol propylene. mol Ga^{-1}. s^{-1}	2.7 ± 0.1
Dehydrogenation Rate: Cracking Rate	41 ± 3
Propylene Selectivity/ %	95
Ethylene Selectivity/ %	2.5
Methane Selectivity/ %	2.5

The stabilized rate of the catalyst is $2.7 \pm 0.1 \cdot 10^{-4}$ mol propylene. mol $Ga^{-1}.s^{-1}$. The rate has been normalized to the total moles of gallium being the weight loading of 3wt% Ga. The catalyst deactivates to approximately 40% of its initial rate. The deactivation of the catalyst after stabilized rate is achieved is about 10%. The deactivation could be attributed to sintering or coking[3].

3.1.2. Blank reactor rates:

The blank reactor rates were measured in an empty reactor because the propane dehydrogenation reaction is known to occur in the gas phase in the absence of catalyst[3].

Propane dehydrogenation reaction was also performed on the SiO_2 support along with the quartz chips and quartz wool in order to test their activity towards the dehydrogenation or cracking reactions. The results are summarized in Table 3. 2. The apparent activation energy for the empty reactor, SiO_2 support and Ga/SiO_2 catalyst has been compared in Figure 3. 2
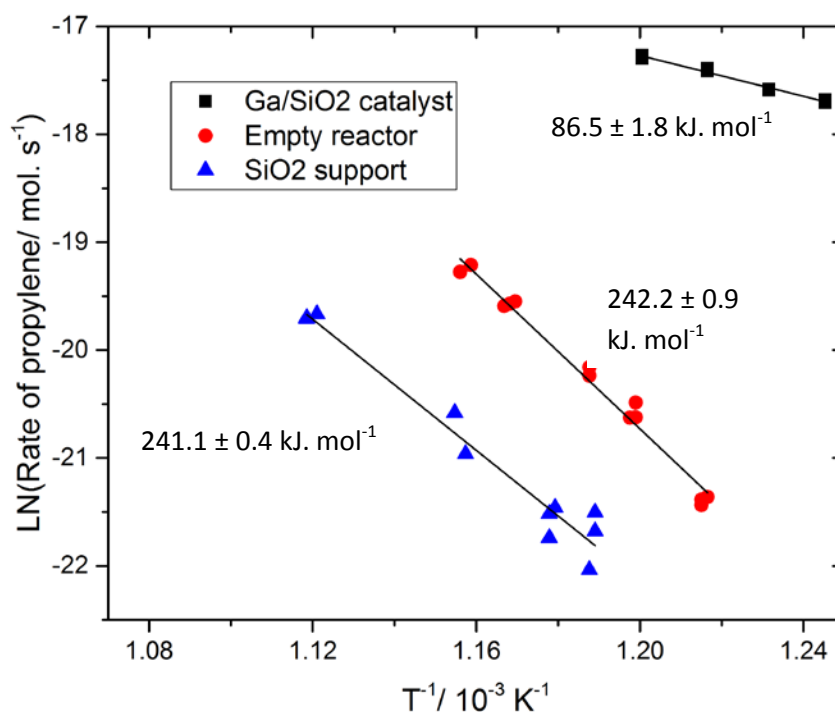
Figure 3. 2: Arrhenius plot comparison of Ga/SiO_2 catalyst with Empty Reactor and SiO_2 support

Table 3. 2: Comparison of results of propane dehydrogenation in empty reactor, SiO_2 and

Ga/SiO_2 at 550°C, 5% propane in inert

	Empty Reactor	SiO_2	Ga/SiO_2
Apparent activation energy of propane dehydrogenation/ kJ. mol^{-1}	242.2 ± 0.9	241.1 ± 0.4	86.5 ± 1.8
Apparent activation energy of propane cracking/ kJ. mol^{-1}	253.8 ± 0.4	259.3 ± 2.9	195.3 ± 5.8
Selectivity of propylene/ %	40%	40%	95%
Selectivity of ethylene/ %	15%	15%	2.5%
Selectivity of methane/ %	45%	45%	2.5%

It can be seen that the catalyst significantly decreases the apparent activation energy for the dehydrogenation reaction. It can be seen that the catalyst also decreases the apparent activation energy for the cracking reaction. However, the activation energy for the dehydrogenation reaction is significantly lower than the cracking reaction. The catalyst

performs the function of more selective C-H vs C-C bond cleavage compared to the gas phase reaction as well as reaction on SiO_2 support.

The order of propane for the dehydrogenation reaction has been measured along with order for cracking reaction. The Figure 3. 3 shows the graphs for the propane order for both the reactions.
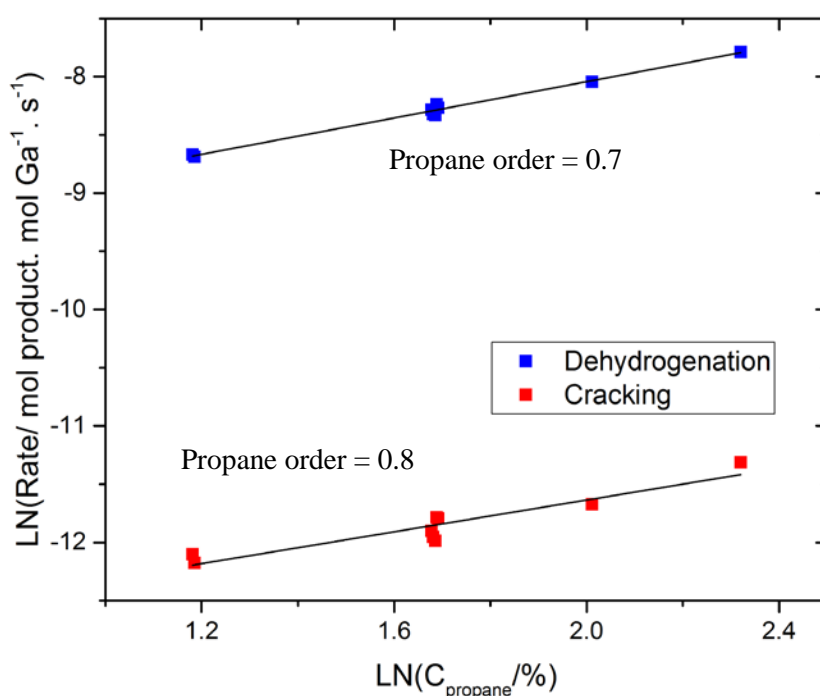
Figure 3. 3: Comparison of propane order on Ga/SiO_2 catalyst for dehydrogenation and cracking reactions

The apparent propane order for the dehydrogenation reaction is equal to 0.8 and is equal to that of the cracking reaction. This would indicate that the first step for propane activation for both the reactions might be the same. The intermediate formed as a result

of the propane activation on the catalyst could then undergo two separate pathways to give the dehydrogenation products and the cracking products.

3.1.3. Effect of catalyst pretreatment:

It has been debated in the literature about the nature of the active Ga for the propane aromatization reaction. Meitzner et al have suggested that the reduced form of Ga is the active form of the catalyst for propane dehydrogenation followed by aromatization on Ga/HZSM-5 catalyst[4]. Rane and co-workers have suggested that Ga^+ cations are the active site for propane dehydrogenation in Ga/HZSM-5 and have suggested that $[GaH_2]^+$ species formed during prereduction steps have lower activity for the propane dehydrogenation reaction[9].

In order to test if this theory also applies to the Ga/SiO_2 catalyst, it was decided to follow three different pretreatment procedures for the catalyst before testing it for propane dehydrogenation reaction. A batch of catalyst was pretreated with helium at 550^oC for 2 hours, a second batch was pretreated with H_2 at 550^oC for 1 hour and a third batch of catalyst was pretreated with H_2 at 650^oC for 1 hour. The stabilization curves are shown in Figure 3. 4 for comparison of the catalyst behavior after the three pretreatment conditions. The initial and final rates on the three samples are summarized in Table 3. 3.
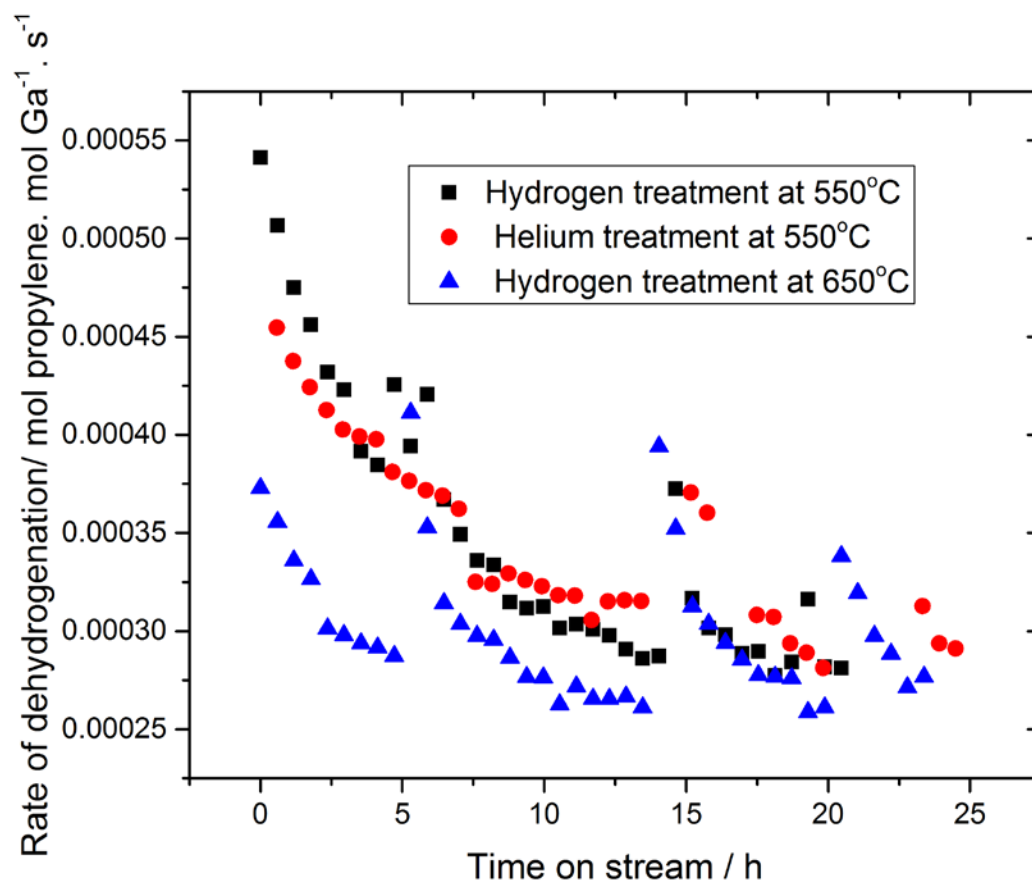
Figure 3. 4: Comparison of stabilization following three different catalyst pretreatment

conditions

Table 3. 3: Initial and final rates of propane dehydrogenation on Ga/SiO_2 catalyst at 550°C, 5% propane in inert under different pretreatment conditions of the catalyst

Pretreatment	Initial rate of dehydrogenation/ mol propylene. mol Ga^{-1}. s^{-1}	Final rate of dehydrogenation/ mol propylene. mol Ga^{-1}. s^{-1}
Helium for 2 h at 550°C	$5.4 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$
H_2 for 1 h at 550°C	$5.1 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$
H_2 for 1 h at 650°C	$3.7 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$

It can be seen that the catalyst samples pretreated with helium or H_2 at 550°C shows the same initial rates whereas the sample pretreated at 650°C with H_2 for 1 hour shows a lower initial rate for propane dehydrogenation by about 1.4 times than the samples treated with H_2 or helium at 550°C. This indicates that the effect of the reduction treatment at 650°C is to transform the Ga into an inactive or a less active form. The final rate of all the samples was equal irrespective of the pretreatment performed.

To verify the effect of the reduction treatment on the stabilized rate of the catalyst, a catalyst sample was subjected to the 4 hour reduction treatment at 650°C as described in Section 2.3. It was observed that the rate of the catalyst after prolonged reduction treatment was 2.5 times lower than the stabilized rate of the catalyst before the treatment. For the latter, the rate of propane dehydrogenation was $1.1 \pm 0.1 \cdot 10^{-4}$ mol. mol $Ga^{-1}.s^{-1}$.

