Graphical Abstract

Catalytic Propane Dehydrogenation over $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3$ Mixed Oxides

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Abstract

We have investigated the catalytic performance of novel $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3$ mixed oxides synthesized by the alcoholic-coprecipitation method for propane dehydrogenation (PDH). Reactivity measurements reveal that the activities of $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3$ catalysts are 1-3 fold (on an active metal basis) and 12-28 fold (on a surface area basis) higher than an $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst in terms of C_3H_8 conversion. The structure, composition, and surface properties of the $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3$ catalysts are thoroughly characterized. $\text{NH}_3\text{-TPD}$ shows that the binary oxide system generates more acid sites than the corresponding single-component catalysts. Raman spectroscopy suggests that catalysts that produce coke of a more graphitic nature suppress cracking reactions, leading to higher C_3H_6 selectivity. Lower reaction temperature also leads to higher C_3H_6 selectivity by slowing down the rate of side reactions. XRD, XPS, and XANES measurements, strongly suggest that metallic indium and In_2O_3 clusters are formed on the catalyst surface during the reaction. The agglomeration of In_2O_3 domains and formation of a metallic indium phase are found to be irreversible under O_2 or H_2 treatment conditions used here, and may be responsible for loss of activity with increasing time on stream.

Keywords

Propane dehydrogenation; In_2O_3 ; Ga_2O_3 ; Mixed metal oxides;

1. Introduction

The catalytic dehydrogenation of short-chain hydrocarbons such as light alkanes is an effective way to increase the value of light alkane streams from fossil-based sources. Dehydrogenation is of renewed interest due to the large availability of new feedstocks derived

from hydraulic fracturing ('fracking') operations [1]. Among this family of reactions, propane dehydrogenation (PDH) is of particular interest, since propylene is a crucial feedstock for polymer production [2]. Total propylene consumption was 83 million tons in 2013 and the global demand is forecast to grow at a CAGR of 4.8% during 2013-2018 [3].

Oxidative dehydrogenation (ODH) of propane is an alternate way to produce propylene. In this scenario, an oxidative gas (O_2 or CO_2) is co-fed with propane. This process has several advantages, such as being exothermic and offering no thermodynamic limitations. However, this approach is faced with problematic over-oxidation (combustion), which can decrease propylene productivity. The most extensively studied catalysts involve Mo/V/Ce based oxides [4-7]. An array of alternate catalysts also continue to be explored, such as metallic alloy (i.e., Cu-Al) catalysts [8] and intermetallic (i.e., Cu-Sn, Cu-Fe-Al) fibers [9]. Several reviews focus on discussing ODH approaches in detail [10-12].

Non-oxidative propane dehydrogenation is an endothermic and equilibrium-limited process that requires relatively high temperature and low pressure conditions to obtain a high yield of propylene. The main issues associated with PDH under such conditions are undesired thermal cracking of the feedstock and products (producing short-chain hydrocarbons) as well as coke formation, which blocks active sites and causes rapid catalyst deactivation [13]. Currently, commercial industrial PDH processes are based on Cr [14, 15] (CATOFIN[®] from CB&I Lummus) and Pt [16-18] (Oleflex from UOP) catalysts. However, these catalytic systems are impacted by rapid deactivation due to coke formation and competitive C-C bond cracking, which causes loss of propylene yield. Hence, a periodic catalyst regeneration step is important in the above-mentioned industrial operations [19]. Many efforts have been made in improving the catalytic performance, including the addition of a second metal such as Sn, In, or Ga into Pt-

based catalysts [20-30], or the modification of Cr-catalysts with alkali additives [31-34]. Meanwhile, other parallel investigations were devoted to systems involving MoO_x [35], VO_x [36, 37], and Zn^{2+} [38]. However, improved PDH catalysts are continuously sought.

Recently, PDH catalysts involving group IIIA metal oxides have attracted attention. It has been reported that supported Ga_2O_3 and bulk Ga_2O_3 show promising catalytic performance for propane dehydrogenation [39-41]. However, the nature of the active site in Ga_2O_3 is still unclear, in part because of its structural complexity and the co-existence of several polymorphs of Ga_2O_3 in mixed oxide materials. Also, the reducibility of Ga_2O_3 strongly depends on its interaction with the support material as well as the potential presence of metals such as Pt [42] and Pd [43]. A proposed reaction mechanism involves heterolytic dissociation, in which H^- adsorbs on a Ga^+ site (gallium hydride) and a C_3H_7^+ carbocation bonds with a neighboring O atom to form a gallium alkoxide [44]. Supported In_2O_3 as a catalyst in presence of weak oxidative gases (i.e., CO_2 , N_2O) was also investigated, and was found to be of interest as a potential new PDH catalyst [45-48]. They proposed that reduced metallic indium at the catalyst surface was the active site due to observation of an induction period.

