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Secondary Reactions of Propylene on Single Site Ga(III) on Alumina Propane Dehydrogenation Catalysts

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Abstract

$Ga/\gamma-Al_2O_3$ catalysts have previously been studied for propane dehydrogenation (PDH); however, the propylene selectivity is lower than that of Ga/SiO_2 or Pt alloy catalysts. In this study, we prepared and characterized 3-15% Ga on $\gamma-Al_2O_3$ by XRD, STEM, and XAS and evaluated these for PDH. At all loadings, the active site structure was an isolated Ga^{+3} ion bonded to the alumina support. The PDH rate and propylene selectivity was identical for all Ga loadings. The propylene selectivity decreased with increasing propane conversion and was lower at higher propane partial pressure. By extrapolating the product selectivities to zero propane conversion, the initial propylene selectivity was near 100%. The selectivities of the light gas by-products, which included methane, ethane, butenes and pentenes, were near 0% at zero propane conversion indicating these are all secondary products of the initially formed propylene. The direct reaction of propylene at the PDH reaction temperature confirmed that methane, ethylene, propane, butenes and pentenes are primary products. Thus, while the intrinsic PDH propylene selectivity is high, these secondary propylene reactions lower the selectivity at higher conversions.

The structure and catalytic performance of Ga/SiO_2 was also determined for comparison with $Ga/\gamma-Al_2O_3$ catalysts. Similar to $Ga/\gamma-Al_2O_3$, the structure of the active site was an isolated Ga^{+3} ion bonded to the silica support. Although the PDH propylene selectivity was higher on Ga/SiO_2, the same by-products were formed including butenes and pentenes. Similar to the $Ga/\gamma-Al_2O_3$ catalysts, extrapolation of the selectivity to zero propane conversion indicates that propylene is a primary product with an intrinsic selectivity near 100%; while the selectivity of the light gases indicates these are secondary products, which was confirmed by the direct reaction of propylene. This latter reaction also suggests that these secondary propylene reactions are occurring on the Ga active site, rather than the support.

Introduction

Propylene is the second largest petrochemical and is used for the production of a variety of products including polypropylene, propylene oxide, acrolein, acrylonitrile, fuels, etc.[1] Propylene is primarily produced by steam cracking of naphtha and fluid catalytic cracking. With the recent large increase in availability of natural gas liquids from horizontal drilling and fracking of shale formations, in the US the naphtha feed to steam crackers has largely been replaced by ethane for production of ethylene. Ethane steam cracking, however, produces little propylene; thus, there is increasing interest in on-purpose production of propylene by propane dehydrogenation (PDH).

For PDH, the two most common commercial technologies are UOP's Oleflex [2] and the Lummus-Clariant's Catofin processes. The former uses a Pt-Sn alloy on alkali modified alumina support; while the latter uses and CrO_x on alumina catalysts.[3–6] However, due to toxicity and environmental hazard of the latter, alternative metal oxide catalysts are being actively researched.[6,7] While many metal oxides have been studied, those based on Ga oxide are appear to be closest to commercialization, e.g., the Dow Fluidized Catalytic Dehydrogenation process.

BP-UOP's Cyclar process, [8] first reported the dehydrogenation activity of gallium oxide supported on ZSM-5 for conversion of propane and butanes to benzene, toluene and xylenes.[9–20] In the bifunctional catalyst, Ga_2O_3 converts alkanes to olefins, which subsequently form aromatics on Bronsted acid sites.[10,14,19–27] For Ga_2O_3 catalysts with few acid sites, however, olefins are the main products.[20,28–32] While Ga on alumina is active, addition of small amounts of Pt, e.g., 0.1%, to Ga (3 wt%) on γ-Al_2O_3 gives a highly active and stable catalyst.[33] This catalyst initially exhibited a decline in catalytic activity over the first day but remained relatively constant for the next 13 days across more than 150 oxidative/reductive cycles using coke oxidation.

In the present study, we have prepared PDH catalysts with up to 15 wt% Ga where every catalytic site is an isolated Ga^{+3} ion with 4 Ga-O bonds stabilized by the γ-Al_2O_3 support. The active site is characterized by XRD, XAS and atomic resolution STEM. For PDH, the propylene selectivity decreases with increasing conversion and is dependent on the propane partial pressure. In addition to the expected PDH reaction products of methane, ethane and ethylene, i.e., due to hydrogenolysis, secondary reactions of propylene form significant amounts of C_4 hydrocarbons, which further lower the propylene selectivity. Although the propylene selectivity is higher on Ga/SiO_2 than that on alumina, secondary reactions of propylene also occur on the former indicating that the Ga catalytic sites are responsible for this reaction.

Experimental section

Catalyst synthesis

The Ga/γ-Al_2O_3 catalysts with different Ga loadings (3, 6, 9, 12, and 15%) were synthesized by incipient wetness impregnation (IWI). To prepare 3% Ga/γ-Al_2O_3, 2.2 g of $Ga(NO_3)_3 \cdot xH_2O$ (Sigma-Aldrich) was dissolved in 8.0 mL deionized water. The solution was then added dropwise to 20.0 g of Alumina (Sasol CATALOX SBA-200; 0.5 cc/g, pore size = 40-100 Å, surface area = 200 m^2/g). The mixture was dried overnight at 110 °C and then calcined for 3 hours in air at 550 °C.

3% Ga/SiO_2 was synthesized using the incipient wetness impregnation (IWI) method. 1.5 grams of Ga $(NO_3)_3xH_2O$ and 1.5 grams of citric acid (Sigma Aldrich) were dissolved in DI 7.5 mL water and added dropwise to 10 grams of Davisil silica grade 636 (0.75 cc/g, pore size = 60 Å, surface area = 480 m^2/g). The catalyst was dried at 125 °C overnight and subsequently calcined at 500 °C for 3 hours.

Catalyst Evaluations

Propane dehydrogenation over 3% Ga/γ-Al_2O_3 catalysts was carried out in a fixed-bed quartz reactor (inner diameter = 10.5 mm).[34] The reactor was heated using an electrical furnace (Applied Test System Series 3210), and the temperature of the catalyst bed was measured using a K-type thermocouple positioned in the middle of the catalyst bed. The 3% Ga/γ-Al_2O_3 catalyst was dried to 150°C in N_2 at 100 mL/min for 1 hr and pretreated in H_2 (100 mL/min) at 550°C for 1 hr. At the reaction temperature, the propane flow rate was adjusted by a mass flow controller (Parker Porter, CM400). The catalysts were initially screened at 6 kPa to determine the Turn Over Rate (TOR) and product selectivity. The 15% Ga/γ-Al_2O_3 was evaluated in more detail at 130 kPa propane. The catalyst mass, e.g., 1.0 g - 0.25 g, and flow rates, 25 – 100 ccm, were varied to obtain propane conversions from 5-35%. Fresh catalyst was tested at each conversion. Other Ga loadings on alumina (6, 9, 12, and 15%) and 3% Ga/SiO_2 were evaluated using the same approach. Reaction products were determined by an online, gas chromatograph (GC) (Agilent 7890A) equipped with a flame ionization detector (FID). The lines from the reactor to the GC were insulated by heat tape (Omega) up 150 ºC. Data points were collected every 15 minutes for PDH. The products were evaluated using an Agilent HP 6890 Series gas chromatograph (GC) equipped with a Restek Rt-Alumina Bond/Na_2SO_4 GC column (30 m in length, 0.32 mm ID, and 0.5 m film thickness) fitted with a flame ionization detector (FID). The reaction products included H_2, methane, ethane, ethylene, propylene, and high molecular weight C_4 and C_5 hydrocarbons.

Catalytic performance for propylene conversion was determined in the same fixed-bed reactor at 550°C and 4-40 kPa (pressure gauge) propylene/balance N_2 for the (3, 12, and 15%)

Ga/γ-Al_2O_3 catalyst. The amounts of catalyst and flow rates were varied to obtain propylene conversions from 5 – 15%.

Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) Spectroscopy

MAS-NMR data were collected through the Purdue Interdepartmental NMR facility. The spectrometer is a Chemagnetics CMX-400 with a wide-bore magnet and a Chemagnetics 5mm H-X-Y triple-resonance MAS probe. For the ^{27} Al spectra, the parameters were as follows: 1-pulse acquisition with no 1H decoupling, pulse width of 2.3us (nominal P90 of ^{27}Al using a solution-state sample of 7 us), relaxation delay of 0.5s, and an acquisition time of 25.6ms. Sample rotation rate was 6 KHz and 1k scans were typically acquired. Data were processed using a left-shift of two data points, exponential multiplication with a line-broadening of 100 Hz and one zero-fill. Each peak was integrated relative to the baseline in order to determine relative occupancy.

Scanning Transmission Electron Microscopy (STEM)

Samples were dispersed in ethanol and inserted on a holey carbon grid in a JEOL NeoARM 200CF scanning transmission electron microscope equipped with a spherical aberration corrector. Images were recorded in annular dark field (ADF) mode as well as in annular bright field mode (ABF).

X-ray Diffraction (XRD)

X-ray diffraction data were collected using a Rigaku SmartLab X-ray Diffractometer using a Cu-target Kα source (λ = 1.54056 Å) in air. Data was collected scanning at 1°/min in steps of 0.004° from 25° to 50° in 2θ.

X-ray Absorption Spectroscopy (XAS)

XAS experiments were performed at the Argonne APS MR-CAT 10-BM beamline. The catalyst materials were scanned at the Ga K edge (10.367 keV) for all of the Ga/Al_2O_3 samples. Samples were pressed into a six-sample holder in a controlled atmosphere *in situ* cell. The samples were scanned as-synthesized in air, during high temperature (550 °C) treatment in 20% O_2, 10% H_2, and 3% C_3H_8 (all in balance He), and after the treatment by cooling to room temperature and scanning in He. A Zn foil (9659 eV) was scanned simultaneously with the sample for energy calibration. The X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) were analyzed using WinXAS v.3.1 software.[35] Ga_2O_3 and gallium (III) acetylacetonate (both Sigma Aldrich) were scanned as standards. All samples were fit using an experimentally generated scattering path from gallium (III) acetylacetonate. An EXAFS fit was performed on the k^2-weighted, Fourier-transform of the sample in R-space as well as on the back-Fourier-transformed (first shell isolated) q-space.