Figure 3. 5 shows the comparison of the catalyst rates during the stabilization and after the 4 hour reduction treatment. This experiment confirms that the catalyst becomes less active after the reduction treatment and this indicates that the reduced form of Ga is less active or inactive for propane dehydrogenation.
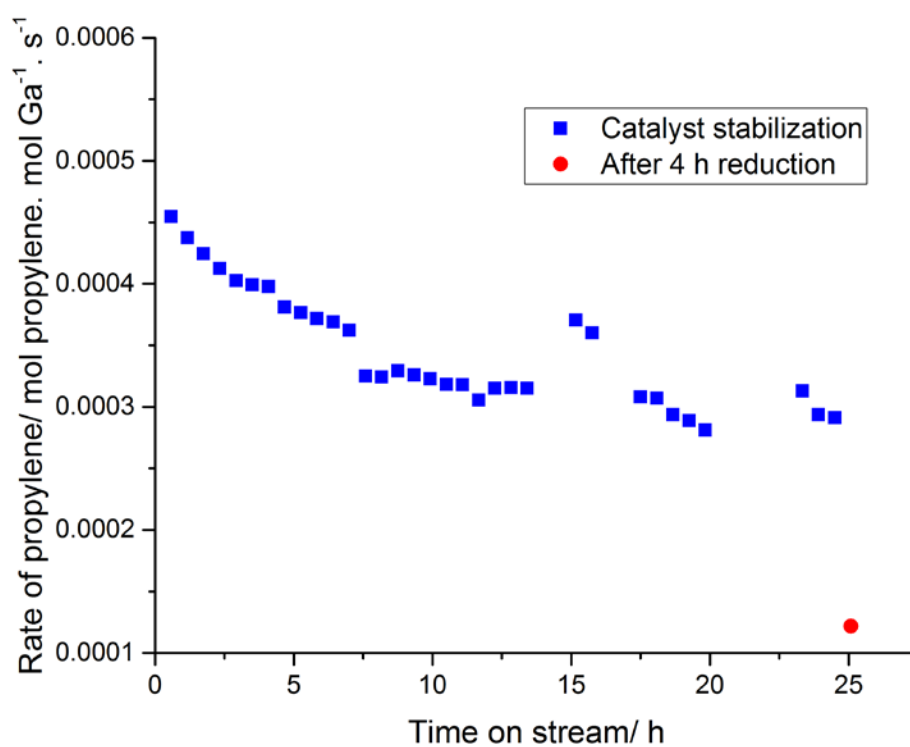
Figure 3. 5: Comparison of propane dehydrogenation rate after 4 h reduction with the stabilized rate of catalyst under 5% propane concentration at a temperature of $550^{o}C$

Following this, to observe if the reduction treatment may result in permanent damage of the gallium active sites for the propane dehydrogenation reaction, the catalyst was

oxidized with air flow at room temperature. The purpose of the catalyst reoxidation at room temperature was separate the effect of reoxidation of the gallium sites from the convolution of combustion of the coke deposited on the catalyst surface. The initial rate of propane dehydrogenation on the catalyst at 550ºC, after reoxidation treatment at room temperature, was higher than the initial rate obtained on fresh catalyst. This is an interesting observation that the catalyst can be reactivated in oxidizing atmosphere at room temperature after prolonged reduction treatment and this has not been reported in the literature. Figure 3. 6 shows the graph of the catalyst during initial stabilization followed by the room temperature reoxidation.
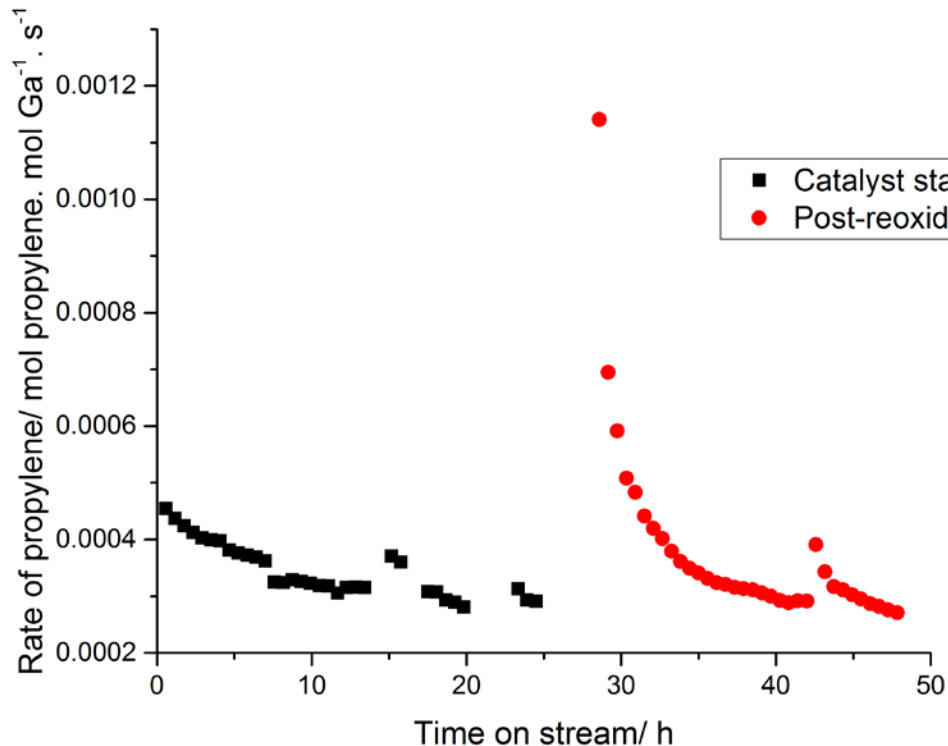
Figure 3. 6: Comparison of the initial stabilization curve of the catalyst with that after the

reoxidation

The stabilized steady state rate of the reoxidized catalyst is the same as the stabilized rate

of the fresh 3% Ga/SiO_2 catalyst indicating that the reduction treatment does not diminish

the catalyst performance permanently. This indicates that the reduced Ga can be

reversibly reoxidized after exposure to air at room temperature. This reoxidized Ga is

similar to Ga^{+3} in the fresh catalyst in terms of its final rates for propane

dehydrogenation. However, the initial rate of the catalyst after the reoxidation is higher

than that of the fresh catalyst which might indicate a different mechanism of the

deactivation of the reoxidized catalyst. The initial rate of the catalyst after the room

temperature reoxidation treatment decreases to the stabilized rate after a period of ~13 hours on stream.

3.2. BET surface area and Thermo Gravimetric Analysis:

The BET surface area of the catalyst was measured to be about 295 m^2/g.

The mass of coke per mass of dry catalyst calculated from the TGA was found to be 0.012. Hence, the total coke formed on the catalyst from the TGA analysis would be about 7 mg. If one assumes a coverage of 10^{15} atoms. cm^{-2} of carbon, then it would account for covering 20% of the BET surface area of the catalyst. However, the catalyst deactivation from the initial rate was shown to be about 40%. Since the metal site for performing dehydrogenation is Ga and the SiO_2 support was shown to be inactive for the reaction, it would be reasonable to say that the coke would cover the Ga sites and this would explain the deactivation[3]. However, we do not have the data showing the number of single site Ga before and after the reaction and hence, sintering of the catalyst cannot be ruled out as the cause of deactivation of the catalyst.

3.3. X-Ray Absorption Spectroscopy:

In order to understand the difference in the reaction rates and to correlate to the oxidation state and the co-ordination number of the gallium in the catalyst, X-Ray Absorption spectroscopy experiments were performed under *operando* conditions. It was observed in the XANES region that the Ga remains in the +3 oxidation state throughout the run when the catalyst is pretreated with H_2 at 550°C, when compared to the Ga_2O_3 and GaAcAc references for the Ga^{+3} as shown in Figure 3. 7.
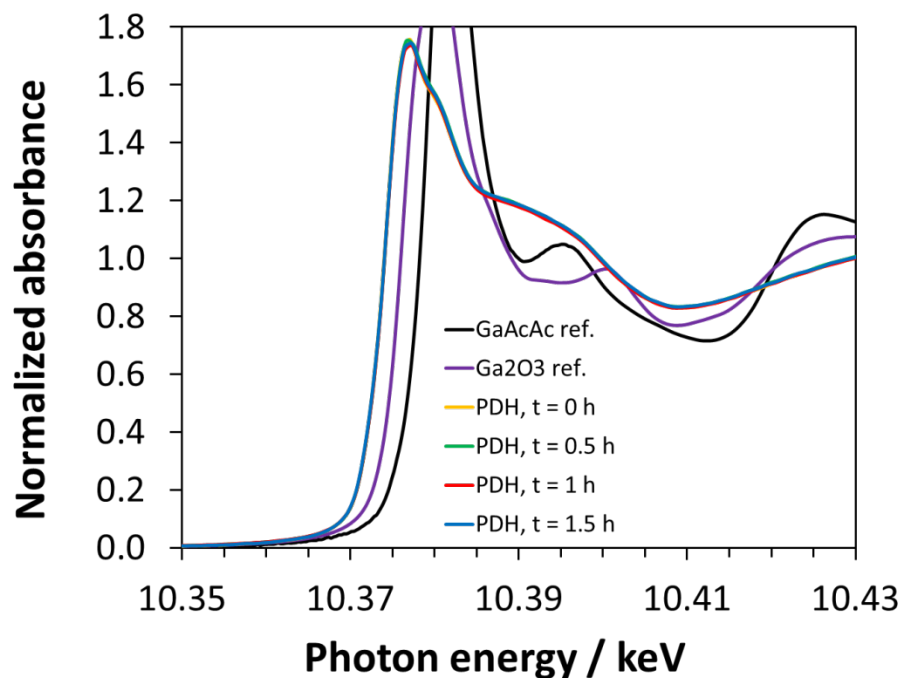
Figure 3. 7: XANES pattern of 3% Ga/SiO$_2$ after treatment with H$_2$ at 550°C for 1 h

At these experimental conditions, the EXAFS data shows that Ga remains 4 co-ordinate throughout the run and the Ga in the catalyst is present in a tetrahedral geometry. The EXAFS isolated first shell data shows that there is only Ga-O co-ordination and no Ga-Ga co-ordination. The EXAFS isolated first shell results also indicate that the Ga-O bond distance remains constant throughout the run at 1.80 Å. This indicates that the active site for the propane dehydrogenation reaction would be a 4 co-ordinate Ga^{+3} site. The results are summarized in Table 3. 4.