However, to the best of our knowledge, there are no reports investigating binary In_2O_3 - Ga_2O_3 mixed oxide catalysts for PDH. Since each single oxide component exhibited some activity, we hypothesized that the mixed In-Ga oxide catalysts could show interesting PDH properties different from the two individual oxide catalysts. To this end, in this work we have prepared a series of mixed In-Ga oxides and evaluated them in detail for the catalytic dehydrogenation of propane. The structural properties of these mixed-oxide catalysts were also elucidated *via* characterization by a range of techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), N_2 -physisorption,

temperature-programmed desorption (TPD) of NH_3 , temperature-programmed reduction (TPR) with H_2 , and elemental analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The deposited carbonaceous species were examined by thermogravimetric analysis (TGA) and Raman spectroscopy. The resulting mixed-metal oxides exhibit a considerably higher activity in terms of propane conversion than previously reported mixed $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$, as well as compared to $\gamma\text{-Ga}_2\text{O}_3$, on both a catalyst mass basis and surface area basis. The origin of this behavior is discussed.

2. Experimental

2.1 Catalyst Preparation

A series of binary $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3$ mixed oxides was synthesized by an alcoholic co-precipitation method [49]. In a typical synthesis, specific amounts of the indium and gallium precursors (nitrate hydrate, Sigma-Aldrich, 99.9%) at different molar ratios were dissolved in ethanol (Alfa-Aesar, 95%). Then, a mixture containing concentrated aqueous ammonia (Sigma-Aldrich, 28 wt%) and ethanol (1:1 in volume) was added dropwise to the precursor solution until no further precipitation occurred ($\text{pH} \approx 8.5$). After aging for 1 hr while stirring at 250 rpm at room temperature, the mixture was centrifuged for 30 min at 6000 rpm. Then the recovered, precipitated gel was dried at 70 °C overnight. Finally, the obtained sample was calcined in air at 600 °C for 6 hrs. The resulting In-Ga binary oxides are labeled as IG x - y , where x and y denote the molar ratio of $\text{In}_2\text{O}_3/\text{Ga}_2\text{O}_3$ in the catalyst (e.g., IG10-90 denotes a material with In and Ga in a 10:90 ratio).

2.2 Catalyst Characterization

N₂ adsorption-desorption isotherms were measured with a Tristar II 3020 apparatus from Micromeritics. The samples were degassed and preheated at 110 °C under vacuum on a Schlenk line for 12 hrs before the measurements. The specific surface area (by the BET method), pore volume (by T-Plot method), and the average pore size (by the BJH method) were obtained with the software of the apparatus.

Elemental analysis for indium and gallium within the catalysts was performed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) by ALS Global.

X-ray diffraction (XRD) measurements were performed on a PANalytical X'pert Pro X-ray diffractometer operating with Ni-filtered Cu K α radiation (0.154187 nm), with generator settings of 45 kV, 40 mA, a scanning step size of 0.008°, and scanning regions of 6-80° 2 θ .

The reducibility of catalysts was assessed with H₂ temperature-programmed reduction (H₂-TPR) in a flow-type fixed bed reactor using an Autochem II Chemisorption Analyzer from Micromeritics. A mixture of 10 vol % H₂/Ar was used as the reducing gas with a total flow rate of 30 sccm. About 100 mg sample was heated from room temperature to 900 °C at a heating rate of 5 °C/min after being pretreated at 150°C for 1 hr in Ar gas flow (50 sccm). The reducing gas was cooled by a cold trap filled with a mixture of acetone and liquid nitrogen to remove the water generated from reduction of catalyst. The reduction signal was recorded by a thermal conductivity detector (TCD).

The surface acidity was assessed by temperature-programmed desorption of NH₃ (NH₃-TPD) at ambient pressure with the above-mentioned equipment. About 100 mg sample was preheated to 500 °C with a ramp of 10 °C/min and maintained for 1 hr, followed by cooling to 120 °C under He flow (25 sccm). Then sufficient NH₃ (5 vol% in He, 30 sccm, 2 hrs) was injected until a saturated sample was obtained, followed by purging with He (25 sccm) for 1 hr.

After obtaining a stable baseline, the sample was heated to 700 °C at a rate of 10 °C/min. The desorbed NH₃ was detected by a thermal conductivity detector (TCD).

Raman spectroscopy was performed using a Thermo Nicolet Almega XR Dispersive Raman Spectrometer, equipped with confocal optics before the spectrometer entrance, and a CCD detector. A microscope was used to focus the excitation laser beam (488nm) with a laser power of ~15 mW on the sample and to collect the Raman signal in the backscattered direction. The acquisition time was 30 s and 30 spectra were recorded for each sample. Moreover, each sample was analyzed by collecting data at 3-5 points to eliminate the effects of the heterogeneity of the sample.