Thermogravimetric analysis (TGA)

The amounts of coke for the propane and propylene reactions were determined by Thermogravimetric analysis (TGA) at two different times: 15 minutes and also 4 hours after the start of the reaction. Thermogravimetric analysis (TGA) experiments were performed on a TA Instruments SDT Q600 thermogravimetric analyzer and differential scanning calorimeter (TGA-DSC) by heating 0.02 g of 15%Ga/ γ-Al_2O_3 in dry air (UHP, 99.999%, Indiana Oxygen) to 800 °C. The coke weight % of catalyst is calculated with Eq (1).

$$Coke\ (wt\%) = \left(1 - \frac{initial\ mass}{final\ mass}\right) * 100 \tag{1}$$

Results

Catalyst Characterization

Alumina support

The alumina was a high purity γ-Al_2O_3 with a BET surface area of 290 m^2/g. In addition, ^{27}Al MAS-NMR gives the relative occupancy of tetrahedral and octahedral Al in the γ-Al_2O_3. Figure 1 shows the normalized MAS NMR spectra for γ-Al_2O_3 as well as the catalyst with the highest Ga loading, 15%Ga/γ-Al_2O_3. The peaks as -78 ppm and -9 ppm correspond with tetrahedral (Td) and octahedral (Oh) coordination, respectively. Integration of the peak areas are summarized for each sample in Table 1, which shows that the Al coordination is approximately 23% Td and 77% Oh, for all samples and is unaffected by Ga loading. These results are consistent with previous studies of MAS-NMR for γ-Al_2O_3.[36]

Table 1 The percentage of tetrahedral and octahedral Al coordination of γ-Al_2O_3 and the Ga/γ-Al_2O_3 catalysts by ^{27}Al MAS-NMR

Sample	**T_d Relative Occupancy (%)**	**O_h Relative Occupancy (%)**
γ-Al_2O_3	22.6	77.4
3%Ga/γ-Al_2O_3	21.3	78.7
6%Ga/γ-Al_2O_3	24.5	75.5
9%Ga/γ-Al_2O_3	22.3	77.7
12%Ga/γ-Al_2O_3	22.9	77.1
15%Ga/γ-Al_2O_3	23.8	76.2

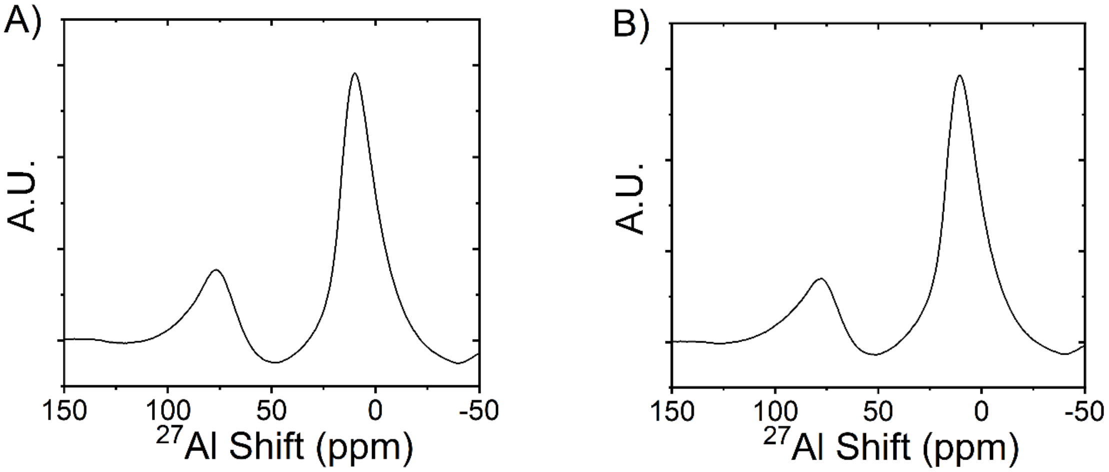


Figure 1 MAS-NMR results for a) γ-Al_2O_3 and b) 15%Ga/γ-Al_2O_3 catalysts.

Ga/γ-Alumina Catalyst

The XRD spectra of γ-Al_2O_3 and the Ga/γ-Al_2O_3 catalysts are shown in Figure 2a. The results show four broad peaks at about 32°, 38°, 40° and 46° 2θ. The peaks are similar to previous results for mixed oxides of γ-Ga_2O_3 and γ-Al_2O_3.[37] There is a systematic shift to lower 2θ for the two peaks at 32° and 38° 2θ; while there is little change in the peaks at 40° and 46° 2θ.

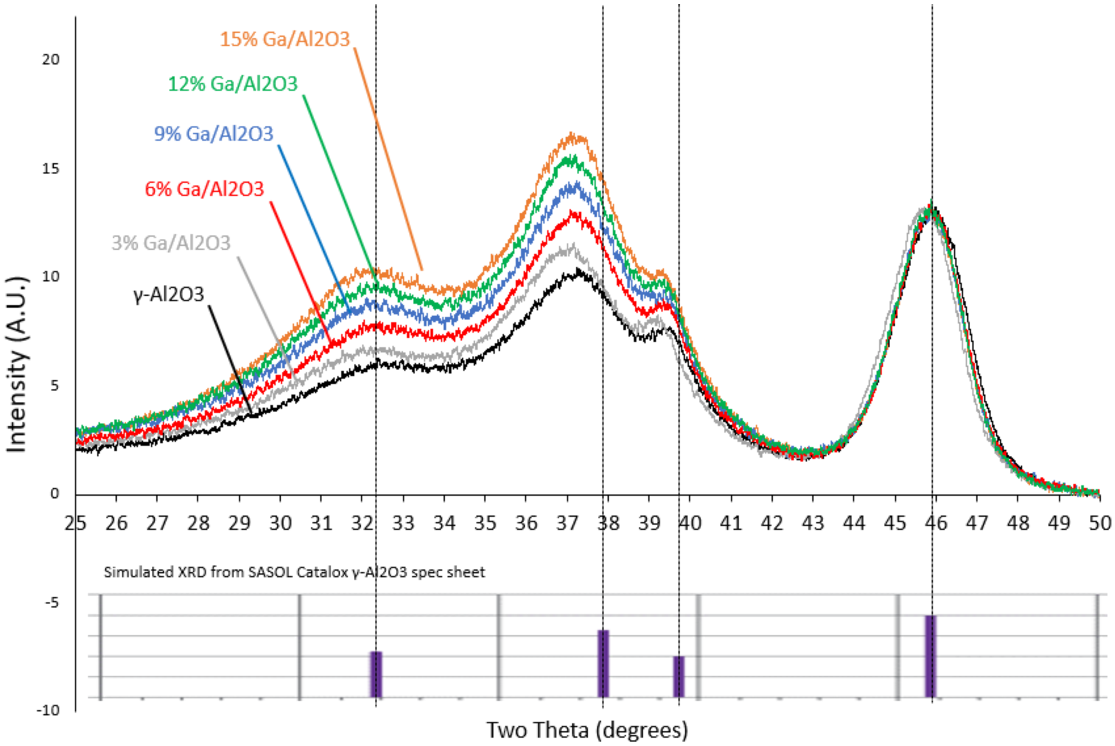


Figure 2 XRD spectra for γ-Al_2O_3 (black), 3%Ga/γ-Al_2O_3 (gray), 6%Ga/γ-Al_2O_3 (red), 9%Ga/γ-Al_2O_3 (blue), 12%Ga/γ-Al_2O_3 (green), and 15%Ga/γ-Al_2O_3 (orange). Simulated XRD spectra from Sasol CATALOX specification sheet.

To better quantify the changes in the XRD with increasing Ga loading, the XRD spectrum of γ-Al_2O_3 was subtracted from the spectrum of each Ga/γ-Al_2O_3 catalyst and shown in Figure 3. The peaks at 40° and 46° 2θ do not change with Ga loading and are absent in the difference spectrum. These are attributed solely to alumina. For the XRD peaks at 32° and 38° 2θ, there is a strong, positive linear correlation (R=0.998 and R=0.996 respectively) between the increase in peak intensity and the Ga weight loading, Figure 4; however, there is little shift in the peak positions suggesting the structure of γ-Al_2O_3 is unaffected by the addition of the Ga.

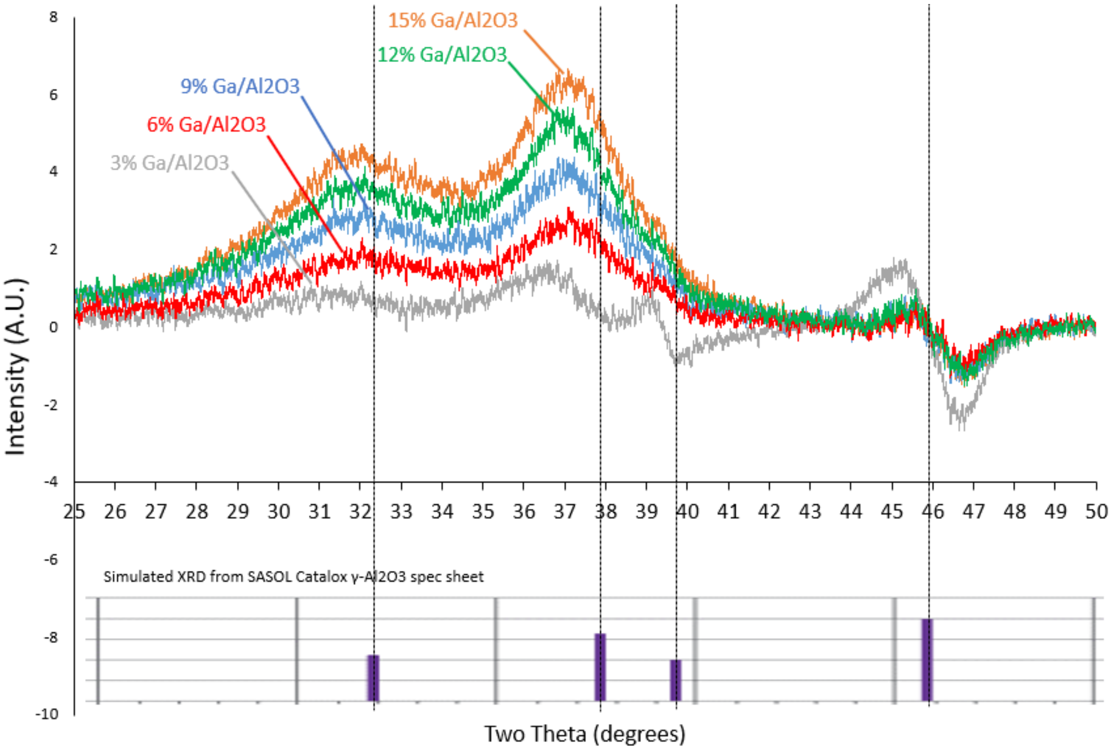


Figure 3 Difference-XRD spectra (Ga/ γ-Al_2O_3 minus γ-Al_2O_3): 3%Ga/γ-Al_2O_3 (gray), 6%Ga/γ-Al_2O_3 (red), 9%Ga/γ-Al_2O_3 (blue), 12%Ga/γ-Al_2O_3 (green), and 15%Ga/γ-Al_2O_3 (orange). Simulated XRD spectra from SASOL Catalox specification sheet.