Table 3. 4: Summary of *operando* XAS results for Ga/SiO$_2$ catalyst pretreated with H$_2$ at 550°C for 1 h during propane dehydrogenation at 550°C, 5% propane in inert

Sample	Rate/ mol C$_3$H$_6$. mol Ga^{-1}. s^{-1}	t/ h	N	R$_{Ga-O}$/Å	σ^2
3% Ga/SiO$_2$ under PDH 550°C	-	0	4.12 ± 0.01	1.80 ± 0.01	0.006
	6.61 × 10^{-4}	0.5	4.07 ± 0.04	1.80 ± 0.01	0.006
	6.25 × 10^{-4}	1	4.01 ± 0.01	1.80 ± 0.01	0.006
	6.42 × 10^{-4}	1.5	4.10 ± 0.04	1.80 ± 0.01	0.006
	6.46 × 10^{-4}	2	4.04 ± 0.04	1.80 ± 0.01	0.006
	6.62 × 10^{-4}	2.5	3.91 ± 0.04	1.80 ± 0.01	0.006
3% Ga/SiO$_2$ under He 550°C		3	4.03 ± 0.04	1.80 ± 0.01	0.006

For the catalyst pretreated with H$_2$ at 650°C for 1 hour, the XANES region exhibited the formation of a shoulder at around 10,370 eV as shown in Figure 3. 8 when compared to Ga^{+3} catalyst which was treated at 550°C for 1 h.
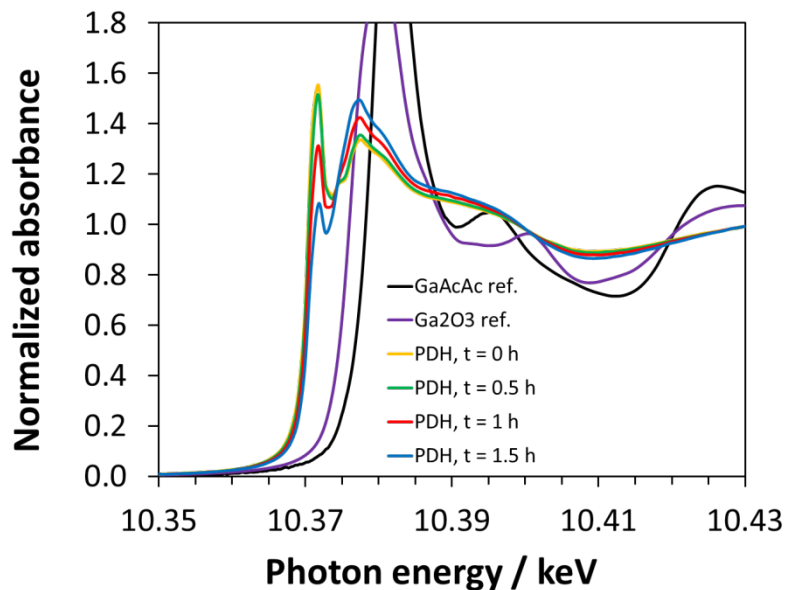
Figure 3. 8: XANES pattern of 3% Ga/SiO$_2$ after reduction in H$_2$ at 650°C for 1 h

This shoulder at ~10,370 eV has been assigned to the lower oxidation state of the gallium

Ga$^{+\delta}$ (δ < 3) after the reduction of Ga^{+3} [4]. The XANES region shows that post reduction

pretreatment, both Ga^{+3} and Ga$^{+\delta}$ are present in the sample. During the course of the

reaction, the Ga$^{+\delta}$ decreases and there is a corresponding increase in the Ga^{+3} in the

sample. The Ga in the sample is initially 2.7 co-ordinate and appears to increase the co-

ordination throughout the run as the Ga$^{+\delta}$ decreases and the Ga^{+3} increases as shown in

Table 3. 5.

Table 3. 5: Summary of *operando* XAS results for Ga/SiO$_2$ catalyst pretreated with H$_2$ at

650°C for 1 h during propane dehydrogenation at 550°C, 5% propane in inert

Sample	Rate/ mol C$_3$H$_6$. mol	t/ h	N	R$_{Ga-O}$/Å	σ^2

	Ga^{-1}. s^{-1}				
3% Ga/SiO$_2$ under PDH 550$^{\text{o}}$C	5.49×10^{-4}	0	2.66 ± 0.04	1.80 ± 0.01	0.006
	7.40×10^{-4}	0.5	2.72 ± 0.04	1.79 ± 0.01	0.006
	4.56×10^{-4}	1	2.96 ± 0.04	1.80 ± 0.01	0.006
	9.06×10^{-5}	1.5	3.21 ± 0.04	1.80 ± 0.01	0.006

The sample pretreated with H$_2$ at 550$^{\text{o}}$C was exposed to the propane dehydrogenation reaction mixture for 3.0 hours whereas the sample pretreated with H$_2$ at 650$^{\text{o}}$C was exposed to the reaction mixture for 1.5 hours. The sample treated at 550$^{\text{o}}$C showed stable rates of propane dehydrogenation whereas the sample treated at 650$^{\text{o}}$C showed decreasing dehydrogenation rates with respect to time on stream. The propylene selectivity in both the cases was > 95%. The initial rates were observed to be the same in both the samples.

Since the rates studies performed previously indicated that the final rate of the catalyst pretreated with H$_2$ 650$^{\text{o}}$C is same as that pretreated with H$_2$ at 550$^{\text{o}}$C, it was essential to study the stability of the Ga$^{+\delta}$ species formed as a result of the reduction pretreatment at 650$^{\text{o}}$C. Figure 3. 9 shows the normalized absorbance of the Ga$^{+\delta}$ species during the reduction treatment at 650$^{\text{o}}$C and after the reduction treatment.
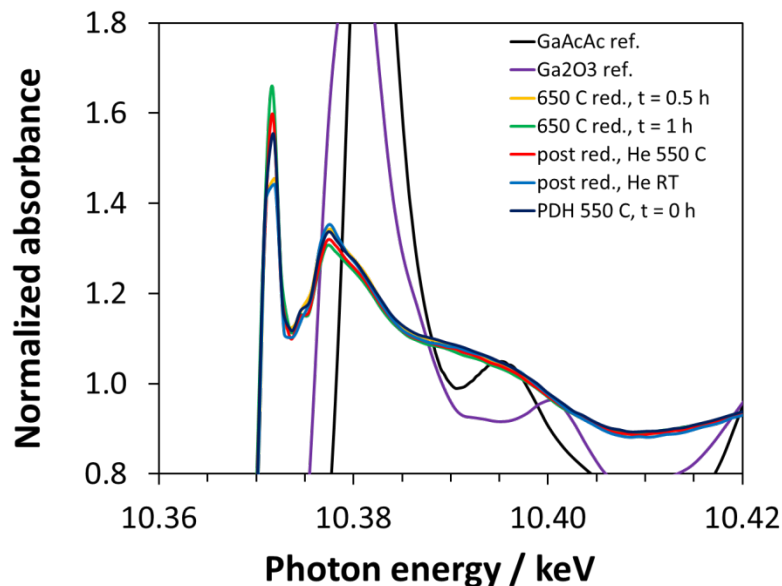
Figure 3. 9: Ga K-edge XANES during H_2 treatment at $650^{\circ}C$ and stability of the $Ga^{+\delta}$ thereafter

It can be seen that the $Ga^{+\delta}$ increases with the reduction time. As the catalyst was cooled under He post reduction to room temperature and back to the reaction temperature to account for the Debye-Waller factor, the $Ga^{+\delta}$ species decreased during the cooling to room temperature and then increased while heating to $550^{\circ}C$ in propane dehydrogenation reaction mixture. The decrease can be attributed to thermal effects. There is a slight total decrease of $Ga^{+\delta}$ species before the start of the propane dehydrogenation reaction at $550^{\circ}C$ compared to the post reduction sample under He at $550^{\circ}C$. Thus it can be seen that the $Ga^{+\delta}$ species remain fairly stable when cooled under helium to room temperature and heated back to the reaction temperature under He. The co-ordination number of the Ga in the catalyst also remains stable to a value of about 2.7 and the Ga-O bond distance also remains stable at 1.8 Å as shown in Table 3. 6.

Table 3. 6: EXAFS isolated first shell results during H_2 reduction at 650^oC

Sample	N	R_{Ga-O}/Å	σ^2
3% Ga/SiO$_2$ under H$_2$ 650 °C, t = 0.5 h	2.69 ± 0.04	1.80 ± 0.01	0.0065
3% Ga/SiO$_2$ under H$_2$ 650 °C, t = 1 h	2.52 ± 0.04	1.79 ± 0.01	0.0065
3% Ga/SiO$_2$ post H$_2$ 650 °C, under He 550 °C	2.63 ± 0.04	1.79 ± 0.01	0.006
3% Ga/SiO$_2$ post H$_2$ 650 °C, under He RT	2.64 ± 0.04	1.80 ± 0.01	0.004
3% Ga/SiO$_2$ post H$_2$ 650 °C, under PDH 550 °C, t = 0 h	2.66 ± 0.04	1.80 ± 0.01	0.006

According to Meitzner et al, the $Ga^{+\delta}$ species are formed at 507^oC under the flow of H$_2$ or propane[4]. They have also observed that the $Ga^{+\delta}$ species are unstable since cooling under H$_2$ resulted in the reoxidation of the $Ga^{+\delta}$ to Ga^{+3} which the authors claim is stabilized by the zeolite framework O atoms. The observations presented by the authors are in contradiction of the results presented in this work. This may be because the catalyst that they have tested is Ga/HZSM-5 which has Bronsted acid sites that are not found in the Ga/SiO$_2$ catalyst. It may be possible that the effect of the presence of Bronsted acid sites is to aid the associative desorption of H$_2$ from the catalyst surface thereby oxidizing the $Ga^{+\delta}$ back to Ga^{+3}.

Meitner et al have performed *in-situ* XAS studies on Ga/HZSM-5 catalyst under various conditions of reduction and propane dehydrogenation followed by aromatization. They have reported that the reduction performed at $507^{o}C$ results in the formation of Ga metal first and as reduction progresses, results in the formation of steady state GaH_x species. The authors claim that the GaH_x species should have Ga in the reduced form and have mentioned in the paper that the oxidation state is between 0 and 1. In a separately performed temperature programmed reduction experiment, the authors have observed that the consumption of H_2 during the TPR is consistent with the decrease in the oxidation state of the Ga from +3 to +1. Since the edge measurements of their XAS data show that there is no Ga^{+3} present in the sample suggest that the $Ga^{+\delta}$ is in fact present in a hydride form stabilized by interactions with the framework O atoms of the HZSM-5 zeolite. The observed co-ordination number of the Ga decreases from 6 (octahedral Ga^{+3}) to 1 during the reduction treatment at $500^{o}C$. This reduction of Ga however, does not occur at room temperature as shown by their XAS as well as H_2 chemisorption results as a function of temperature. The authors have claimed that the active state of Ga in the Ga/HZSM-5 catalysts during propane dehydrogenation/aromatization is $Ga^{+\delta}$. According to the authors, these Ga sites cause the recombinative desorption of the hydrogens in the propane dehydrogenation/ aromatization reactions which causes the Ga to follow a redox cycle[4].

Rane and co-workers have synthesized a Ga/HZSM-5 catalyst using a synthesis route that involves vapor phase deposition of tri-methyl gallium (TMG) over HZSM-5 support followed by removal of the methyl ligands by reduction under H_2 flow at $550^{o}C$. They

claim that the resulting catalyst has a mixture of $[GaH_2]^+$ and Ga^+ species which charge balance the framework O atoms of the zeolite and by their IR studies observed that the zeolite has no Bronsted acid sites. The authors have performed *in-situ* XAS studies in which they have reduced the TMG/HZSM-5 sample under H_2 at different temperatures (150°C to 520°C). They observe that the absorption maximum of Ga shifts to a higher energy which is attributed to the formation of $[GaH_2]^+$ species. At temperatures higher than 400°C, a shoulder is observed with a maximum at 10371.5 eV which the authors have attributed to the presence of Ga^+ which they claim is formed as a result of decomposition of the hydride. On cooling of the sample under H_2, the authors observe a decrease in the shoulder and they have assigned this behavior to the oxidative addition of the H_2 to the Ga^+ to form $[GaH_2]^+$. This behavior was also observed by Meitzner et al who have assigned this behavior to the increased interaction of the Ga species with the framework O atoms. The authors have tested the reduced TMG/HZSM-5 catalyst for propane dehydrogenation reaction and have observed that the conversion of the reduced catalyst samples at 550°C increases with time. They propose that this observation indicates the slow decomposition of $[GaH_2]^+$ species formed during the reduction of Ga into Ga^+ cations and that the Ga^+ cations are the active site for propane dehydrogenation reaction. However, no evidence of the state of gallium under propane dehydrogenation conditions has been presented[9].

Hensen et al have described the procedure for the synthesis of TMG/ZSM5 catalyst used in the study by Rane and co-workers[7]. They have studied the removal of the ligands using *in-situ* XAS and have observed that for the as synthesized catalyst, the Ga is co-ordinated

with two C atoms and one O atom. Their studies on *in-situ* IR spectroscopy show that the catalyst has no Bronsted acid sites[9]. This means that monovalent methyl gallium species have charge substituted the zeolite. On reduction, it was observed that methane is generated and a pre-edge feature at lower absorption energy is observed in their XANES spectra. We observe a similar pre-edge feature at lower energy after the reduction of the Ga/SiO$_2$ catalyst. The authors have attributed the shift that they have observed to formation of Ga$^+$ cations. The authors have already shown that it is unlikely to form $[GaH_2]^+$ species[10]. However, they have not commented on their EXAFS results for the Ga-O co-ordination for the reduced samples. Frash and Van Santen in their earlier findings had proposed that the ethane activation during ethane dehydrogenation occur on $[GaH_2]^+$ species based on first principles calculation[11]. However, they have revised their results to show that $[GaH_2]^+$ is unstable and decompose to Ga$^+$. From their H$_2$/D$_2$ switch experiments, the authors have concluded that the GaO$^+$ species are more likely to activate H$_2$ than the Ga$^+$ species. Based on this, the authors have surmised that the rate of alkane activation on Ga$^+$ is small because of the weak interaction of Ga$^+$ with hydrocarbon molecules that they expect[7].