Thermogravimetric analysis (TGA) was carried out by using Netzsch STA 449 F3 Jupiter TG-DSC. About 30 mg sample was loaded in a pan. Then it was heated from 20 °C to 900 °C in air with flow rate of 90 ml/min.

XPS analysis was carried out using Thermo K-Alpha spectrometer employing a monochromatic Al K α X-ray source. Pressures near 5×10^{-8} Torr were observed in the analytical chamber during surface analysis. The binding energies (BE) of all elements were referenced to the C 1s peak of contaminant carbon at 284.6 eV with an uncertainty of ± 0.2 eV.

XAS measurements were carried out at the beamline of the materials research collaborative access team (MRCAT, 10BM-A,B) at the Advanced Photon Source (APS), Argonne National Laboratory. Samples were measured in transmission mode using ion chambers with 2% N₂ in Ar. Data were collected with a cryogenically cooled double-crystal Si (111) monochromator. The X-ray beam size was ca. 1.5×1.5 mm². An indium foil spectrum was measured simultaneously to calibrate the energy. The XANES pre-edge energy analysis of indium was performed using *WinXAS 3.2* software package according to standard data analysis procedures.

2.3 Catalyst Evaluation

The PDH reaction was performed in a U-shape fixed bed quartz reactor (ca. 3.5 mm i.d., 80 cm long) with a measured amount of catalyst (pellet size 150-212 μm) under atmospheric pressure at 600 $^{\circ}\text{C}$. The sieved powder was held in the reactor by quartz wool. The reactor was then heated to 600 $^{\circ}\text{C}$ in an Al_2O_3 fluidized bath (Techne FB-08) under 20 sccm N_2 flow. The reactant flow contained C_3H_8 with balancing N_2 . The hydrocarbon products as well as H_2 were analyzed on line by a gas chromatograph (SHIMADZU GC-2014) equipped with a RESTEK Column (Rt-Alumina BOND/ Na_2SO_4 , 30 m $\times$ 0.25 mm $\times$ 4 μm) and a TCD, respectively (See supporting material, Figure S1). The data were collected after flowing the reactant mixture for 10 min. The mass balance based on carbon had a maximum deviation of 10%. The conversion and molar selectivity were calculated by using the following equations:

$$\text{C}_3\text{H}_8 \text{ Conversion (\%)} = \frac{\text{C}_3\text{H}_{8\text{in}} - \text{C}_3\text{H}_{8\text{out}}}{\text{C}_3\text{H}_{8\text{in}}} * 100\%$$
$$\text{Product Selectivity (\%)} = \frac{X_{\text{out}}}{\text{C}_3\text{H}_{8\text{in}} - \text{C}_3\text{H}_{8\text{out}}} * 100\% \quad (X = \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_2\text{H}_4, \text{C}_3\text{H}_6, \text{etc.})$$

After reaction, the catalyst was purged with N_2 , cooled down to room temperature under its protection and removed from the reactor for ex-situ measurements.

3. Results and discussion

3.1 Structural characterization

Figure 1 depicts the diffractograms for three In_2O_3 - Ga_2O_3 mixed oxides as well as synthesized bulk In_2O_3 and Ga_2O_3 samples for comparison. The bulk In_2O_3 exhibits a well-crystallized structure. The 2θ angles at 21.7 $^{\circ}$, 30.6 $^{\circ}$, 35.6 $^{\circ}$, 37.7 $^{\circ}$, 41.9 $^{\circ}$, 45.7 $^{\circ}$, 51.2 $^{\circ}$ and 60.8 $^{\circ}$ are identified as characteristic of the cubic bixbyite phase of In_2O_3 (JCPDS 6-0416) [50]. In

contrast, the broad diffraction lines of the as-synthesized Ga_2O_3 indicate its mostly amorphous structure. The peaks at 31.9° , 35.4° and 64.6° are assigned as (220), (311) and (440) planes of γ - Ga_2O_3 (JCPDS 20-0426) [51]. Such low crystallinity is common in the γ -polymorphs of gallia, although other phases (i.e., α -, β -) may also coexist [52]. For the series of IG mixed oxides, no obvious diffraction lines were observed, suggesting the low concentration of indium precluded the formation of large crystalline domains. The patterns suggest the indium oxide may be well-dispersed during the co-precipitation and calcination process.

Table 1 summarizes the textural properties (BET surface area, pore volume and average pore size) of the IG catalysts. The physisorption isotherms are shown in the supporting information (Figure S2). The bulk In_2O_3 has the largest pore size but lowest surface area, while the bulk Ga_2O_3 exhibits the opposite behavior, a large surface area with a small pore size less than 4 nm. As the indium-gallium ratio is adjusted within the mixed oxide samples, the properties follow the above trend within the limits of instrumental error.