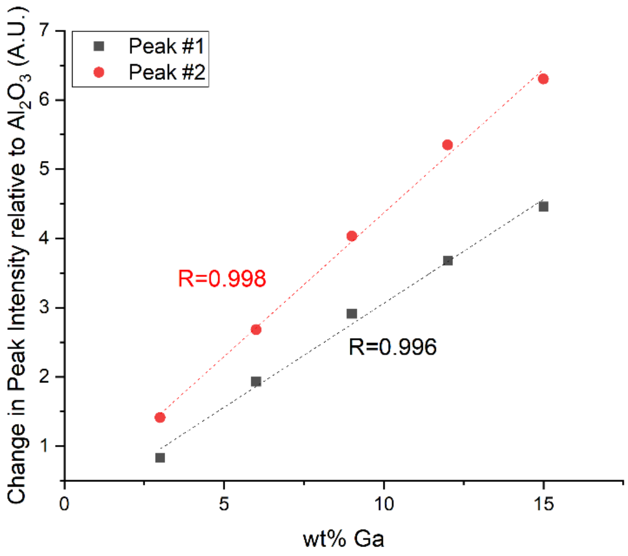


Figure 4 Change in XRD peak intensity versus the Ga weight loading; Peak #1 (black square) refers to the peak at 31° and peak #2 (red circle) refers to the peak at 37°

The Ga K-edge X-ray absorption near edge spectra (XANES) and X-ray absorption fine spectra (EXAFS) were obtained on the Ga/γ-Al_2O_3 catalysts to determine the oxidation state and coordination geometry, for example, number of Ga-O bonds and bond distance. The XANES energy is the inflection of the leading edge. The XANES energy of (octahedral) Oh Ga^{+3} ions, for example, in $Ga(AcAc)_3$ occurs at 10.3768 keV, see Figure 5. The XANES energy of Ga_2O_3, which has 50% Td (tetrahedral) and 50% Oh coordination, is 10.3740 keV, see Table 2. The XANES energy of Td Ga occurs at lower energy than Oh Ga ions; thus, for Ga_2O_3 the XANES energy is consistent with Ga with Td coordination. The XANES spectra of the as synthesized catalysts for 3, 6, 9, 12 and 15% Ga are identical and the XANES energy, 10.3747 keV and is consistent with Td coordinated Ga^{+3} ions and indicates that the structure of all Ga/γ-Al_2O_3 catalysts is the same.

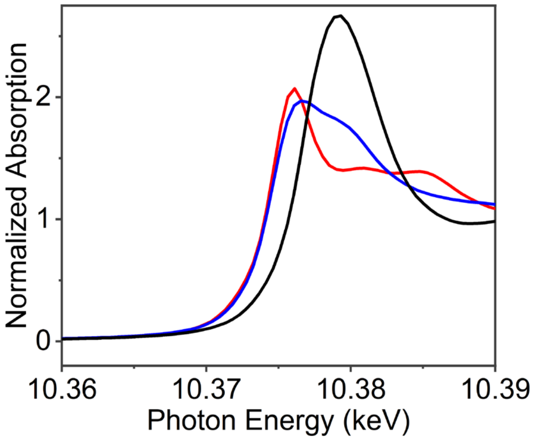


Figure 5 The Ga K-edge XANES from 10.36 – 10.39 keV of a) as-synthesized 3%Ga/γ-Al_2O_3 (Red), 3%Ga/SiO_2 (Blue) and $Ga(AcAc)_3$ reference (Black)

The magnitude of the k^2-weighted EXAFS of 3% Ga/γ-Al_2O_3 (Red) and the $Ga(AcAc)_3$ (Black) reference are shown in Figure 6. The Ga-O scattering peak at about 1.9 Å (phase uncorrected distance) of Ga(AcAc)$_3$, which has 6 Ga-O bonds at 1.95 Å, is larger and shifted to higher R than that of the Ga/alumina and Ga/silica catalysts. A fit of the first shell EXAFS of the Ga/ γ-Al$_2$O$_3$ gives 4 Ga-O bonds at 1.84 Å, Table 2. The EXAFS of the 3% Ga/γ-Al$_2$O$_3$ catalyst also has a small, higher-shell peak due to Ga-(O)-Al scattering. This was fit with 4 Ga-(O)-Al neighbors at 3.25Å. The EXAFS of all Ga/alumina catalysts give similar results to that of 3% Ga/γ-Al$_2$O$_3$, see Table 2. The EXAFS of 3% Ga/SiO$_2$ (Blue) was also fit giving 4 Ga-O bonds at 1.84 Å similar to Ga/Al$_2$O$_3$.[38]

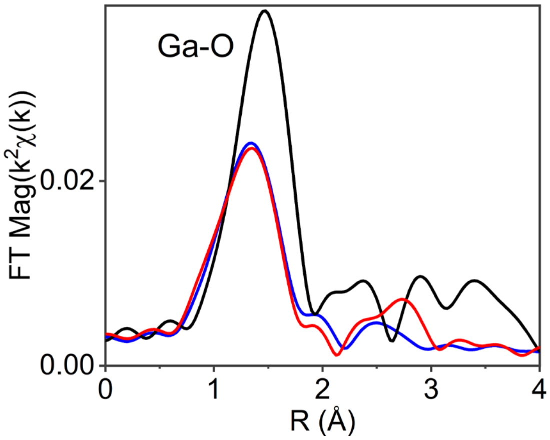


Figure 6 The Ga K-edge magnitude of the k^2-weighted EXAFS from k = 2.5 – 10.5 Å^{-1} of the as-synthesized samples of 3% Ga/γ-Al$_2$O$_3$ (Red) and 3% Ga/SiO$_2$ (Blue).

Previously, for Ga/SiO$_2$ catalysts, the Ga-O first shell coordination decreased at above about 400 °C in H$_2$ and during propane dehydrogenation.[32,38] Thus, the XANES and EXAFS of the Ga/γ-Al$_2$O$_3$ catalysts were also determined at 550 °C in He, H$_2$ and propane. There is no change in the XANES of the 6%Ga/γ-Al$_2$O$_3$ in He, H$_2$ or propane, Figure 7b, at 550 °C suggesting there is no change in the coordination geometry. Figure 8 and fits in Table 2 of the first shell Ga-O coordination number confirm that the Ga-O coordination does not change under any gas treatments at high temperature. Similar results were obtained for 3 Ga catalyst. Additionally, the EXAFS of

9% Ga/γ-Al_2O_3 in He, H_2 or propane was determined at 550 C. At this higher temperature, there is a larger $\sigma\Delta^2$ due to the large thermal disorder. The fits, Table 2, also show no change in the Ga-O coordination geometry at elevated temperature.

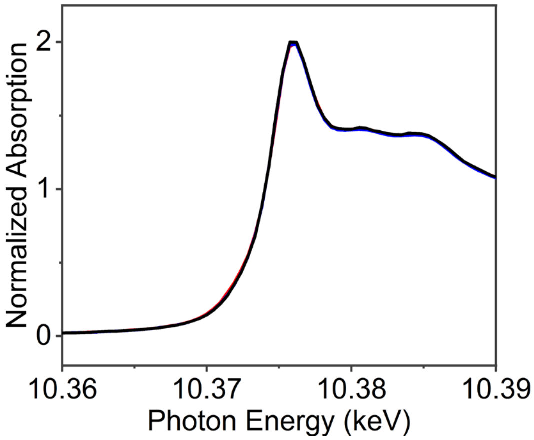


Figure 7 The Ga K-edge XANES from 10.35 – 10.39 keV of the 6%Ga/γ-Al_2O_3 at 550 °C in 20% He (blue), 10% H_2 (red), and 3% C_3H_8 (black).

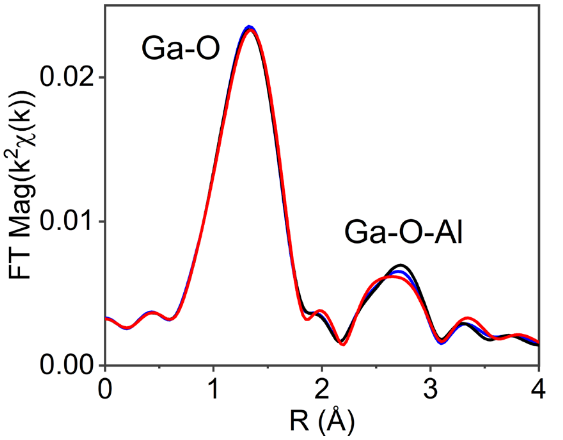


Figure 8 The magnitude of the k^2-weighted EXAFS from k = 2.5 – 10.5 $Å^{-1}$ of the 6%Ga/γ-Al_2O_3 at 550 °C in 10% He (blue), 10% H_2 (red), and 3% C_3H_8 (black).

Table 2 Ga K-edge EXAFS fitting results of as received Ga/ γ-Al_2O_3 after drying at 550 °C and gas treatments in air, H_2 or propane at 550 °C.