This study indicates that the result of the reduction treatment at 650°C is the formation of a low co-ordinate Ga$^{+\delta}$. This species is stable for the time period of the measurements performed at the synchrotron source. However, the results in this work show that after keeping the catalyst at 550°C under inert overnight results in rates that are similar to Ga^{+3}. This might suggest that the Ga$^{+\delta}$ species formed might not be stable at 550°C under inert for long period of time. Due to the absence of a reference compound for oxidation

states of Ga lower than +3, it was not possible to quantify the amount of $Ga^{+\delta}$ or the relative ratio of Ga^{+3}:$Ga^{+\delta}$ or identify δ. However, it is possible that δ is +3 but the Ga is bonded to H atoms and is 3 co-ordinate with O atoms of the silica surface.

3.4. X-Ray Photoelectron Spectroscopy:

Table 3. 7 lists the binding energies for the detected elements on the Ga/SiO_2 catalyst surface after different treatment conditions described in Section 2.5.4. The peak fitting procedures are described in Section 2.5.4.

Table 3. 7: XPS binding energy of electrons for elements detected in Ga/SiO_2 catalyst

Peak	As-is sample binding energy/ eV			Pressed sample binding energy/ eV		
	Room Temperature	550^oC under H_2	650^oC under H_2	Room temperature	550^oC under H_2	650^oC under H_2
Ga2p (HBE)	1118.8	1119.0	1119.0	1118.4	1119.0	1119.1
Ga2p (LBE)	1117.4	1117.6	1117.6	1117.0	1117.6	1117.8
O1s (HBE)	533.9	533.9	533.9	533.9	533.9	533.9
O1s (LBE)	532.5	532.5	532.5	532.2	532.5	532.6
O2s	25.3	25.4	25.2	25.3	25.4	25.0
Ga3d (HBE)	21.0	21.0	21.0	21.0	21.0	21.0

Ga3d (LBE)	19.7	19.7	19.7	19.7	19.7	19.7
Si2p	103.3	103.4	103.3	103.3	103.4	103.4

All the XPS spectra were calibrated to Si2p region which was fixed at a value of 103.4 eV binding energy. A slight variation in the binding energy of the Si2p can be seen which arises out of fitting component peak within the Si2p region. In order to remove the complications of sample charging and reference energy, the binding energy difference of various peaks were compared to the literature values. The O1s peak observed in this work at binding energy of 532.5 eV maintains a difference of 429.1 eV with respect to the Si2p peak at 103.4 eV. This difference is close to that reported in the literature which is 429.4 eV for Ga_2O_3/SiO_2 catalyst and Ga_2O_3/HZSM-5 and is also typical of values for SiO_2[12,13,14]. A small component peak can also be found for the O1s at a binding energy of 533.9 eV as shown in Figure 3. 10.
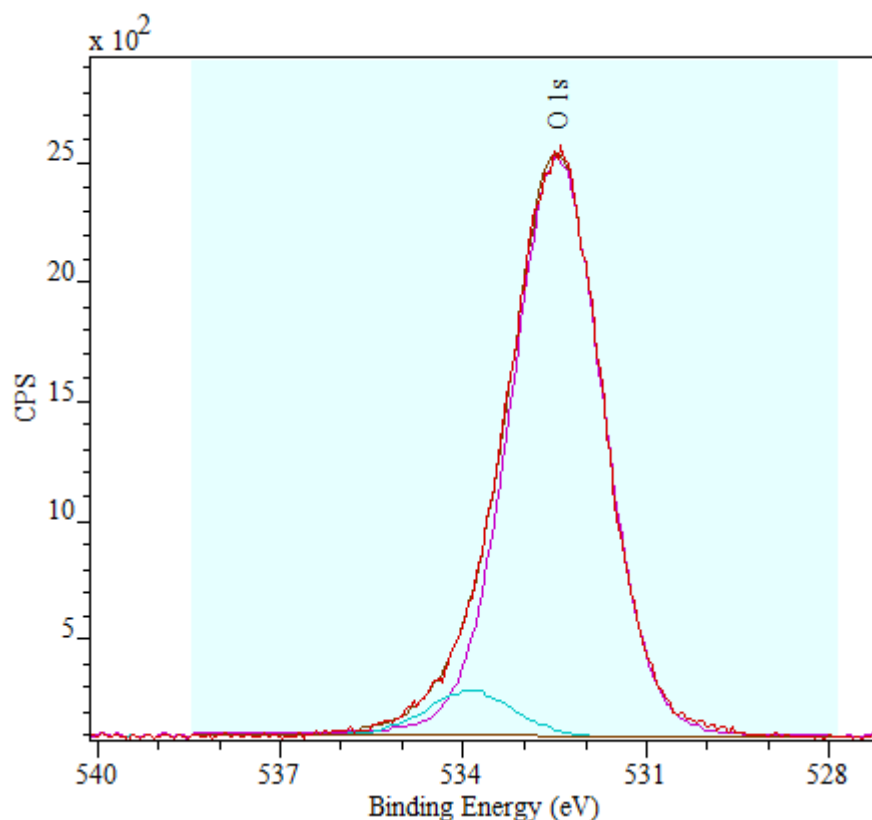
Figure 3. 10: XPS high resolution scan of O1s region

It was noted that this binding energy does not correspond to O1s peak of any possible surface Ga_2O_3 because the O1s of surface Ga_2O_3 is expected to be at about 531 eV[12,15,16]. Hence, this peak can be assigned to the bridging oxygen atom in the SiO_2 support[17]. The binding energy difference between the O1s low binding energy peak and the O2s peak is about 507.3 eV and matched with the literature values[13,12]. The assignment of other peaks was made based on the comparison with literature values of the difference in the binding energy of the peak and the Si2p peak. Comparison was also made of the difference in binding energy of a given peak and the O1s peak with the literature values and it yielded

similar results. All comparisons with literature matched within a binding energy of ± 0.5 eV or less.

In regard to this, the Ga2p peak at 1119 eV was assigned to Ga^{+3} [12,16,18]. Similarly, the Ga3d peak at 21 eV has been assigned to Ga^{+3} [13,18,19]. Figure 3. 11 and Figure 3. 12 show the two peaks for Ga^{+3} in the Ga2p and the Ga3d region.
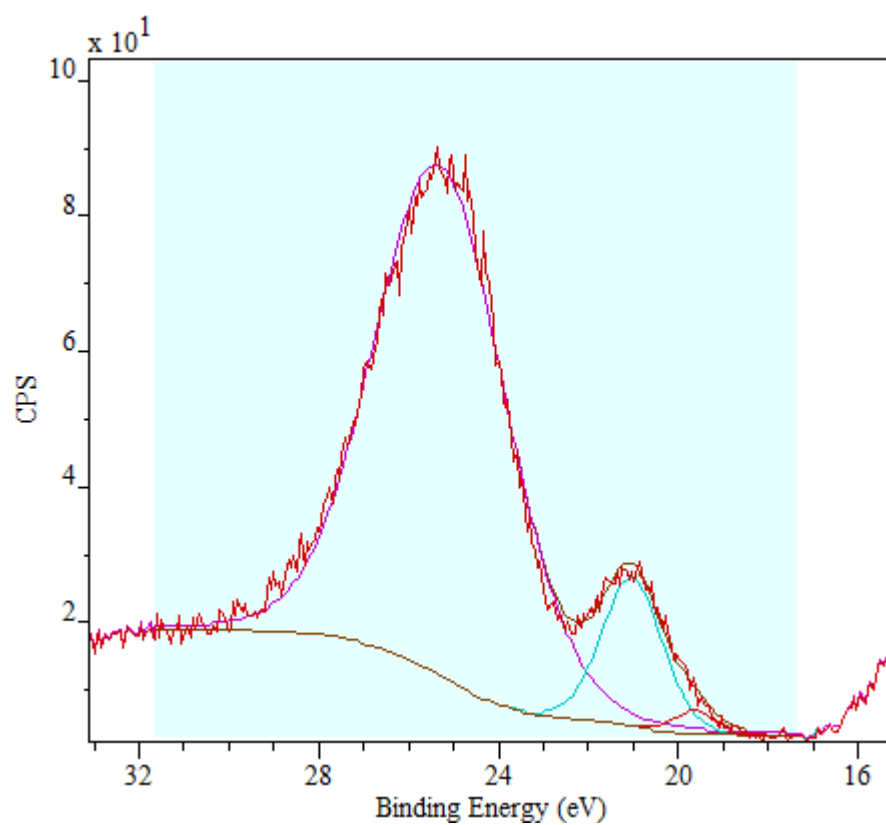
Figure 3. 11: XPS high resolution scan of O2s and Ga3d region for Ga/SiO$_2$ catalyst treated with H$_2$ at room temperature
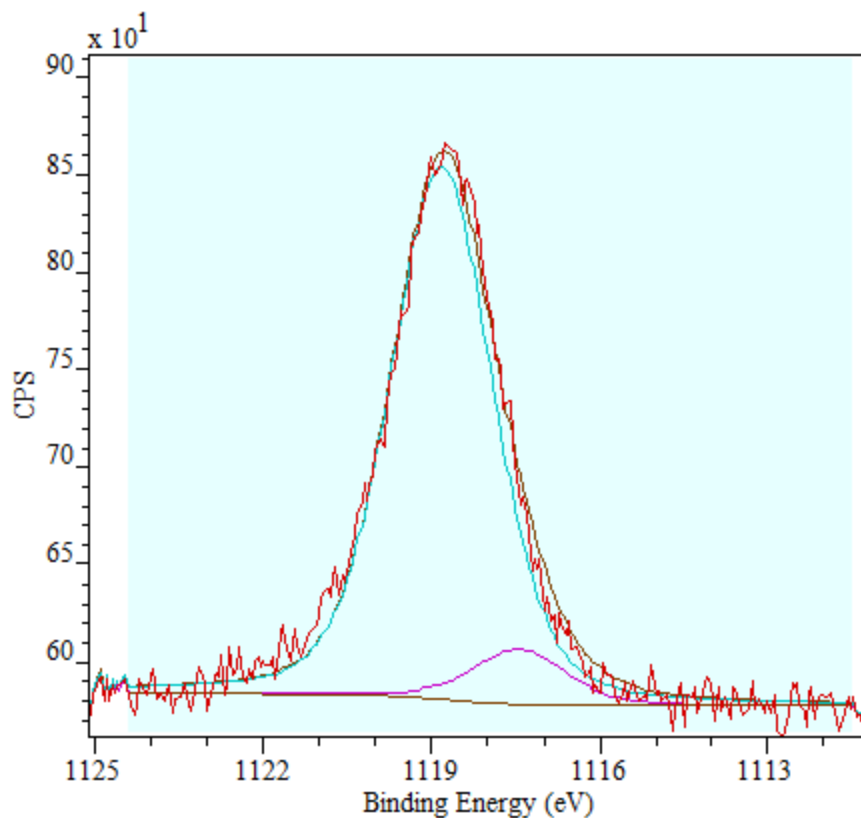
Figure 3. 12: XPS high resolution scan of Ga2p region for Ga/SiO$_2$ catalyst treated with

H$_2$ at room temperature

The Ga3d region overlaps with the O2s region as shown in Figure 3. 11. The low binding energy component peak for the Ga fits appears as a result of the peak fitting procedures as described in Section 2.5.4. Hence, for the sample that was not subjected to any reduction treatments, all the Ga was present in the +3 oxidation state as also confirmed by our XAS results.