Among the surface properties of the catalysts that affect catalytic performance, acidity plays a key role in many reactions [53]. Hence, the surface acidity of the In-Ga catalysts was examined by NH_3 -TPD (See supporting material, Figure S3). The results are summarized in Table 2. All the mixed metal oxides exhibit two TPD peaks: one broad peak at 120-450 $^\circ\text{C}$, and a smaller peak between 450-600 $^\circ\text{C}$. These two peaks correspond to acid sites with weak and medium strength, respectively. It is difficult to explicitly correlate the acid properties of binary oxide systems, since the resulting acidity can be influenced by many factors such as the type of metals, the synthetic method, and the relative population of metals [54]. However, it is widely accepted that the combination of two metal oxides can usually generate more acidic sites than that of a single component oxide [55-57]. It can be seen from Table 2 that the In-Ga samples

contain more acid sites (normalized by the mass of catalyst) than pure In_2O_3 and Ga_2O_3 . Pure In_2O_3 exhibits the most acid sites based on surface area, and the value monotonically decreases when increasing the Ga_2O_3 percentage.

3.2 Redox properties characterization

The redox properties of the IG mixed oxides were characterized by H_2 -TPR. Figure 2 shows the H_2 -TPR profiles of the bulk In_2O_3 , Ga_2O_3 , and various In_2O_3 - Ga_2O_3 mixed oxides. A broad peak centered at $\sim 710^\circ\text{C}$ is assigned to the reduction of bulk In_2O_3 to In^0 [58, 59]. The calculated H_2 uptake is $\sim 8.9 \text{ mmol/g}_{\text{cat}}$, indicating $\sim 80\%$ of the In_2O_3 species are reduced to indium metal under these conditions. Similarly, the reduction extents for In-Ga binary oxides samples containing indium are calculated and listed in Table 1. In contrast, no peaks are observed for reduction of bulk Ga_2O_3 , suggesting Ga_2O_3 could not be reduced in H_2 in the current temperature region [60]. For the case of In-Ga mixed oxides, the reduction peak appears at a lower temperature (ca. $500\text{--}600^\circ\text{C}$) with much weaker intensity, although no peak was observed for the IG2-98 sample, possibly due to the extremely small amount of indium in the sample. The shift of the reduction peak is generally accepted for reduction of supported In_2O_3 with different particle sizes. Smaller particles lead to lower reduction temperatures. Taking in account that highly-dispersed In_2O_3 could be reduced in the range of $200\text{--}500^\circ\text{C}$ [58, 59], the observed shift suggests the formation of moderately-dispersed In_2O_3 in the mixed oxide. The appearance of a single reduction peak suggests that only one type of In_2O_3 phase may exist in the IG samples, an observation that is different from the previous study on In-Al mixed oxides [46].

3.3 Propane dehydrogenation reactions

Propane dehydrogenation over the In-Ga mixed oxides was carried out at 600°C under 1 atmosphere total pressure. The main products are propylene and hydrogen. Other side products

formed include short chain hydrocarbons, such as methane, ethane, and ethylene. Trace amounts of higher hydrocarbons (i.e., butane, pentane) are also observed. Prior to the reaction, blank tests were carried out under the same conditions (i.e., temperature, gas mixture composition, residence time, etc.) to investigate the extent of thermal cracking. These results indicate that less than 4.5% conversion can be associated with thermal reactions (See supporting material, Table S1).

Two ranges of reactivity were investigated in this study. First, the reactions were run such that the initial propane conversion was less than 10% to assess the intrinsic reactivity of the catalysts. The gas mixture composition was fixed at 5 vol% C_3H_8 balanced with N_2 , with a total flow rate of 20 sccm, while the catalyst amount was varied. The residence time was ca. 4 seconds. As can be seen in Figure 3a, a deactivation was observed for the three catalysts during the initial 90 min, after which the conversion became stable. The IG2-98 catalyst shows a constant C_3H_6 selectivity ranging from 30-40%, while for the IG5-95 and IG10-90 catalysts, the selectivity decreases to ca. 20% after 150 min. However, the initial selectivity during the first 30 min of reaction is higher for these catalysts than for the IG2-98 material (Figure 3b). Fitting the reactivity data from the steady-state region and extrapolating back to time zero, an extrapolated initial conversion ('intrinsic activity') was estimated for each catalyst. Our data suggest the In-Ga mixed oxides exhibit higher intrinsic activity as the indium percentage decreased (on both catalyst mass basis and surface area basis). Given the observed trend, it is worthwhile to examine whether bulk Ga_2O_3 would be the most active catalyst. Hence, a control experiment was carried out under the same conditions with γ - Ga_2O_3 (See supporting material, Figure S4). Interestingly, the calculated initial activity for this material is similar to IG5-95. The initial reaction rates on both catalyst mass basis and surface area basis were calculated and are summarized in Table 3. The highest values for IG2-98 are $25.5 \mu\text{mol/hr/m}^2$ and $2.1 \mu\text{mol/hr/g}_{\text{cat}}$, respectively. To have an