Sample	Treatment, Scan	XANES Energy, keV	Scatter	CN	R (Å)	σ^2	ΔE_0, eV
Ga_2O_3 Reference	25 °C He	10.3740		-	-	-	-
$Ga(AcAc)_3$	25 °C He	10.3768	Ga-O	6.1	1.95	0.002	0.6

Reference							
3%Ga/SiO_2	550 °C He 25 °C He	10.3746	Ga-O	4.0	1.84	0.004	-1.0
3%Ga/γ-Al_2O_3	550 °C He 25 °C He	10.3746	Ga-O	3.8	1.82	0.003	0.9
			Ga-O-Al	4.1	2.37	0.003	-5.5
3%Ga/γ-Al_2O_3	As synthesized 25 °C He	10.3746	Ga-O	3.8	1.82	0.003	0.9
6%Ga/γ-Al_2O_3	As synthesized 25 °C He	10.3746	Ga-O	3.9	1.83	0.003	0.5
			Ga-O-Al	4.1	3.26	0.003	-6.3
9%Ga/γ-Al_2O_3	As synthesized 25 °C He	10.3747	Ga-O	3.8	1.83	0.003	1.0
			Ga-O-Al	3.9	3.26	0.003	-6.6
12%Ga/γ-Al_2O_3	As synthesized 25 °C He	10.3747	Ga-O	4.1	1.84	0.003	-0.3
			Ga-O-Al	3.8	3.26	0.003	-7.3
15%Ga/γ-Al_2O_3	As synthesized 25 °C He	10.3747	Ga-O	4.0	1.81	0.003	-1.1
			Ga-O-Al	3.7	3.25	0.003	-7.2
9%Ga/γ-Al_2O_3	550 °C He 550 °C He	10.3747	Ga-O	3.8	1.83	0.006	0.9
9%Ga/γ-Al_2O_3	550 °C H_2 550 °C H_2	10.3747	Ga-O	3.8	1.82	0.006	0.6
9%Ga/γ-Al_2O_3	550 °C C_3H_8 550 °C C_3H_8	10.3747	Ga-O	3.8	1.83	0.006	0.6

Atomic-resolution STEM images were obtained for the as-synthesized 15%Ga/γ-Al_2O_3 catalyst, Figures 9a and 9b. The lattice images from the γ-Al_2O_3 are seen in both figures. In addition, individual bright spots (circled in yellow Figure 9) are consistent with isolated Ga atoms. There are no indications of Ga oxide clusters, despite the high Ga loading suggesting that the Ga ions are atomically dispersed.

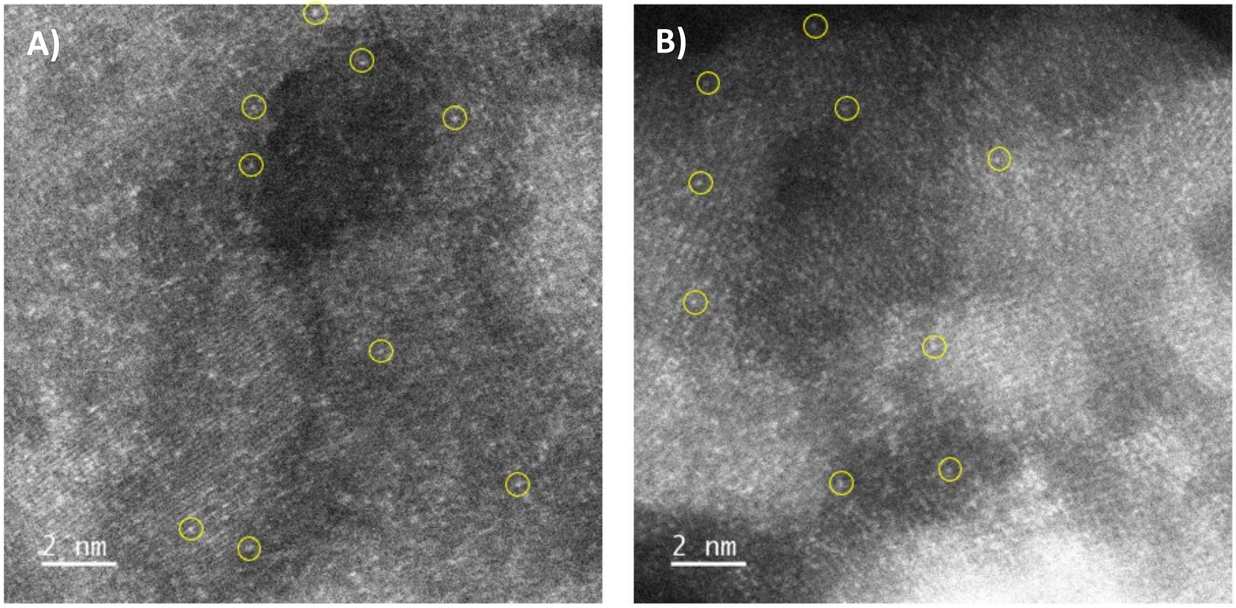


Figure 9 STEM images for 15%Ga/γ-Al_2O_3 sample; Ga ions are denoted with yellow circles.

Catalyst performance

Propane dehydrogenation

Each of the Ga/γ-Al_2O_3 catalysts with different Ga loadings (3, 6, 9, 12, and 15 wt%) was evaluated for propane dehydrogenation (PDH) at a propane partial pressure of 6 kPa and 550 °C to determine the difference in selectivity and rate with Ga loading.

Table 3 gives the PDH product selectivity and TOR rates for the Ga/γ-Al_2O_3 catalysts. The propylene selectivity is higher at low conversion and decreases at higher conversion. Within the error of the measurements, the propane conversion rates per Ga, i.e., the turnover rate (TOR), are the same, 1.2×10^{-3} moles C_3H_8/mole-Ga s^{-1}, for each Ga loading from 3-15%. At low conversions of less than about 10%, the propylene selectivity is near 95% but decreases to about 85% at 25-30% conversion. The by-products include methane and C_2's (ethane and ethylene), but there are also small amounts of C_4 and C_5 products. The selectivity to higher molecular weight products increases with increasing conversion.

Table 3 Propane dehydrogenation rates and selectivity of Ga/γ-Al_2O_3 catalysts, 6 kPa propane at 550 °C.

	3% Ga/γ-Al_2O_3		**6% Ga/γ-Al_2O_3**		**9% Ga/γ-Al_2O_3**		**12% Ga/γ-Al_2O_3**		**15% Ga/γ-Al_2O_3**	
Conversion (%)	7.5	28.8	8.2	27.7	7.6	29.4	8.6	32.2	9.5	33.8
Selectivity (%)										
Methane	0.9	2.7	0.9	2.5	0.9	2.7	1.1	3.1	1.1	3.4
C_2s	1.9	7.9	2.4	6.9	1.7	7.9	2.2	9.4	2.2	10.0
Propylene	95.8	84.5	95.2	86.3	96.1	83.9	95.1	81.7	95.1	80.7
C_4s	1.4	4.7	1.5	4.1	1.3	5.3	1.6	5.6	1.6	5.7
C_5s	-	0.2	-	0.2	-	0.2	0.0	0.2	0.0	0.2
PDH TOR rate*	1.2×10^{-3}		1.2×10^{-3}		1.2×10^{-3}		1.2×10^{-3}		1.2×10^{-3}	

*Turn Over Rate (TOR): (mol C_3H_8)/(mole Ga-s)

The product selectivity of each catalyst was determined from about 5-35% propane conversion. The propylene selectivity is shown in Figure 10 and the by-product selectivities are shown in Figure 11. As shown in Figure 10, the propylene selectivity linearly decreases with increasing propane conversion. At about 35% propane conversion, for example, the propylene selectivity is near 80%. In addition, the selectivity is independent of the Ga loading suggesting that the structure of the active site in each catalyst is identical. The by-product methane, C_2s (ethane and ethylene), and total C_4 selectivities are shown in Figure 11 for each Ga/γ-Al_2O_3 catalyst. The selectivity of each by-product increases with increasing conversion, and all catalysts have identical selectivities. Iso-butylene is the major C_4 hydrocarbon (> 60%). The C_2 hydrocarbons were > 70% ethylene. The selectivity towards methane is about 3%. The product selectivity at each conversion and each catalyst is given in Tables S1-S6.