It was observed in the Ga2p region, that a second peak forms at a binding energy of 1117.5 eV after reduction treatment at 650°C as seen in Figure 3. 13. This peak has been assigned to Ga$^{+\delta}$ where $0 < \delta < 3$ [12,18,19]. This peak is more pronounced in the Ga3d

region which is observed at a binding energy of 19.6 eV as shown in Figure 3. 14 and can similarly be assigned to $Ga^{+\delta}$, where $0 < \delta < 3$ [13,18,19]. However, due to the low signal to noise ratio, this peak was not used for quantification. It has been much debated in the literature about the value of δ.
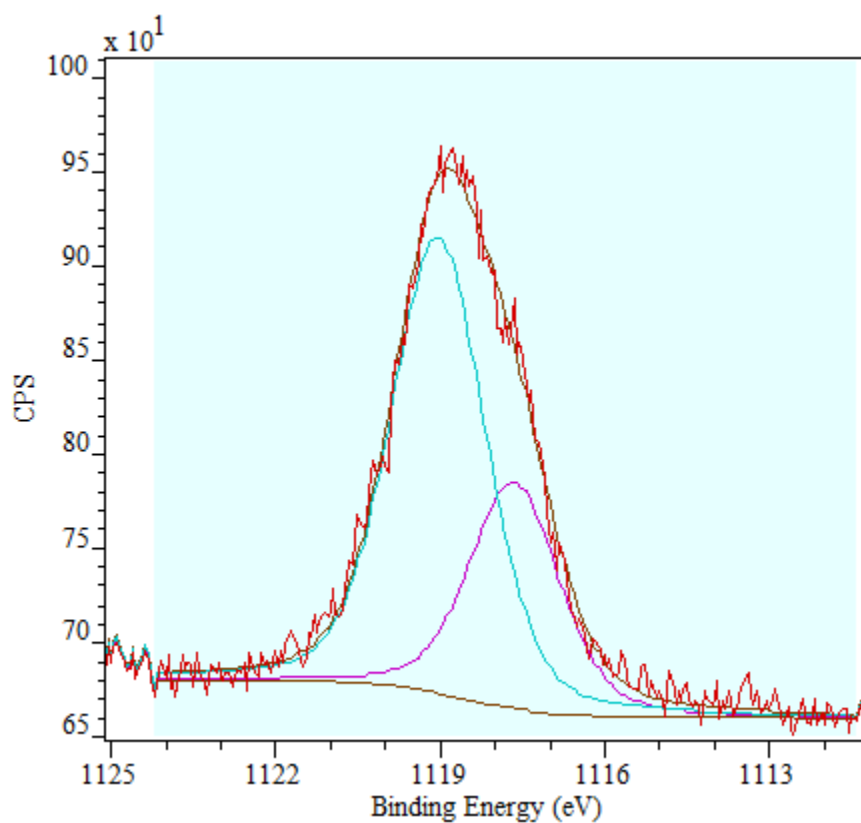
Figure 3. 13: XPS high resolution scan of Ga2p region for Ga/SiO$_2$ catalyst treated with
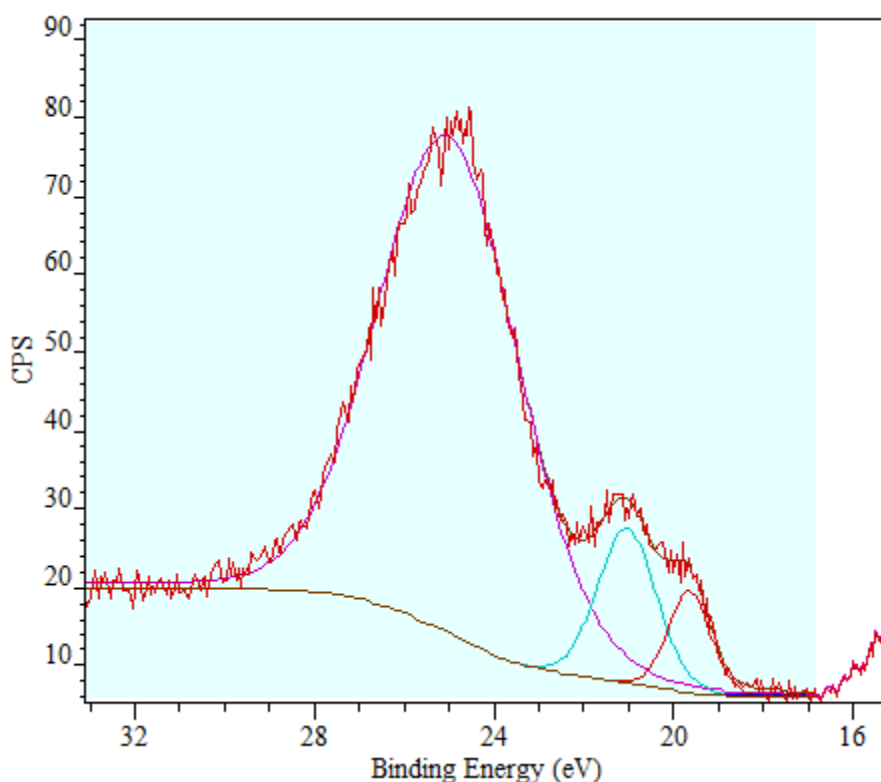
H$_2$ at 650°C

Figure 3. 14: XPS high resolution scan of Ga3d region for Ga/SiO$_2$ catalyst treated with

H$_2$ at 650°C

Collins and co-workers have performed reduction treatments on Ga$_2$O$_3$/SiO$_2$ catalyst and characterized the catalyst using XPS. They have looked at the Ga3d region in the XPS spectra and they observe two shoulders for the Ga3d core level signal which are overlapped with the O2s signal. They have assigned the low binding energy component of Ga3d to a reduced form of Ga. From their Temperature Programmed Reduction (TPR) experiments, they have shown that some of the Ga^{+3} are reduced under the similar treatment conditions. Although the authors have not provided evidence that disproves the formation of Ga^0 or presented additional characterization to conclude the oxidation state

of the Ga in the reduced catalyst or the stoichiometry of the H_2 consumed in the TPR experiments, they have proposed that $0 < \delta < 2$ [13].

Carli and Bianchi have studied the reaction between Ga_2O_3 and metallic Ga at 773-823 K using XPS measurements. They have reported the formation of a new peak in the Ga3d region, the binding energy of which lies in between the binding energy of Ga^0 and Ga^{+3} in Ga_2O_3. They have assigned this new peak to Ga^{+1} in Ga_2O formed as a result of a disproportionation reaction that they claim to occur between Ga_2O_3 and metallic Ga. However, they have clearly mentioned in their paper that they have not provided any evidence to conclude the oxidation state of the new Ga species formed and this hypothesis is required to be tested in the future [20].

Carli et al have also performed reduction studies on Ga_2O_3 deposited on HZSM-5 catalyst and characterized the samples using XPS [21]. A comparison of the XPS spectrum of the Ga3d region of the reduced and the unreduced catalyst revealed the formation of a new Ga3d peak for the reduced sample. They have assigned this new peak to Ga^{+1} using a reference compound which they claim to be Ga_2O, synthesized using methods mentioned in the literature [22]. However, the authors have not characterized the reference compound to confirm that it was indeed Ga_2O. No other characterization techniques have been used in their paper to deduce the oxidation state of the Ga in the reduced catalyst sample. Nevertheless, it is reasonable to conclude that they had formed a new species of Ga after the reduction of the catalyst and one possibility is that the oxidation state of this new species is less than 3.

Kanazirev and co-workers have also performed reduction treatments on the Ga_2O_3/HZSM-5 catalyst and studied the catalyst using XPS [12]. They have also observed the formation of a new peak in the Ga3d region after the reduction treatment of the catalyst. They have compared the binding energy of the peaks observed in the Ga3d region to the literature and have assigned the high binding energy peak to Ga^{+3} and the low binding energy peak to a Ga species having oxidation state between +3 and +1. Here as well, the authors have not presented any evidence that corroborates beyond doubt that the new Ga species formed after the reduction of the sample indeed has an oxidation state between +3 and +1.

Seykh et al have performed reduction treatments on Ga_2O_3/HZSM-5 and Ga_2O_3/SiO_2 catalysts and have characterized the samples using XPS[18,19]. They have also observed the formation of an additional low binding energy Ga peak in the Ga3d region of the reduced samples. They have cited the papers by Carli et al to compare the binding energy values to literature and have also proposed that the low binding energy peak can be assigned to Ga^{+1}. The authors argue that the binding energy of this new peak formed is lower than the binding energy for Ga^{+3} but higher than the binding energy of metallic Ga and hence, they have assigned this peak to Ga^{+1} cations formed from the reduction treatment. However, the authors have not reported any other evidence that could confirm the oxidation state of the Ga in the reduced catalyst samples.

Hence, it would be difficult to conclude about the oxidation state of the reduced Ga species since the true nature of these species have been debated in the literature and no conclusive evidence using XPS have been presented until now. It could be possible that

these new Ga species have an oxidation state lower than +3. It is known from our XAS results that the average Ga-O co-ordination number decreases after the reduction treatment. Hence, it could also be possible that the reduction treatment results in the formation of Ga^{+3} species bonded to H co-ordinated to three O atoms. As H is lower in electronegativity compared to O, it is possible that the binding energy of this species decreases and these species could be reflected in the low binding energy peak of the XPS spectrum. However, this conclusion cannot be made for certain based on the available data.

Based on these fits for the XPS data, quantification was made for the elemental composition of the sample which was scanned in pressed as well as as-is conditions described in Section 2.5.4. This has been summarized in Table 3. 8.

Table 3. 8: Quantification of elements in Ga/SiO_2 from XPS peak fitting analysis

Species	As-is sample atomic %			Pressed sample atomic %		
	Room Temperature	$550^{o}C$ under H_2	$650^{o}C$ under H_2	Room temperature	$550^{o}C$ under H_2	$650^{o}C$ under H_2
Ga^{+3}	1.5	1.1	1.0	1.4	0.8	0.9
$Ga^{+\delta}$	0.1	0.2	0.7	0.2	0.2	0.3
O (HBE)	7.6	6.4	4.2	3.6	4.6	8.1
O (LBE)	58.5	63.8	60.7	62.8	57.5	57.0
Total O	66.0	70.2	64.9	66.3	62.2	65.2
Si	32.4	28.6	33.0	32.1	36.8	33.7

Si:O	0.5	0.4	0.5	0.5	0.6	0.5
$Ga^{+\delta}: Ga^{+3}$	0.1	0.1	0.5	0.2	0.3	0.3
Total Ga	1.6	1.2	2.1	1.6	1.1	1.2

It can be seen that the atomic % ratio of Si to O is 1:2 which is expected for SiO_2. It can also be observed that the total gallium content for the untreated samples is same for the pressed and the as-is sample. This indicates that the total gallium is distributed uniformly in the SiO_2 support and the surface concentration is equal to the bulk concentration. However, more evidence is required to conclude this beyond doubt. The data for the pressed and the as-is catalyst 650^oC reduced samples do not show the same total gallium content. It is not clear yet whether this effect arises because the variation is within the error of measurement or whether it is a real effect.

It can be seen that the ratio of the atomic % of the $Ga^{+\delta}$ to Ga^{+3} progressively increases as the reduction temperature increases. Thus is expected since with higher reduction temperatures, we expect more Ga to be reduced.

It can be observed that the binding energy of the Ga2p peak for the as is sample increases by 0.2 eV as the temperature of H_2 treatment increases from room temperature to 650^oC. This is accompanied by progressive increase in the atomic % of Ga. A possible explanation for this is that the reduction treatment causes a decrease in the co-ordination number of the Ga as corroborated by the XAS results. A decrease in the co-ordination number causes an increase in the binding energy and this can explain why there is a shift in the binding energy of the Ga2p peak. Serykh et al have reported the observation of an

increase in the atomic % of Ga after their reduction treatment. They have suggested that the reduction treatment causes some of the Ga to reduce to metallic form[18]. They have proposed that this Ga metal rises to the surface and sinters to form particles of Ga on the surface which results in a total increase in the atomic % of Ga in their observed XPS spectra. For the pressed sample there is a higher shift in the binding energy of about 0.7 eV. However, there is no significant change in the atomic %. Since the effect of crushing the particles on the chemistry of gallium on the SiO_2 support is not known for certain it would be difficult to comment on this result. As mentioned previously, it is possible that this effect is not real and is merely resulted from the error in the measurement.