accurate comparison with the literature, the instantaneous activities associated with the first data point were also calculated and are reported in Table 3. For an alternate comparison, the mass based activity of the reference catalyst IA10-90 was calculated by considering only In_2O_3 species as active. While for the current IG series, both In_2O_3 and Ga_2O_3 are considered to provide activity. The results suggest the catalysts of the IG series exhibit higher activity than the Al_2O_3 -supported In_2O_3 catalysts reported previously by a factor of 12-28 (surface area basis) and 1-3 (active metal basis) at the same reaction temperature [46], noting that the current WHSV is 4 times that used in the previous literature report (0.54 hr^{-1} vs. 0.135 hr^{-1}). In addition, the superior activities of IG5-95 and IG2-98 compared with $\gamma\text{-Ga}_2\text{O}_3$ suggest a synergistic effect due to incorporation of indium into a dominant Ga_2O_3 phase.

A second series of experiments was aimed at reaching a higher conversion regime that is more relevant to industrial operation. For these runs, the reaction conditions were fixed for all three catalysts, giving the results are shown in Figure 4. The residence time was ca. 8 seconds. As before, a deactivation period is observed in the initial 90 min of reaction, as shown in Figure 4a. Subsequently, a steady activity is obtained over the In-Ga mixed oxides in the order of IG2-98 > IG5-95 > IG10-90. The calculated intrinsic activities were 0.9, 0.7, and $0.5 \mu\text{mol/hr/g}_{\text{cat}}$, respectively. Regarding the C_3H_6 selectivity data shown in Figure 4b, IG2-98 provided a value of ~25% over the course of the reaction. For the case of IG5-95 and IG10-90, although the initial selectivity value was higher (ca. 28%) but then dropped to a lower steady-state selectivity (ca. 13% and 10%, respectively) with the following order: IG2-98 > IG5-95 > IG10-90. The main side-products are CH_4 , C_2H_6 and C_2H_4 . The product distributions are shown in Figure 5. The quantities are in the following order: $\text{C}_3\text{H}_6 > \text{CH}_4 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_6$.

Zhuang et al. previously proposed that metallic In^0 generated from highly dispersed In_2O_3 over Al_2O_3 support is the active site for PDH [46, 47], based on evidence of an induction period in terms of conversion. In contrast, in the current study, no such phenomenon was observed. Taking into account the fact that metallic indium has a melting point at ca. 157 °C, at the current reaction temperature the generated In^0 could be highly mobile, leading to sintering of the indium domains. Given the catalytic performance of the IG catalysts for propane dehydrogenation with no observable induction period, one may surmise the active sites may be different from the proposal for the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ system.

The most active catalyst (IG2-98) was chosen to evaluate the effect of the reaction temperature with the aim of finding an optimal operating condition. As shown in Figure 6, the steady values of conversion decrease along with a decrease of reaction temperature. Meanwhile, a rough trend of C_3H_6 selectivity was observed: lower temperature led to higher selectivity, as expected (although the data in Figure 6b have relatively larger scatter than those in Figure 6a). This observation can be rationalized by the fact that lower hydrocarbon ($\text{C}_1\text{-C}_2$) byproducts formed through cracking and pyrolysis processes become kinetically and thermodynamically unfavorable at lower temperature [61]. Thus, an optimal temperature needs to be carefully chosen to suppress the side reactions while keeping the desired route kinetically active.

Ex-situ XPS measurements were carried out to reveal the surface In/Ga ratio of the catalysts. The results for the series of catalysts before and after reaction are summarized in Table 4. It can be seen that the In/Ga ratio at the surface increases after the reaction. This may be due to the migration and agglomeration of indium from the bulk phase to the surface during the reaction. In addition, considering the redox properties of indium oxide, the dispersed In_2O_3 species at the surface can be simultaneously reduced by the formed H_2 during the dehydrogenation, which

leads to removal of surface oxygen and consequently causes an increase of the indium mass percentage at the surface.

Indium K-edge XANES was used to evaluate the electronic state of the In-Ga catalysts before and after reaction, and the fitting results are summarized in Table 4 as well. The raw XANES data and fitting curves are available in the supporting information as Figure S5 and S6. From the data, it is clear that no metallic indium exists in the as-synthesized In-Ga catalysts. However, after dehydrogenation, all the In-Ga catalysts contain metallic indium to varying extents, suggesting that indium oxide domains are easily reduced under the reaction conditions employed. There is no obvious trend that correlates the $\text{In}^0/\text{In}^{3+}$ ratio with the overall In-Ga composition. This is possibly due to the complexity of the binary metal oxide system (i.e., how the guest In_2O_3 disperses in the primary Ga_2O_3 , the domain size of In_2O_3 , etc.). It should be mentioned that metallic indium is quite stable to oxidation at room temperature and could hardly be oxidized to In_2O_3 under an ambient air environment, though it has been reported to form a ~4 nm oxide layer after heating at 130 °C in air for 120 min [62]. In addition, although metallic indium can exhibit intermediate oxidation states at high temperature, in the current study, it is unlikely to occur as a stable species, since preparation of In_2O from In_2O_3 was reported to require heating at 700 °C under vacuum conditions, while InO was only detected in the vapor phase [63].