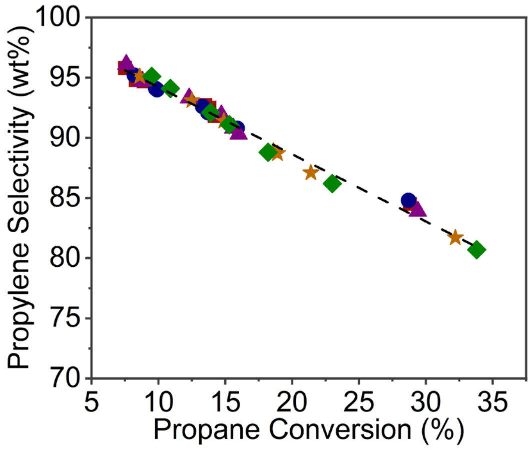
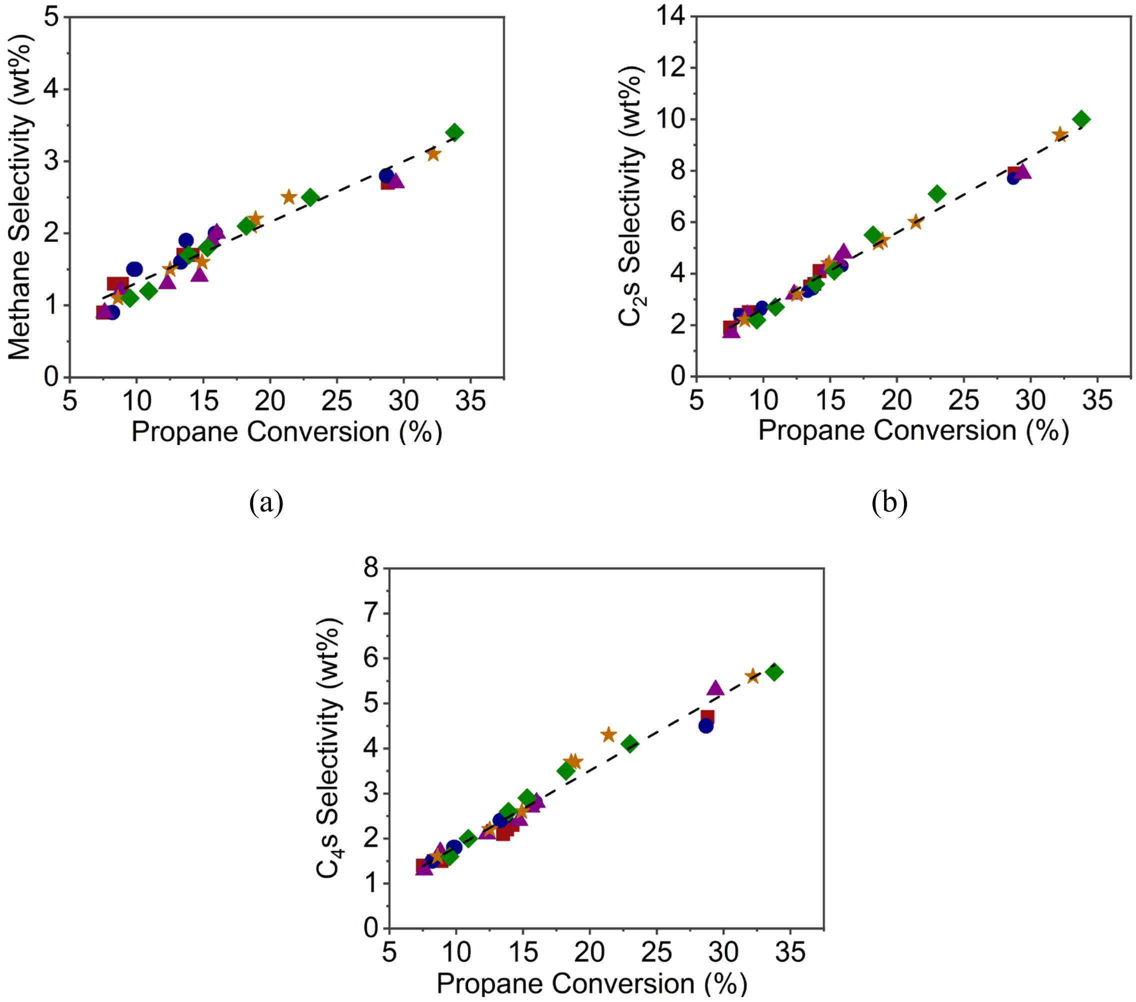


Figure 10 Weight % propylene selectivity verses propane conversion of Ga/γ-Al_2O_3 catalyst at 550 ºC and 6 kPa (Red Square: 3% Ga/γ-Al_2O_3 $_3$, Blue Circle 6% Ga/γ-Al_2O_3, Purple Triangle: 9% Ga/γ-Al_2O_3, Yellow Star: 12% Ga/γ-Al_2O_3, and Green Diamond: 15% Ga/γ-Al_2O_3).



(a)

(b)

(c)

Figure 11 Weight % by-product selectivities at different conversions: a) methane, b) C_2s, and c) total C_4s at different for the Ga/γ-Al_2O_3 catalysts at 550°C and 6 kPa (Red Square: 3% Ga/γ-Al_2O_3, Blue Circle 6% Ga/γ-Al_2O_3, Purple Triangle: 9% Ga/γ-Al_2O_3, Yellow Star: 12% Ga/γ-Al_2O_3, and Green Diamond: 15% Ga/γ-Al_2O_3).

Since all catalysts have identical rates and selectivity, the catalytic performance of the 15% Ga/γ-Al_2O_3 catalyst was tested under more practical conditions, i.e., 550 °C and 130 kPa propane partial pressure. Figure 12 compares propylene selectivity at 6 and 130 kPa at different conversions. At the higher pressure, the selectivity is significantly lower. The by-product selectivity of 15% Ga/γ-Al_2O_3 at different partial pressure is shown in Figure 13. The by-products methane, C_2s (ethane and ethylene), and total C_4 hydrocarbon selectivities are linearly increasing with increasing propane conversion. But at the higher pressure, in comparison to the lower pressure, the selectivity of each by-product significantly increases. The product selectivity at each conversion is given in Table S6.

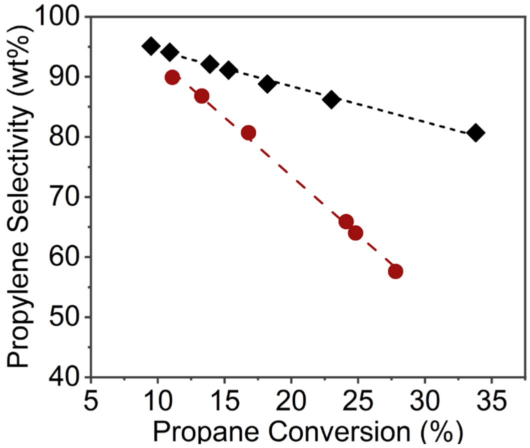
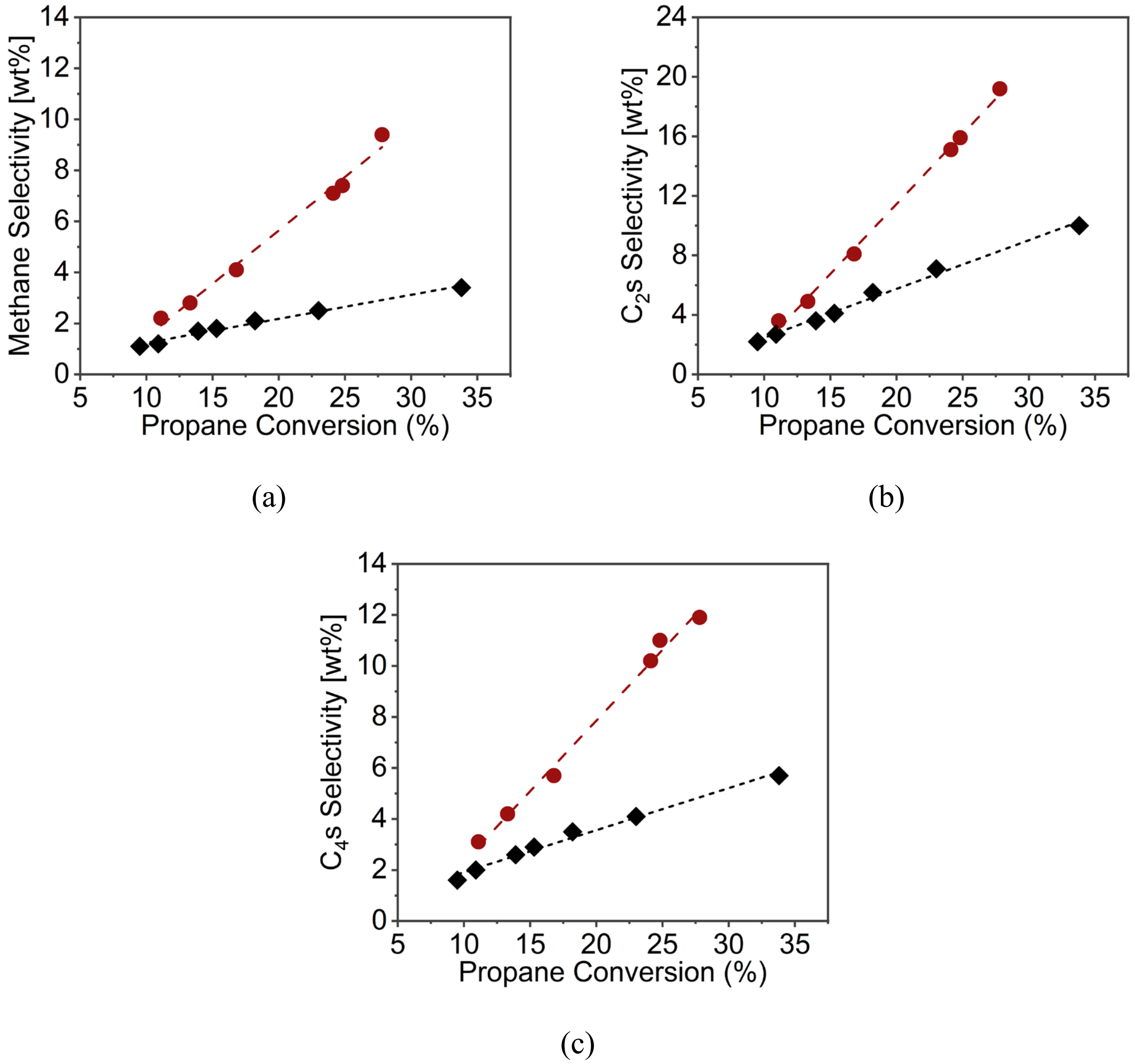


Figure 12 Weight % propylene selectivity versus propane conversion of 15% Ga/γ-Al_2O_3 catalyst at 550 °C and different partial pressure (Black Diamond: 6 kPa, and Red Circle: 130 kPa).



(a)

(b)

(c)

Figure 13 Weight % by-product selectivity, verses propane conversion of 15% Ga/γ-Al_2O_3 catalyst at 550 ºC and different partial pressure: a) methane, b) C_2s, and c) total C_4s (Black Diamond: 6 kPa, and Red Circle: 130 kPa).