3.5. *In-situ* FTIR spectroscopy:

3.5.1. *In- situ* H_2 reduction treatment:

The spectra of the sample in inert was subtracted from the spectra of the sample in H_2 to simplify the analysis and to avoid the deconvolution of the results with the clean wafer peaks. Figure 3. 15 shows the region between wavenumbers 2300 cm^{-1} and 2125 cm^{-1}.
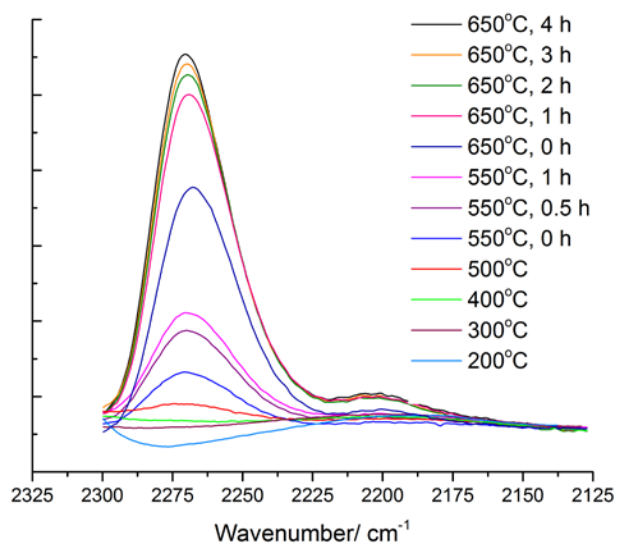
Figure 3. 15: FTIR spectra of Ga/SiO$_2$ catalyst from 2300 cm^{-1} and 2125 cm^{-1} in H$_2$ environment at different temperatures

It can be seen that as the temperature increases, a peak at 2270 cm^{-1} starts forming at a temperature of 500°C and higher. This peak becomes intense at a temperature of around 650°C. This peak can be attributed to the formation of Si-H bonds in the SiO$_2$. It was shown by Hosono et al that SiO$_2$ when subjected to high temperature reduction treatment (600°C– 1000°C) results in the formation of Si-H bonds[23]. The author has claimed that the SiO$_2$ glass contains several Si-Si linkages and reduction treatment results in the breaking of the Si-Si bond to form Si-H bond. The frequency of the Si-H bond reported by the author is 2260 cm^{-1}. The peak observed at 2270 cm^{-1} in this work can be assigned to the formation of the Si-H bonds in the catalyst. A shoulder to the peak at a wavenumber of about 2200 cm^{-1} starts forming at a temperature of 650°C. This peak can also be attributed to the formation of Si-H on the surface of the catalyst as a result of the

high temperature reduction treatment. The region from 2270 cm^{-1} to 2100 cm^{-1} is associated with the formation of Si-H bonds[24].
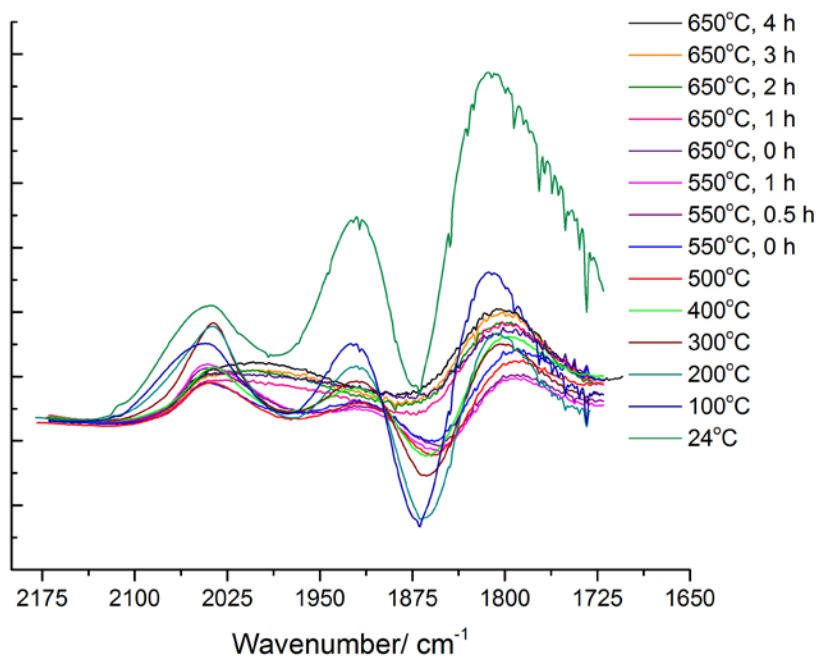
Figure 3. 16: FTIR spectra of Ga/SiO$_2$ catalyst from 2175 cm^{-1} and 1600 cm^{-1} in H$_2$ environment at different temperatures

The IR spectra between wavenumbers 2175 cm^{-1} and 1600 cm^{-1} in Figure 3. 16 show the presence of three intense peaks at wavenumbers 2038 cm^{-1}, 1915 cm^{-1} and 1800 cm^{-1}. The peak observed at 2038 cm^{-1} has been reported to correspond to the Ga-H bond stretching vibration[25,26]. It can be seen that as the temperature is increased from room temperature to 650°C, the intensity of this peak decreases. This peak, however, does not disappear and is present at all temperatures from room temperature to 650°C. The region between wavenumbers 2010 cm^{-1} and 1950 cm^{-1} shows the formation of a broad peak.

This peak is formed only at 650^oC and is not formed at 550^oC in H_2 flow. This region has been attributed to the formation of several different types of Ga-H species such as Ga-H bond formed on tetrahedral Ga (2003 cm^{-1}) and octahedral Ga (1980 cm^{-1}) [27]. Since our XAS results suggest that most of the Ga was present as tetrahedral Ga, we would expect a higher contribution of the peak at wavenumber 2003 cm^{-1} to the broad peak observed between 2010 cm^{-1} and 1950 cm^{-1}.

3.5.2. *In-situ* Propane Dehydrogenation:

Figure 3. 17 shows the peaks formed in the region from 2500 cm^{-1} to1700 cm^{-1} during exposure of the catalyst to propane dehydrogenation reaction mixture and heated from 150^oC to 550^oC.
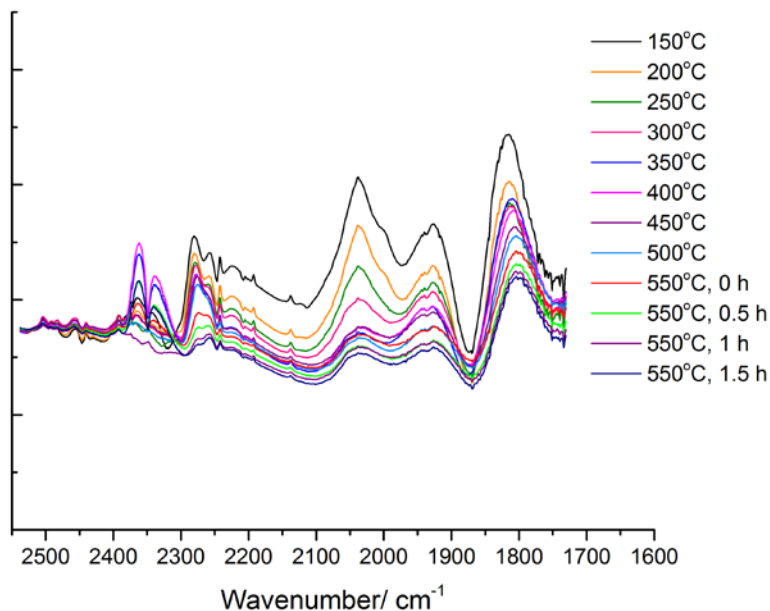
Figure 3. 17: FTIR spectra of Ga/SiO$_2$ catalyst from 2500 cm^{-1} to1700 cm^{-1} in 5% propane in inert at different temperatures

The peaks observed at 2335 cm^{-1} and 2365 cm^{-1} are due to the presence of CO$_2$ in the path of the IR beam. The peak present at 2270 cm^{-1} which has been attributed to the formation of the Si-H bond decreases in the presence of the propane dehydrogenation mixture as the temperature is increased to 550°C from room temperature. Simultaneously, the peak associated with the Ga-H bond at 2038 cm^{-1} also decreases significantly in intensity. It was also observed that the peaks present at 1915 cm^{-1} and 1800 cm^{-1} also decrease in intensity as the temperature is increased to 550°C. It has been reported in the literature that the vinyl hydrocarbon compounds have vibration overtones in the region from 1850 cm^{-1} to 1800 cm^{-1} [24].

Figure 3. 18, Figure 3. 19 and Figure 3. 20 show the region from 1610 cm^{-1} to 1310 cm^{-1},

2920 cm^{-1} to 2850 cm^{-1} and 3010 cm^{-1} to 2915 cm^{-1}.
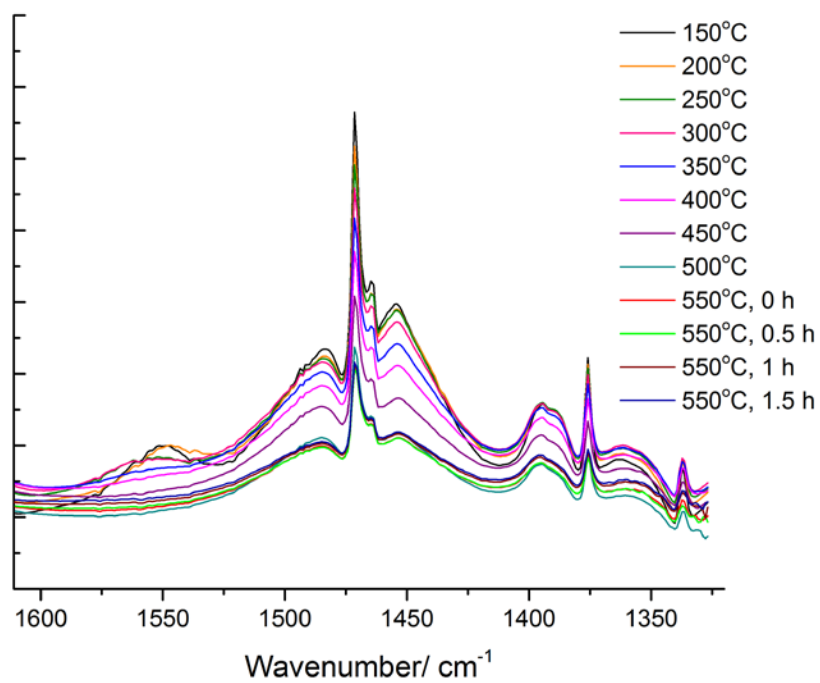
Figure 3. 18: FTIR spectra of Ga/SiO$_2$ catalyst from 1610 cm^{-1} to 1310 cm^{-1} in 5%

propane in inert at different temperatures
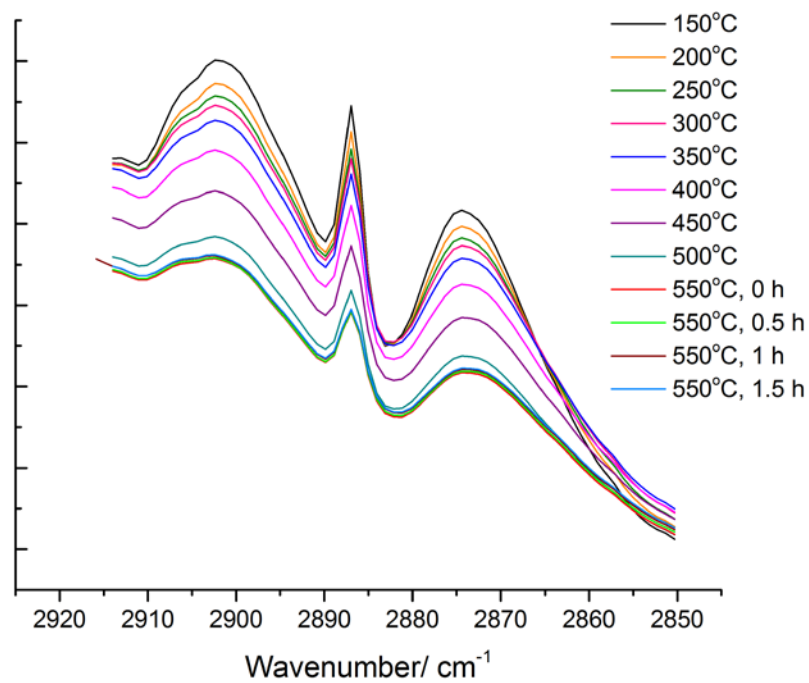
Figure 3. 19: FTIR spectra of Ga/SiO$_2$ catalyst from 2920 cm^{-1} to 2850 cm^{-1} in 5%