In parallel with the XANES investigation, ex-situ XRD measurements were carried out to examine any changes in crystallinity of the In-Ga catalysts after the reaction, and the results are summarized in Figure 7. For the IG10-90 and IG5-95 samples, characteristic peaks assigned to In_2O_3 (JCPDS 6-0416) appeared after the dehydrogenation reaction, consistent with indium sintering during reaction. Moreover, it is noteworthy that some diffraction peaks associated with

metallic indium (JCPDS 85-1409) also appear [64]. This is due to the partial reduction upon exposure to reducing reaction conditions (600 °C with H₂ and hydrocarbons). Such a conclusion is also supported by the H₂-TPR experiments. Along with the XPS and XANES results, this provides evidence for the formation of In⁰ during the reaction. No obvious change was found for the IG2-98 sample in the XRD pattern, likely due to the low indium loading, although the XANES spectra support the formation of some In⁰ domains in this material as well.

To gain insights into the stability and recyclability of the In-Ga catalysts, a re-oxidation step at 600 °C was added and IG10-90 was investigated over the course of two re-oxidation cycles after an initial period of activity. From Figure 8, it is clear that after the re-oxidation step, the activity modestly increases during the first 20 min. However, overall, the activity and selectivity of the catalyst remains mostly unchanged, even after re-oxidation. An XRD measurement for IG10-90 catalyst after the re-oxidation step was also carried out and is shown in Figure 7, where it can be observed that after exposing to air at the reaction temperature for one hour, the main peak for the (101) plane of In⁰ slightly decreases in intensity, suggesting the In⁰ domains could be partly re-oxidized. Aside from this, the overall pattern is almost identical to that of the sample before re-oxidation. This observation suggests during the reaction, the agglomeration of well-dispersed In₂O₃ to larger domains occurs and may be responsible for the loss of activity. Such a process, at least under the current re-oxidation treatment, is believed to not be completely reversible.

H₂ pretreatment was also applied to an example of IG10-90 prior to the reaction at 600 °C, and the results are shown in Figure 9. It can be seen that the initial conversion is ~16%, and drops to a steady conversion of ~12.5% after 70 min. After a 1-hr H₂-regeneration, the IG10-90 catalyst regains its original activity while decreasing again to the steady state conversion again

within 70 min. Meanwhile, it should be noted that for this IG catalyst after the H₂-treatment, the C₃H₆ selectivity is poorer than in the case of the O₂-treatment. A H₂-pretreatment (reducing some In₂O₃ to In⁰) could significantly change the surface properties (acidity, surface area) of the solid. Therefore, an H₂-TPR followed by NH₃-TPD over bulk In₂O₃ was investigated. After reduction by H₂, the produced In⁰ shows a weak NH₃ signal, indicating the sample lost most of the surface acidity (see supporting material, Figure S7). Our findings indicate that reduced In⁰ under reaction conditions may melt and migrate/agglomerate as a non-porous material, causing a dramatic loss of surface area and acidity, which is proposed to contribute to the loss of activity. In addition, the increase of In₂O₃ domain size (from ex-situ XRD) might be another reason for loss of catalytic performance.

3.4 Coke analysis

As the main issue associated with deactivation in the PDH process is coke formation, Raman spectroscopy was used to examine the deposited carbonaceous species at the catalyst surface. The spectra were deconvoluted into a combination of 4 bands. The individual peak parameters (position, intensity, FWHM) were set based on visual inspection. Then the residuals between the raw data and overall fit were minimized in a least squares regression. The G band was fitted by a Lorentzian function, while a Gaussian function was used to fit other bands. Figure 10 shows the stack of obtained Raman spectra as well as the fitted results for the spent IG catalysts that were used for the experiments shown in Figure 3. As can be seen, four distinguishable bands appeared in the region of 1000-1800 cm⁻¹. The most intensive band at ca. 1590 cm⁻¹ was assigned as the G band, which is due to a perfectly crystalline carbonaceous material (i.e., a graphitic lattice) [65]. The second most intense band at ~1360 cm⁻¹ is the D₁ band due to in-plane defects and heteroatoms in the carbon lattice. In addition, the D₃ band at