Figure 14 shows the deactivation for PDH at 130 kPa and 550 °C, i.e., propane conversion verses time, for the 15% Ga/γ-Al_2O_3 catalyst. The initial conversion drops from about 33% to 25% during the first hour and then declines more slowly at longer time. The amount of coke on the catalyst was also determined for PDH after 15 minutes and 4 hours. The weight loss of coke (Eq. (1)), was determined by temperature programmed oxidation up to 800 ºC and is reported in Table

4. Nearly 7% coke was formed after 15 minutes, while an additional 3% coke is formed in about 4 hours.

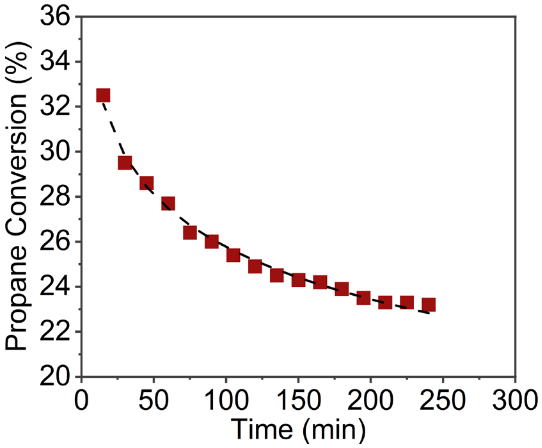
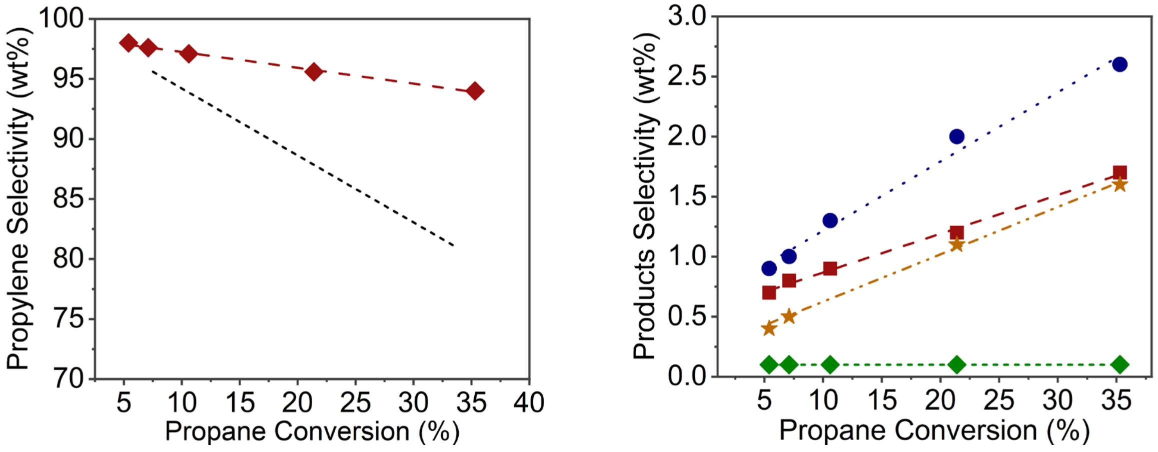


Figure 14 PDH deactivation for 15% Ga/γ-Al_2O_3 catalyst at 550 °C and 130 kPa propane partial pressure.

Table 4 The amount of coke formed at 550 °C during PDH and propylene reaction.

Catalyst	Feed	Partial pressure (kPa)	Time (min)	Coke (wt%)
15% Ga/γ-Al_2O_3	Pure Propane	130	15	6.8
			210	10.2
	30% Propylene	40	15	10.3
			210	14.9

To compare the performance of the (3-15)% Ga/γ-Al_2O_3 catalysts with that of 3% Ga/SiO_2, the latter was also tested under the same operating conditions used for Ga/γ-Al_2O_3, e.g., 550 °C, 6kPa. The propylene selectivity with increasing propane conversion is shown Figure 15a along with the average selectivity of Ga/γ-Al_2O_3 (dotted line). The by-product selectivities with increasing conversion are shown in Figure 15b. As the propane conversion increases, the propylene selectivity linearly decreases (Figure 15a). At a propane conversion close to 35%, propylene selectivity is 94%, which is significantly higher than that for Ga/γ-Al_2O_3, which is about 81%. The selectivity of methane, C_2s, and C_4s are reported in figure 15b for the 3% Ga/SiO_2 catalyst. The selectivity of by-products increases with the increase in propane conversion. Almost 40% of C_4s products are isobutylene, and 80% of C_2s products are ethylene. The TOR of 3% Ga/SiO_2 in the PDH process is 4.6×10^{-4}, approximately 2.5 times less than that for Ga/γ-Al_2O_3. The product selectivities of Ga/SiO_2 at each conversion are given in Table S7.



(a)

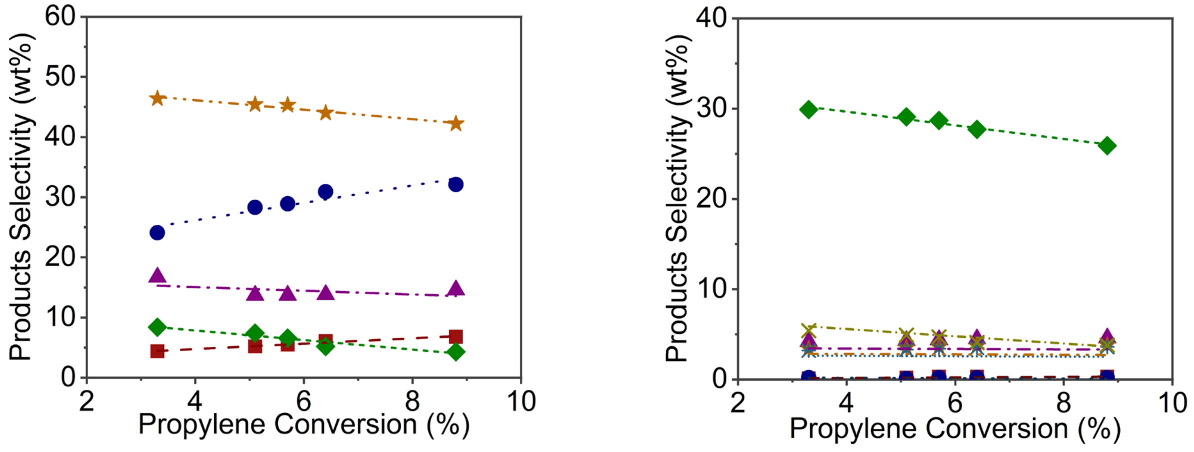
(b)

Figure 15 Weight % product selectivities verses propane conversion for the 3% Ga/SiO_2 catalyst at 550 ºC and 6 kPa a) Propylene (red squares: 3% Ga/SiO_2, and green dotted line: average value for Ga/γ-Al_2O_3) b) side-products (red square: methane, Blue Circle: C_2s, yellow stars: C_4s, and Green Diamond: C_5s)

Propylene conversion

The formation of small amounts of C_4 and C_5 hydrocarbons during PDH suggests that the product propylene is undergoing secondary reactions. Thus, the reaction of propylene at the same concentrations and temperature as that for PDH was investigated. Since the propylene partial pressure is lower than that of propane due to the partial conversion, initially, the 3% and 12%Ga/γ-Al_2O_3 catalysts were evaluated at a propylene partial pressure of ca. 4 kPa.

Figure 16 shows the propylene product selectivity with increasing conversion up to about 10%. In Figure 16a, the total C_4 hydrocarbons and C_2s were the major products. The selectivity was 45% but decreased slightly with increasing propylene conversion. The next highest selectivity was C_2 hydrocarbons at 25-30%. The C_2 hydrocarbons were > 95% ethylene. Approximately, although propylene was reacted without added H_2, 15% propane is produced. The methane and C_5 selectivities each are about 5%. Figure 16b shows the distribution of C_4s products with increasing propylene conversion for 12% Ga/γ-Al_2O_3. The most abundant product among C_4s is iso-butylene, which is about 60% of C_4s products. As the propylene conversion increases to 10%, the iso-butylene and 1,3-butadiene selectivities decrease, while the other C_4s products increase. The selectivities for 3% Ga/γ-Al_2O_3 are very similar to those for the 12% Ga/γ-Al_2O_3 catalyst. The selectivity of all products for the 3% and 12% Ga/γ-Al_2O_3 catalysts are given in Tables S8, and S9. Finally, the propylene TOR was 3.4×10^{-4} moles C_3H_6/mole-Ga s^{-1}, about 3.5 times lower than the TOR for PDH at 550 °C.



(a)

(b)

Figure 16 The propylene conversion product verses selectivities for 12% Ga/γ-Al_2O_3 at 550 °C and 4 kPa: a) all products (Red Square: methane, blue circle: C_2s, Purple Triangle: propane, Yellow Star: C_4s, and Green Diamond: C_5s), b) C4s products (Red Square: iso-butane, Blue Circle: butane, Purple Triangle: t-2-butane, Yellow Star: 1-butane, Green Diamond: iso-butylene, Light Blue Asterisk: c-2-butane, and Light Green X: 1,3-butadiene).

The reaction products for propylene conversion at higher partial pressures were also determined with the 15% Ga/γ-Al_2O_3 catalyst. Figure 17 shows the selectivity for propylene conversion product up to about 40%. Propane, C_2s, and C_4s were the major products. Although propylene was reacted without added H_2, the propane selectivity was 47% but decreased slightly with decreasing propylene conversion. The next highest selectivity was C_2 hydrocarbons at 18-19%, and the selectivity to C_4 hydrocarbons was 17-20%. The methane selectivity during the reaction decreases slightly from 17% to 12% with increasing conversion. The C_5s selectivity is low at about 2%. The complete propylene conversion product selectivity at each conversion is given in Table S10.

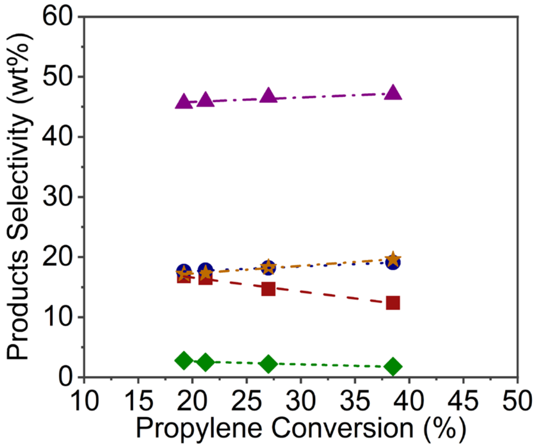


Figure 17 The propylene conversion product vs selectivities for 15% Ga/γ-Al_2O_3 at 550 °C and 40 kPa for all products (Red Square: methane, Blue Circle: C_2s, Purple Triangle: propane, Yellow Star: C_4s, and Green Diamond: C_5s).