propane in inert at different temperatures
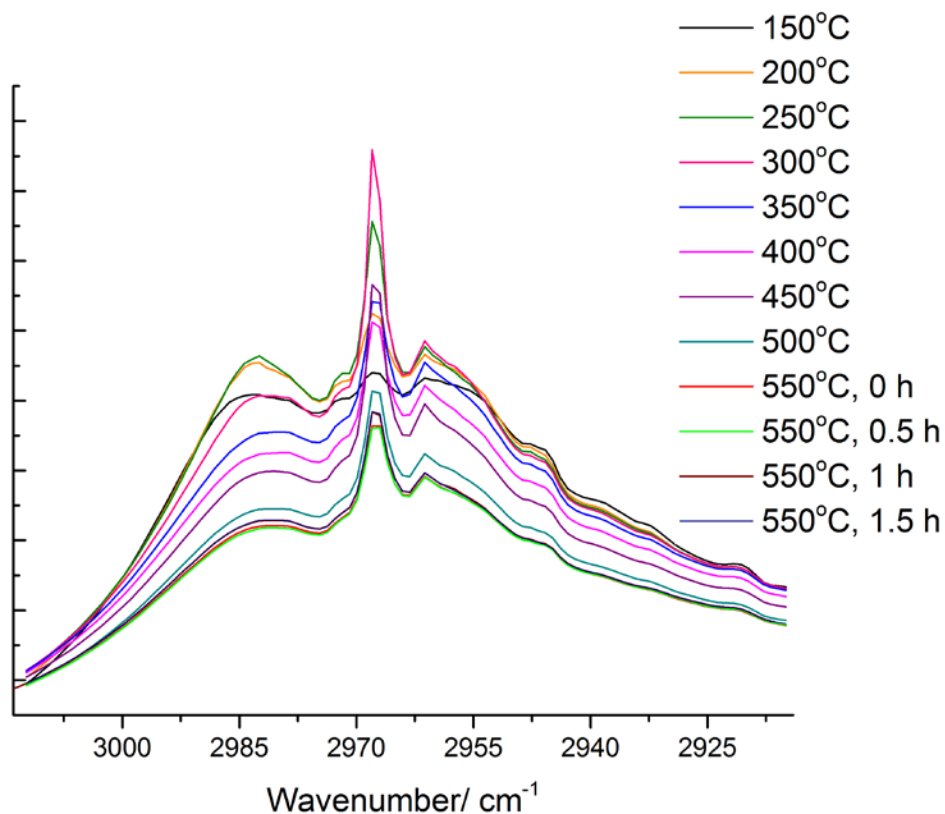
Figure 3. 20: FTIR spectra of Ga/SiO$_2$ catalyst from 3010 cm^{-1} to 2915 cm^{-1} in 5%

propane in inert at different temperatures

The two peaks observed at 2900 cm^{-1} and 2905 cm^{-1} are convoluted into one broad peak. It is possible that there are more peaks under this broad peak which would be clear only after deconvolution of the broad peak. The peak at 2900 cm^{-1} has been attributed to symmetric stretch of the CH$_3$-Ga bond and the peak at 2905 cm^{-1} has been attributed to the presence of Ga-OH species[24]. The peaks at 2890 cm^{-1} and 2874 cm^{-1} can be associated with many possible peaks and it was not possible to conclude the type of species associated with this band with the existing data. Acylic CH is reported to have C-H stretching vibrations from 2890 cm^{-1} to 2880 cm^{-1}. Aliphatic CH$_3$ fragment is also

reported in the literature to have C-H stretching symmetric vibrations from 2890 cm^{-1} to 2865 cm^{-1} [24]. This peak could also be observed due to the presence of CH_3 attached to an unsaturated hydrocarbon fragment since the symmetric C-H stretching of the CH_3 group is reported to be observed from 2945 cm^{-1} to 2880 cm^{-1} [24]. The intensity of this peak decreases as the temperature of the catalyst is increased in the flow of the propane dehydrogenation reaction mixture. The peak observed at 2874 cm^{-1} also decreases in intensity as the temperature is increased. This peak could correspond to the CH_2-Ga symmetric stretch which is reported to be observed at 2877cm^{-1} [26]. The peak observed in Figure 3. 20 at wavenumber 2961 cm^{-1} and 2967 cm^{-1} can be assigned to CH_3-Ga antisymmetric stretching[26]. It was observed that this peak increases in intensity as the temperature is increased from 150°C to 300°C. On heating in the propane dehydrogenation reaction mixture beyond 300°C, this peak decreases in intensity. The peak at 2985 cm^{-1} can be assigned to several different possible species on the catalyst surface. The CH_3 group attached to unsaturated hydrocarbons except acetylene is reported to have an asymmetric stretch vibration in the range of 2995 cm^{-1} and 2905 cm^{-1} [24]. The CH_3 group attached to aliphatic hydrocarbons is also reported to have an asymmetric stretch in the range of 2975 cm^{-1} and 2950 cm^{-1} [24]. The asymmetric CH_3 stretch of the CH_3 group attached to an aromatic ring also lies in the general region from 3005 cm^{-1} to 2965 cm^{-1} [24]. However, it cannot be concluded for certain whether this species indeed exists on the catalyst surface since the Gas Chromatograph data does not detect the presence of Toluene or Xylenes in the exit product stream. It could be possible that all or some of these species could exist on the catalyst surface resulting in the convolution of their peaks into one broad peak observed at ~ 2985 cm^{-1}. The region from

2955 cm^{-1} to 2920 cm^{-1} shows the presence of some peaks which could be due to the presence of many different species on the surface such as acyclic CH_2 group (2940-2915 cm^{-1} asymmetric stretch), CH_3 attached to an aromatic ring (3000-2935 cm^{-1} asymmetric stretch) or CH_3 attached to an unsaturated hydrocarbon molecule (2995-2905 cm^{-1} asymmetric CH_3 stretching, 2945-2880 cm^{-1} symmetric CH_3 stretching) [24]. Figure 3. 18 shows several peaks observed in the region from 1610 cm^{-1} to 1310 cm^{-1}. The alkane C-H deformation vibrations and the deformation vibrations of the CH_3 group attached to unsaturated hydrocarbons are reported to lie in the general range of 1480 cm^{-1} to 1320 cm^{-1} [24]. All of the peaks observed in the figure are seen to decrease in intensity as the temperature increases.

CHAPTER 4. DISCUSSION

From the kinetic studies, it is evident that H_2 treatment at 550^oC did not alter the activity of the catalyst in any way. However, the H_2 treatment of the catalyst at 650^oC results in the formation of a less active Ga species. When the catalyst is subjected to the H_2 treatment at 550^oC, it was observed using XAS that the Ga is 4 co-ordinate with neighboring O atoms and is in the +3 oxidation state when turning over for propane dehydrogenation reaction. This indicates that the 4 co-ordinate Ga^{+3} is the active site for propane dehydrogenation. Reduction of the catalyst with H_2 at 650^oC results in the formation of a new Ga species as indicated by formation of a low energy pre edge feature. From our XPS results it is also clear that the reduction treatment does result in the formation of a new Ga species. However, whether this species is $Ga^{+\delta}$ ($\delta < 3$) or a Ga^{+3} in the hydride form is not known for certain. As mentioned in Section 3.1.3., the initial rate of propane dehydrogenation normalized to the total moles of Ga for the samples treated with H_2 at 650^oC is $3.7 . 10^{-4}$ mol propylene. mol total $Ga^{-1}. s^{-1}$. Table 4. 1 shows the initial rate of propane dehydrogenation of the sample pretreated with H_2 at 650^oC for 1 h normalized to the moles of Ga^{+3} which is obtained from XPS under this treatment condition.

Table 4. 1: Initial rate of propane dehydrogenation ($550^{\circ}C$, 5% propane in inert) of

Ga/SiO$_2$ pretreated with H$_2$ at $650^{\circ}C$ normalized to moles of Ga^{+3}

Catalyst sample treated with H$_2$ at $650^{\circ}C$ for 1 h	Initial rate of propane dehydrogenation/ mol propylene. (mol Ga^{+3})$^{-1}$. s^{-1}
As-is sample	$5.4 \cdot 10^{-4}$
Pressed sample	$5.0 \cdot 10^{-4}$

As mentioned in Section 3.1.3., the initial rate of propane dehydrogenation for the sample treated with H$_2$ at $550^{\circ}C$ is $5.4 \cdot 10^{-4}$ mol propylene. mol total Ga^{-1}. s^{-1}. From our XAS results, it is known that the catalyst under these conditions has Ga in the +3 oxidation state and co-ordinated to four O atoms. This analysis shows that when the initial rate of propane dehydrogenation of the sample treated with H$_2$ at $650^{\circ}C$ for 1 h is normalized to the total moles of Ga^{+3}, the rate matches with the rate of the fresh catalyst sample. This is thus an additional evidence to show that the active site for propane dehydrogenation on single site Ga/SiO$_2$ catalyst is Ga^{+3} and not the reduced Ga species. The *in-situ* IR spectroscopy data shows the presence of the band at 2038 cm^{-1} which has been assigned to the Ga-H bond. The role of the Ga-H species responsible for this peak in the propane dehydrogenation reaction is not clear. Reduction at $650^{\circ}C$ with H$_2$ shows the formation of additional broad peak in the region of 2010 cm^{-1} to 1950 cm^{-1}. This peak has been assigned to the formation of several different types of Ga-H species, one of them being tetrahedral Ga-H. From our XAS results, it is clear that the Ga^{+3} in the catalyst is terahedrally co-ordinated to the O atoms of the SiO$_2$. Hence, it is hypothesized that the

reduction of the catalyst at 650°C results in the formation of a tetrahedral Ga-H species which is not formed during the reduction treatment at 550°C and this species is not active for propane dehydrogenation reaction. It was also observed in the IR spectra in Figure 3. 17 that the peak in the region of 2010 cm^{-1} to 1950 cm^{-1} decreases in intensity with time as the catalyst is exposed to the propane dehydrogenation reaction mixture. This is in agreement with our XANES results which show the decrease in the intensity of the shoulder assigned to reduced Ga species as the reaction proceeds with a simultaneous increase in the intensity of the Ga^{+3} peak. This is also in congruence with the results from the plug flow kinetic studies described in Section 3.1.3 which suggest that the final rate of propane dehydrogenation in the sample pretreated with H$_2$ at 650°C is equal to that of the sample pretreated with H$_2$ at 550°C. This suggests that the reduced Ga species is unstable in the presence of propane dehydrogenation reaction mixture at 550°C and get reoxidized to Ga^{+3}.

CHAPTER 5. CONCLUSIONS AND FUTURE WORK

The Ga/SiO$_2$ catalyst is active and selective for propane dehydrogenation reaction. The active site for the reaction was shown to be Ga^{+3} co-ordinated to four O atoms of the SiO$_2$ support. Treatment of the Ga/SiO$_2$ catalyst with H$_2$ at 650°C results in the formation of a reduced Ga species. The reduced Ga species results in lower rates of propane dehydrogenation reaction and are unstable in the presence of the propane dehydrogenation reaction mixture as they get reoxidized to Ga^{+3} with time on stream. The exact nature of the reduced Ga species is not known for certain. It is known that the reduced Ga species is bonded to three O atoms and to H atoms. The number of H atoms bonded to the Ga is not known. Hence, for future experimentation, it is suggested to perform a temperature programmed reduction (TPR) for the catalyst and measure the moles of H$_2$ consumed which will help in understanding the number of H atoms attached to the Ga. This will help in a better interpretation of the existing characterization data.

It is also suggested to perform the H$_2$/D$_2$ switching for *in-situ* IR experiments. This will help in understanding the nature of the various Ga-H species observed in the wavenumber range of 2010 cm^{-1} to 1950 cm^{-1} and at 2038 cm^{-1}.