1500 cm^{-1} and the D_4 band at 1220 cm^{-1} are assigned as amorphous carbon (out-plane defect) and a disordered graphitic lattice, respectively [66]. Previous study tried to correlate the G band position to the graphite particle size, (1575 cm^{-1} for larger and perfect graphite crystals, while a blue shift to 1590 cm^{-1} indicated a decrease of the crystallite size) [67]. For the catalysts studied here, a clear correlation of the band position vs. In-Ga ratio was not observed. However, the G band positions for the IG samples were all around 1590 cm^{-1} , suggesting small graphite crystals amongst the deposited coke. An important parameter to describe degree of organization of the carbonaceous materials is the intensity ratio of the D_1/G bands (R_1 ratio). These values are listed in Table S2, where it can be seen that a decrease in the In/Ga ratio corresponds to the D_1/G ratio dropping from 0.88 to 0.70. This indicates that a catalyst with a lower indium percentage tends to produce coke with a more ordered and graphitic nature. This might suggest a correlation between the nature of the coke formed and the steady state value of the C_3H_6 selectivity: coke with more graphitic nature is correlated with catalysts that yield a higher C_3H_6 selectivity, perhaps by suppressing side reactions that lead to low molecular weight (cracking) products. This would be consistent with Weckhuysen's previous study over Pt-based catalysts [66].

It should be mentioned that the accurate quantitative analysis of coke in the catalysts by TGA is difficult in the current In-Ga-O system because the indium species reduced under reaction conditions are reoxidized during TGA experiments aimed at assessing the coke content on the catalysts. In this study, two methods were applied to estimate the total amount of formed coke: (i) based on direct TGA measurements with simplifying assumptions to deconvolute indium oxidation vs. carbon combustion, and (ii) examining the carbon percentage of the remaining spent catalyst by elemental analysis. The TGA results are shown in the supporting information (Figure S8). It should be noted that the mass loss during the 350-600 $^{\circ}\text{C}$ ramp range

is the overall effect of mass loss due to the coke decomposition and mass gain due to oxidation of metallic indium produced under PDH conditions. In this way, the coke percentage was estimated by subtracting the indium re-oxidation (assuming all In^0 atoms are oxidized. The indium content in each sample was measured by elemental analysis). The calculated deposited coke percentage as well as the carbon balance from both methods are summarized in Table 5. It can be seen that the general trend suggests that higher gallium content leads to more coke formation. In general, calibrated results based on these methods show good consistency, although method 1 provides a little higher coke estimate than method 2. The carbon balance after calibration using these methods is generally higher than 90%.

4. Conclusions

In this work we have explored $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3$ mixed-oxide catalysts for non-oxidative propane dehydrogenation reactions. This family of catalysts is shown to exhibit high intrinsic activity in terms of C_3H_8 conversion. Among the In-Ga catalysts, we report that IG2-98 provides maximum activity of $58.6 \mu\text{mol/hr/m}^2$ (28 fold) and $4.9 \mu\text{mol/hr/g}_{\text{cat}}$ (3 fold) higher than the previously studied $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts even at a 4 times higher WHSV, although the steady value of C_3H_8 selectivity is less than half of that observed in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (ca. 35% vs. 85%). For the best catalyst operating at higher conversions, a stable conversion of ca. 25%, was achieved with a modest ca. 25% C_3H_6 selectivity. As expected, a lower reaction temperature helps to suppress side reactions (cracking) to enhance C_3H_6 selectivity, while suppressing overall productivity. H_2 -TPR measurements suggest the incorporation of In-O-Ga linkages improves the dispersion and reducibility of In_2O_3 domains. NH_3 -TPR experiments demonstrate a generation of acidic sites in the mixed oxides compared to the single component oxides. Raman analysis

indicates that catalysts with deposited coke with more disordered structures have lower C_3H_6 selectivity, while catalysts with graphite-like coke better suppress side reactions and maintain higher level of C_3H_6 selectivity. Ex-situ XPS, XRD, and XANES analysis illustrates the agglomeration of dispersed In_2O_3 domains and production of In^0 are responsible, at least in part, for the loss of activity during use. These processes are not completely reversible under O_2/H_2 regeneration treatments.

The present study indicates that the In/Ga binary oxide system has potential as a new catalyst for the propane dehydrogenation reaction. However, due to the low/moderate propene selectivity and catalyst deactivation, substantial improvements in catalyst preparation would have to be achieved to reach a performance comparable to commercial Cr-based and Pt-based catalysts for this reaction.

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Tables

Table 1. The chemical and physical properties of In-Ga mixed oxide catalysts.

Catalyst	$S_{\text{total}}^{\text{a}}$ (m^2/g)	$V_{\text{total}}^{\text{b}}$ (cm^3/g)	Pore Size ^b (nm)	In/Ga ratio ^c	Reduction extent ^d (%)
In ₂ O ₃	11	0.05	19.1	-	81.1
IG10-90	75	0.05	3.7	0.14	31.7
IG5-95	87	0.07	3.7	0.06	57.3
IG2-98	83	0.07	4.1	0.03	35.9
Ga ₂ O ₃	84	0.07	3.8	-	-

^a Calculated by BET method

^b Calculated by BJH method

^c Molar ratio of bulk phase was obtained by ICP-OES

^d Percentage of In₂O₃ reduced to In⁰ during H₂-TPR experiment

Table 2. NH₃-TPD data of In-Ga mixed oxide catalysts.