The propylene deactivation rate was also determined, and the loss in conversion with time is shown in Figure 18. The initial deactivation rate is higher and decreases at longer times on stream, similar to PDH deactivation, Figure 12. The amount of coke on the catalyst was also determined for propylene conversion after 15 minutes and 4 hours. The weight loss of coke is reported in Table 4. Similar to PDH, propylene conversion gave higher coking rates at 15 minutes, ca. 10%, while at 4 hours the amount of coke was 15%. The coking rate of propylene was about 30% higher than for PDH.

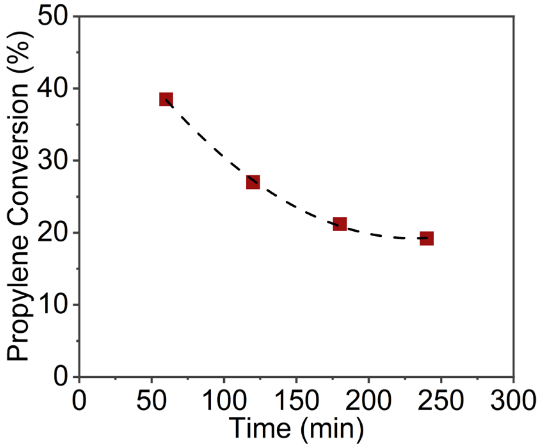
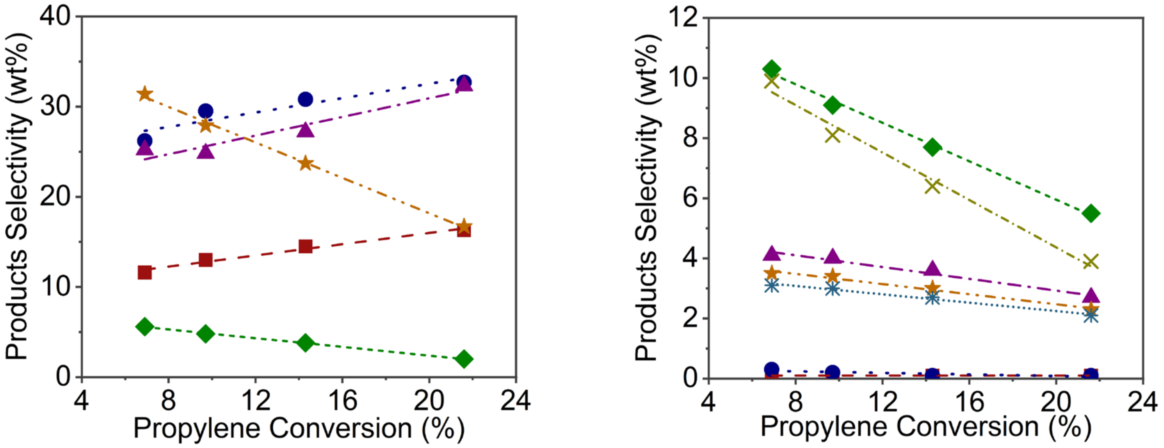


Figure 18 Propylene deactivation for 15% Ga/γ-Al_2O_3 catalyst at 550 °C and at 40 kPa.

As shown in Figure 15b, PDH with 3% Ga/SiO_2 also produces some higher molecular weight products, indicating secondary propylene reactions. Thus, the propylene conversion rate and product selectivities were determined at the PDH reaction conditions. As shown in Figure 19a, the majority of products include C_2s, propane, and C_4s. With increasing propylene conversion from 7-22%, the C_4 selectivity decreases from 31% to 17%; while the C_2s and propane selectivities increase. Almost 70% of C_2 products are ethylene. Despite the absence of H_2 in the feed, propylene produces about 30% propane. With an increase in propylene conversion from 7 to 22%, the methane selectivity also increases from 11 to 16%. The selectivity of C_5s is less than 7%. Figure

19b shows the distribution of C_4s products for propylene conversion reaction utilizing 3% Ga/SiO_2. The major C_4s products are iso-butylene and 1,3-butadiene. With increasing propylene conversion, there is a decrease in the C_4 selectivity, with increasing selectivity to methane, C_2 and propane, Figure 19a. The 3% Ga/SiO_2 TOR is 1.1×10^{-4}, which is approximately 4 times lower than that for PDH. The propylene product selectivity at each conversion is given in Table S11.



(a)

(b)

Figure 19 The propylene conversion product verses selectivities for 3% Ga/SiO_2 at 550 °C and 4 kPa: a) all products (Red Square: methane, Blue Circle C_2s, Purple Triangle: propane, Yellow Star: C_4s, and Green Diamond: C_5s), b) C4s products (Red Square: iso-butane, Blue Circle: butane, Purple Triangle: t-2-butane, Yellow Star: 1-butane, Green Diamond: iso-butylene, Light Blue Asterisk: c-2-butane, and Light Green X: 1,3-butadiene).

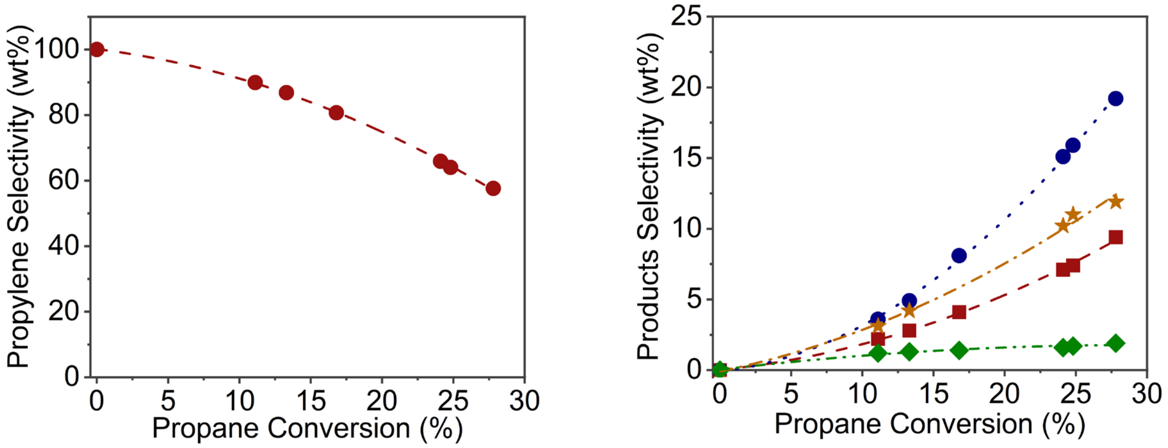
Discussion

Ga/γ-Al_2O_3 PDH catalysts with Ga loadings from 3-15% were synthesized and their structures were determined by XRD, XAS and STEM. The XRD diffraction pattern of γ-Al_2O_3 has 4 broad peaks, Figure 3. As the Ga loading increases, the peaks at 40° and 46° 2θ do not change, while there is a continual increase in the peak intensity at 32° and 38° 2θ, Figures 3 and 4. The XRD is consistent with Ga occupying similar coordination sites on alumina at all loadings.

The Ga oxidation state and local coordination geometry were determined by XANES and EXAFS, respectively. The XANES energies of all catalysts were identical and is consistent with 4 coordinate Ga^{+3} ions. The EXAFS fits of all catalysts were also identical, with 4 Ga-O bonds at 1.84 Å. This bond distance is also consistent with Td Ga coordinations.[39] The higher shell fit gives 4 Ga-O-Al bonds at about 3.25 Å. Attempts to fit the higher shell peaks with a Ga-O-Ga scattering path gave poor fits. Thus, XAS analysis suggests that the structure of the catalyst is an isolated, 4 coordinate Ga^{+3} ion bonded to the alumina support. The single site Ga ions were confirmed for the 15% Ga/ γ-Al_2O_3 catalysts by atomic resolution STEM, Figure 9, where individual Ga ions are observed with no visible Ga oxide clusters.

The PDH product selectivities and TORs were determined for Ga/γ-Al_2O_3 catalysts. At all Ga loadings as the conversion increases, there is a decrease in propylene selectivity and all catalysts have very similar product distributions, see Figures 10 and 11 plus Tables S1-S5. The propylene selectivities at equivalent conversion are consistent with those reported in the literature.[33] In addition to propylene, the by-products include the expected methane and ethane in an approximate 1:2 weight ratio, see Figure 11a, 11b and Table 3, consistent with formation by hydrogenolysis reactions. Unexpectedly, there is also a significant by-product selectivity to C_4 hydrocarbons, Figure 11c. The most abundant C_4 product is iso-butene, with smaller amounts of 1-butene and 2-butenes, see Tables S1b-S5b. In addition to similar product selectivities, the TORs are also very similar, ca., 1 x 10^{-3} sec^{-1}. The catalytic performance is consistent with the characterization indicating that all catalytic sites are identical up to 15 wt% Ga.

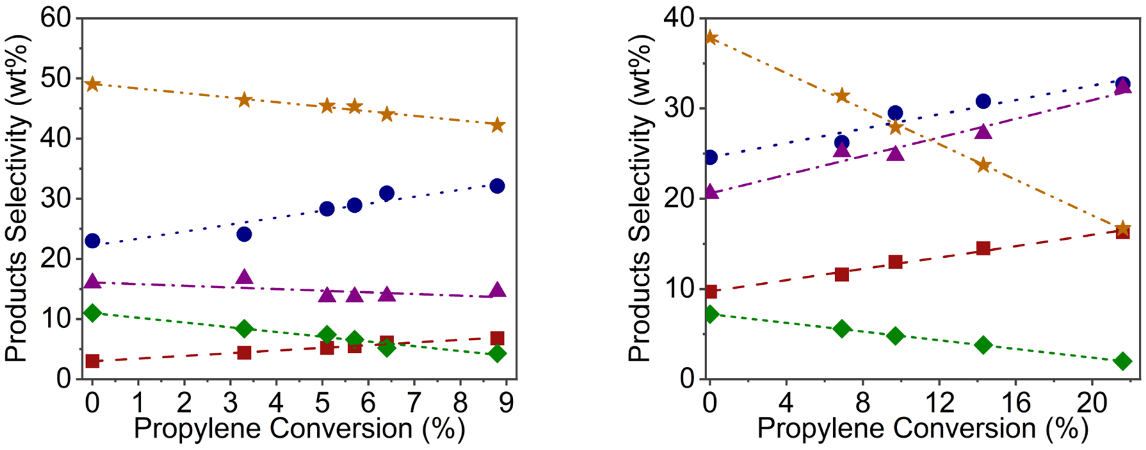
PDH at higher propane partial pressure gives the same reaction products but with lower propylene selectivity, Figure 12. The lower propylene selectivity is due to higher selectivities for methane, ethane and butenes, Figure 13. The product selectivities for 15% Ga/γ-Al_2O_3 at 134 kPa were extrapolated to zero conversion to determine the primary and secondary reaction products, Figure 20. Although the propylene selectivity is about 50% at 30% propane conversion, see Figure 12, the intrinsic selectivity, i.e. the selectivity extrapolated to zero propane conversion is very high and close to 100%, Figure 20a. Consistent with the high intrinsic propylene selectivity, the light gas intrinsic selectivities, Figure 20b, are near 0% at zero propane conversion indicating these are all secondary PDH products. Typically, for Pt alloy PDH catalysts, hydrogenolysis products, methane and ethane, are primary products and not secondary products.