In this work, we have not provided evidence to show that the Ga sites are monoatomically dispersed. Although the XAS data does not show the presence of Ga-Ga co-ordination or Ga-O-Ga co-ordination, more evidence is needed to conclude that the Ga

in the catalyst is indeed single site. Schweitzer et al have studied single site Zn/SiO_2 catalyst for propane dehydrogenation and propylene hydrogenation. They have used pyridine to poison the Lewis acidic Zn^{+2} sites on the catalyst and have shown a linear trend of the propylene hydrogenation rate normalized to the total moles of Zn^{+2} with the poison equivalents with slope = 1. This shows that all the Zn^{+2} sites in the catalyst are similar in nature. This result combined with their XAS results shows that the Zn^{+2} is monoatomically dispersed on the SiO_2 surface. Similar studies can be performed on the Ga/SiO_2 catalyst to show that the Ga sites are monoatomically dispersed on the SiO_2 support[28].

A pyridine chemisorption experiment on the catalyst is needed to show that the Ga^{+3} is a Lewis acid site. This experiment will also help in quantifying the Ga sites that are Lewis acidic in nature. The results can be combined with Atomic Absorption Spectroscopy to find out the % of Lewis acidic Ga sites. These results can be further used to understand the mechanism of the C-H vs C-C bond scission of the propane which results in high selectivity for the dehydrogenation reaction as against the cracking reaction.

In this study, we have also not checked the kinetic results for mass and heat transfer limitations. A part of the future work of the project would be to perform the Koros-Novak test to ensure that the results are free of transfer limitations.

The room temperature reoxidation of the catalyst after the 4 hour reduction treatment with H_2 at $650^{o}C$ has also not been studied further in this work. It would be interesting to pursue this study by observing the changes to the Ga^{+3} sites under these conditions by using techniques such as *in-situ* XAS and IR spectroscopy.

It has been shown in the literature that Pd-Ga is able to selectively hydrogenate the triple bond of alkane to a double bond. Pd is shown to form an intermetallic alloy with Ga and surrounded with Ga_2O_3 [29,30]. The authors have claimed that the reason for the selective hydrogenation of acetylene to ethylene is a combination of electronic effects and geometric effects between Pd and Ga. It is claimed that Ga modifies the Fermi level of Pd and also causes isolation of the Pd atoms by decreasing the Pd-Pd co-ordination which is responsible for the high activity and selective hydrogenation of acetylene to ethylene. It would be expected that the catalyst is a good potential candidate for propane dehydrogenation and it will be interesting to understand the synergistic effects between Ga and Pd.

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APPENDICES

APPENDIX A

It is known that the propane dehydrogenation is an equilibrium limited reaction. Hence, it becomes necessary to calculate the equilibrium conversion of propane to ensure that we operate far from equilibrium to measure the true forward rate of the reaction. The reaction under consideration was:

$$C_3H_8 \leftrightarrow C_3H_6 + H_2$$
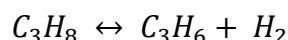
The values for standard enthalpy of formation were obtained from the NIST database. The values for standard entropy of formation were obtained from Perry's Chemical Engineering Handbook. The variation of specific heat (Cp) with temperature has also been incorporated in the calculations. The values for Cp at different temperatures were obtained from the NIST database for both propane and propene. The resulting integrals were solved numerically using MathCad 15 software.

Calculation of equilibrium constant for propane dehydrogenation reaction:

$$C_3H_8 \leftrightarrow H_2 + C_3H_6$$
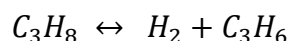
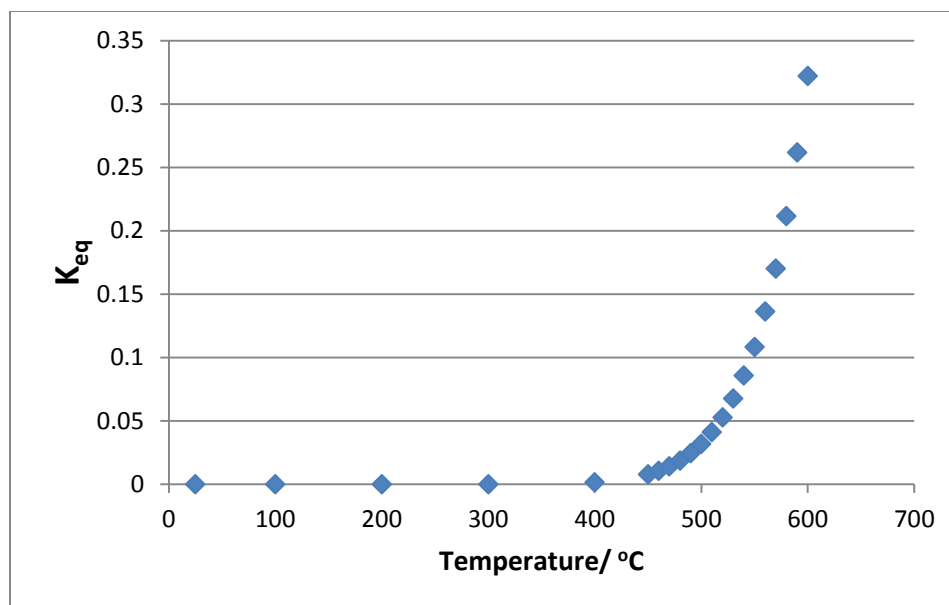Solving the governing equations, we get a graph Keq with temperature as shown in Figure A 1:

Figure A 1: Variation of equilibrium constant with temperature for propane dehydrogenation reaction
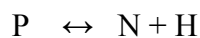
Now, consider the reaction:

$$P \leftrightarrow N + H$$

Table A 1: Equilibrium Mole Ratios for propane dehydrogenation reaction

Component	Propane (P)	Propene (N)	Hydrogen (H)
Initial moles/s	n	0	0
Equilibrium moles/s	n-x	x	x
Equilibrium mole ratios	(n-x)/(n+x)	x/(n+x)	x/(n+x)

$$K_{eq} = \frac{P_N \times P_H}{P_P} \ atm$$

$$K_{eq} = \frac{\left(\frac{x}{n-x}\right) \times P \times \left(\frac{x}{n-x}\right) \times P}{\left(\frac{n-x}{n+x}\right) \times P} \; atm$$

$$K_{eq} = \frac{x^2 \times P}{(n-x) \times (n+x)} \; atm$$

$$K_{eq} = \frac{x^2 \times P}{(n^2 - x^2)} \; atm$$

$$P = 1 \; atm$$

$$n = \; initial \; moles/s \; of \; propane$$

$$n - x = equilibrium \; moles/s \; of \; propane$$

$$equilibrium \; conversion \; of \; propane = c = \frac{x}{n}$$

Using this, we calculate the equilibrium concentration of propane and thus the equilibrium % conversion of propane. The equilibrium curve for the reaction is thus obtained as:
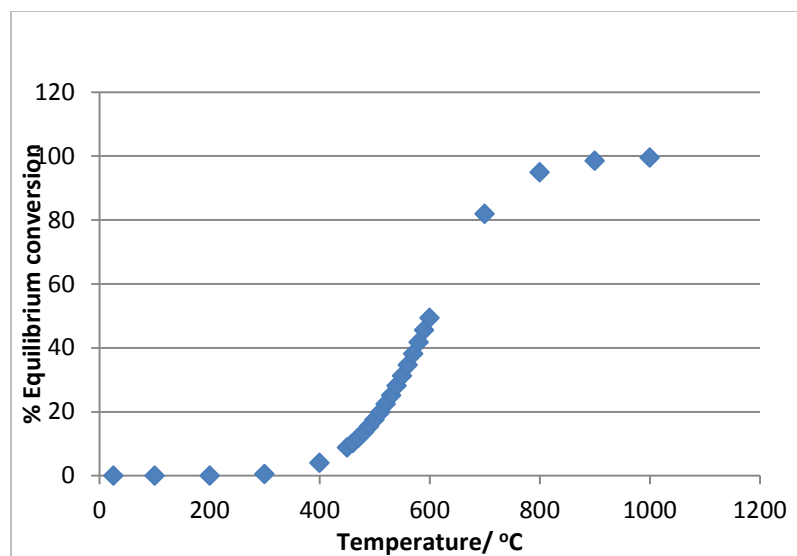
Figure A 2: Equilibrium conversion variation with temperature for propane dehydrogenation reaction with 5% propane in feed

From this graph we can see that the equilibrium conversion of propane is ~30% at 550°C
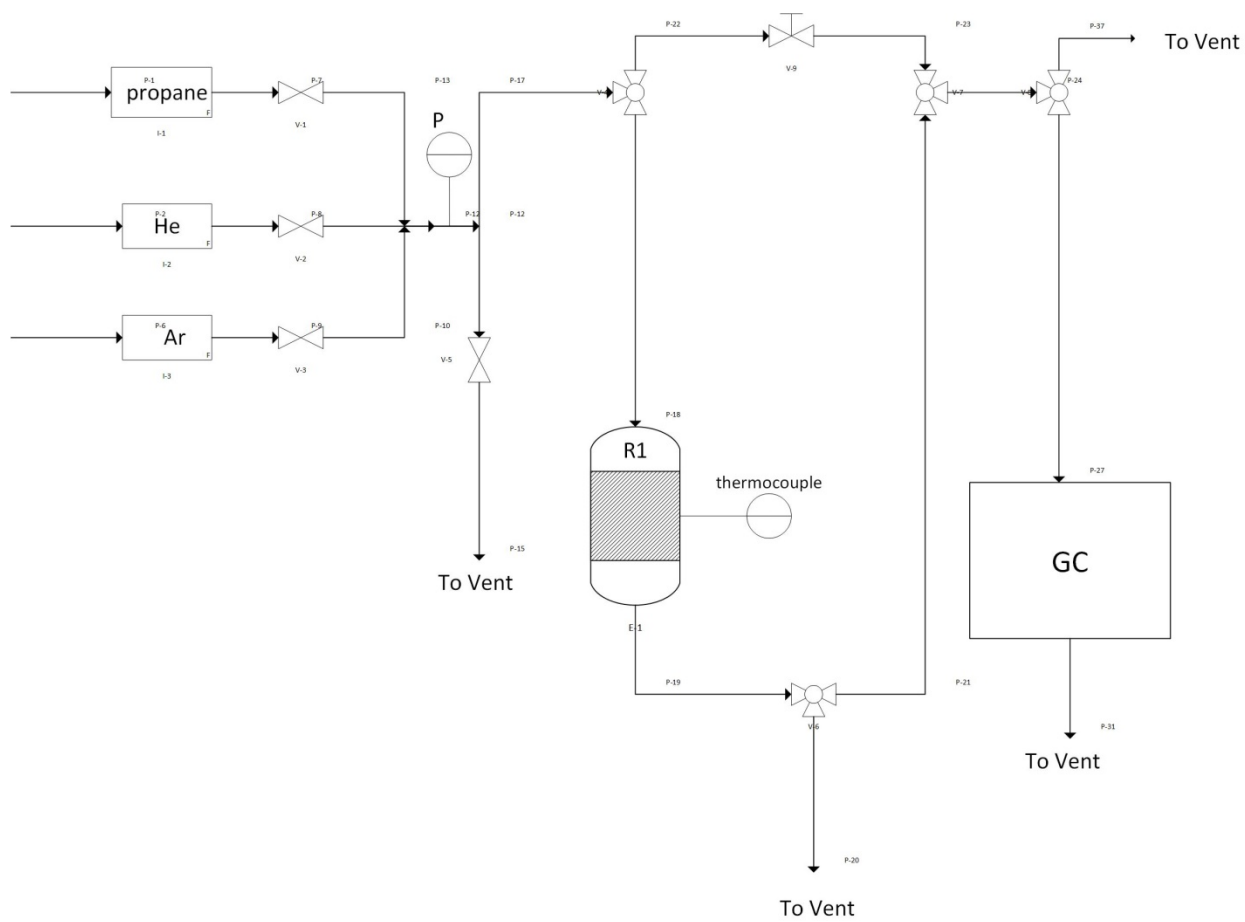
APPENDIX B

Figure B 1: Process flow diagram for measurement of kinetics of propane dehydrogenation reaction