(a) (b)

Figure 20. Weight % product selectivities verses propane conversion of 15% Ga/γ-Al_2O_3 catalyst at 550 ºC and 134 kPa a) Propylene b) side-products (Red Square: methane, Blue Circle: C_2s, Yellow Star: C_4s, and Green Diamond: C_5s); data taken from Table S6.

If the light gas formation is due to secondary reactions of propylene during PDH, these should be primary products for the direct conversion of propylene. The primary products of propylene conversion are methane, ethylene, propane, butenes and pentenes. The selectivities extrapolated to zero propylene conversion are shown in Figure 21a, and the selectivities at zero conversion are given in Table 5.



(a) (b)

Figure 21. The propylene conversion verses products selectivities for a) 12% Ga/γ-Al_2O_3 and b) 3%Ga/SiO_2 at 550 °C and 4 kPa (Red Square: methane, Blue Circle: C_2s, Purple Triangle: propane, Yellow Star: C_4s, and Green Diamond: C_5s); data taken from Tables S9, and S11.

Table 5. The selectivity at zero percent conversion of propylene at 550 C and 4 kPa.

Product	% Selectivity	
	12% Ga/γ-Al_2O_3	3%Ga/SiO_2
Methane	3	10
Ethylene	23	25
Propane	16	21
Butenes	49	38
Pentenes	11	7

Although the propylene reaction with 12% Ga/γ-Al_2O_3 was conducted in the absence of H_2, there were nevertheless saturated products, for example, propane. This is perhaps not surprising since Ga catalysts have hydrogenation and dehydrogenation activities at this temperature. An initial selectivity to propane indicates that there are hydrogen transfer reactions occurring during propylene conversion. The products of ethylene and butenes, however, are unexpected primary products from the reaction of propylene. In 12% Ga/γ-Al_2O_3, the weight ratio of 23:49 ethylene to butenes is close to a 1:1 molar ratio suggesting that propylene is undergoing a disproportionation reaction, i.e. 2 propylene gives 1 ethylene + 1 butene. A similar reaction was recently reported for propylene conversion on γ-Al_2O_3 at 260°C and 1.5 atm.[40] Finally, with increasing conversion, the selectivities of butenes and pentenes decrease suggesting that these are also reactive on the Ga catalyst.

The reaction rate for propylene conversion and propane dehydrogenation are given in Table 6. The rate of propylene conversion is 0.28 times that of PDH. Thus, although Ga/γ-Al_2O_3 has a high intrinsic PDH propylene selectivity, the significant rate of secondary reactions of propylene gives additional non-propylene products lowering the propylene selectivity as observed in Figures 10 and 12.

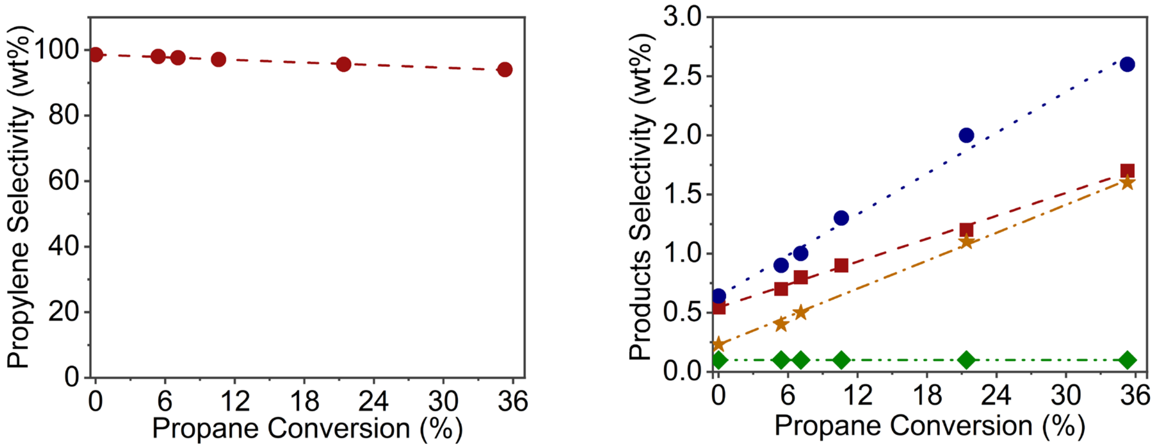
Table 6 Propylene reaction (4 kPa propane at 550 °C) and Propane dehydrogenation (6 kPa propane at 550 °C) rates and selectivity of Ga/γ-Al_2O_3 and Ga/SiO_2 catalysts.

Catalyst	**PDH**			**Propylene Reaction**
	Conversion (%)	**Selectivity (wt%)**	**TOR (mol C_3H_8)/(mole Ga.s)**	**TOR (mol C_3H_6)/(mole Ga.s)**
Ga/Al_2O_3	34	81	1.2×10^{-3}	3.4×10^{-4}
Ga/SiO_2	35	94	4.6×10^{-4}	1.1×10^{-4}

Since these secondary propylene reactions also occur on alumina at the PDH reaction temperatures,[40] to determine whether the reactions are occurring on the alumina support or the Ga catalytic site, a Ga/SiO_2 was also prepared. The XAS characterization indicate that the Ga coordination and oxidation state are very similar to those on alumina, i.e., Ga^{+3} ions with 4 Ga-O bonds at 1.84 Å. While the local coordination geometry and oxidation state are very similar, the

XANES is not the same as that on alumina, see Figure 5, suggesting that the energy of the valence 4p orbitals are slightly different. In addition, previously it was shown that reduction of Ga/SiO_2 in H_2 at PDH temperatures leads to a loss in Ga-O bonds for Ga/SiO_2,[32,38,41]which is not observed for these Ga/γ-Al_2O_3 catalysts. These differences suggest that the support modifies the chemical nature of the Ga active site.

For the Ga/SiO_2 the PDH propylene selectivity is higher than that of Ga/γ-Al_2O_3, see Figure 15a and the TOR, Table 6, of the former is lower than that of the latter, e.g., 4.6×10^{-4} and 1.2×10^{-3} sec^{-1}, respectively. Similar to Ga/γ-Al_2O_3 the by-products are the same, i.e., methane, ethane, butenes and pentenes, Figure 15b. The PDH product selectivities extrapolated to zero propane conversion are shown in Figure 22. Similar to Ga/γ-Al_2O_3, the intrinsic propylene selectivity is nearly 100%, i.e., it is a primary product, Figure 22a; while the selectivities of the light gases are near 0% at zero propane conversion, Figure 22b, suggesting these are secondary PDH products.



(a) (b)

Figure 22. Weight % product selectivities verses propane conversion of 3% Ga/SiO_2 catalyst at 550 ºC and 4 kPa a) Propylene b) side-products (Red Square: methane, Blue Circle: C_2s, Yellow Star: C_4s, and Green Diamond: C_5s); data taken from Table S7.

The primary products for propylene reaction on Ga/SiO_2 are shown in Figure 21b, and the selectivities extrapolated to zero propylene conversion are given in Table 5. The methane and propane selectivities are higher; while, the butenes and pentenes are lower again suggesting change in the catalytic performance due to the type of support. Finally, these reaction products on Ga/SiO_2 indicate that the isolated Ga^{+3} ions, and not γ-Al_2O_3, are catalytic sites for the secondary propylene PDH reactions.

Conclusion

Ga/γ-Al_2O_3 catalysts with 3-15% by weight of Ga were synthesized using the IWI method and calcination at 550C. Characterizations, by XRD, STEM, and XAS indicate that at all loadings isolated, four coordinate Ga^{3+} ions are bonded to γ-Al_2O_3. In addition, the PDH catalytic rates and product selectivities of all Ga/γ-Al_2O_3 were identical. The PDH propylene selectivity decreases with increasing conversion and was also dependent on the propane partial pressure. The PDH by-products included methane, ethane and unexpectedly butenes and pentenes. Extrapolation of the PDH products to zero propane conversion indicates that the intrinsic propylene selectivity is near 100%, i.e., is a primary product. The selectivity of all light gases extrapolated to zero propane conversion, however, indicates these are secondary reactions. Consistent with this conclusion, the reaction of propylene on Ga/γ-Al_2O_3 at PDH conditions gives primary products of methane, ethylene, propane, butenes and pentenes. Thus, although the PDH intrinsic propylene selectivity is very high, these secondary reactions of the initial product lead to lower selectivity at higher conversions.

A 3% Ga/SiO_2 was also prepared and has a very similar structure to that of Ga/γ-Al_2O_3, i.e., isolated, four coordinate Ga^{3+} ions. Although, the PDH propylene selectivity of the former was higher than that of the latter, the same by-products were formed, including butenes and pentenes. Similar to the Ga/γ-Al_2O_3 catalysts, extrapolation of the selectivity to zero propane conversion indicate that propylene is a primary product with an intrinsic selectivity near 100%. Likewise, the selectivity of the light gases extrapolated to zero conversion indicate these are secondary products, which was confirmed by the direct reaction of propylene. This latter reaction also suggests that these secondary propylene reactions are occurring on the Ga active site, rather than the support. The differences in the rates and selectivities for PDH and propylene conversion of Ga/γ-Al_2O_3 and Ga/SiO_2 also suggests that that the catalytic performance is dependent on the support type.

Acknowledgements

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