Catalyst	α -peak (120-450 °C)		β -peak (450-600 °C)		Total	
	NH ₃ (mmol/g _{cat})	NH ₃ (μ mol/m ²)	NH ₃ (mmol/g _{cat})	NH ₃ (μ mol/m ²)	NH ₃ (mmol/g _{cat})	NH ₃ (μ mol/m ²)
In ₂ O ₃	0.16	14.2	0.01	0.8	0.17	15
IG10-90	0.46	6.1	0.01	0.1	0.46	6.2
IG5-95	0.43	4.9	0.05	0.6	0.48	5.5
IG2-98	0.43	5.2	0.03	0.4	0.46	5.6
Ga ₂ O ₃	0.32	3.9	0.03	0.3	0.35	4.2

Table 3. Catalytic performance of In-Ga mixed oxide catalysts.

Catalyst	Conversion ^a (%)	C ₃ H ₆ Selectivity ^b (%)	Activity ^c ($\mu\text{mol/hr/m}^2$)	Activity ^c ($\mu\text{mol/hr/g}_{\text{cat}}$)
IG2-98	7.9	33.7 (35)	25.5 (58.6)	2.1 (4.9)
IG5-95	7.2	39.7 (18)	14.8 (33.5)	1.3 (2.9)
IG10-90	6.1	45.5 (16.5)	10.9 (25.1)	0.8 (1.9)
Ga ₂ O ₃	9	30.2 (16.2)	14 (22)	1.2 (1.9)
IA10-90 ^d	12	30 (83)	- (2.1)	- (1.7)

^a The initial conversion obtained by extrapolating the linear region to zero time.

^b Initial selectivity at 10 min. Numbers in parenthesis are estimated steady-state value of selectivity.

^c Intrinsic activity calculated on surface area and active metal (In and Ga) basis. Numbers in parenthesis are instantaneous activity by using actual data point at 10 min (in the same way as [46]).

^d Data from [46].

Table 4. Ex-situ XPS and XANES analysis for the IG catalysts before (pre) and after (post) reaction.

Catalyst	Composition from XANES		In/Ga molar ratio from XPS
	In ³⁺ (%)	In ⁰ (%)	
IG2-98 pre	100	-	0.05
IG2-98 post	84	16	0.12
IG5-95 pre	100	-	0.09
IG5-95 post	60	40	0.16
IG10-90 pre	100	-	0.17
IG10-90 post	78	22	0.45

Table 5. Carbon balance and coke formation over the catalysts.

Sample	Carbon balance (%)		Coke ^c (%)	
	Before calibration ^d	After calibration ^d	Method 1	Method 2
IG2-98 ^a	97	98.3	1.3	^e
IG5-95 ^a	95	96.2	1.2	^e
IG10-90 ^a	96	97.1	1.1	^e
IG2-98 ^b	86	96.4 (95.5)	10.4	9.5
IG5-95 ^b	87	91.4 (91.2)	4.4	4.2
IG10-90 ^b	86	90.7 (90.1)	4.7	4.1

^a: IG catalysts used in Figure 3.

^b: IG catalysts used in Figure 4.

^c: Values based on total carbon in feed gas.

^d: Calibration refers to the process of applying method 1 and method 2 (numbers in parenthesis).

^e: Sufficient coked sample unavailable for analysis.

Figure Captions

Figure 1. XRD patterns of bulk In_2O_3 , Ga_2O_3 , and various In_2O_3 - Ga_2O_3 mixed oxides.

Figure 2. H_2 -TPR profiles of bulk In_2O_3 , Ga_2O_3 , and various In_2O_3 - Ga_2O_3 mixed oxides.

Figure 3. C_3H_8 conversion (a) and C_3H_6 selectivity (b) of various In_2O_3 - Ga_2O_3 mixed oxides at low conversions. Reaction condition: 5 vol% C_3H_8 in N_2 ; total flow rate: 20 sccm; Temperature: 600 °C; catalyst amount: IG2-98 0.1g, IG5-95 0.15g, IG10-90 0.2g.

Figure 4. C_3H_8 conversion (a) and C_3H_6 selectivity (b) of various In_2O_3 - Ga_2O_3 mixed oxides at a fixed catalyst loading. Reaction condition: 3 vol% C_3H_8 in N_2 ; total flow rate: 10 sccm; Temperature: 600 °C; catalyst amount: 0.3g.

Figure 5. Product distribution of PDH over IG series catalysts. Reaction condition: 3 vol% C_3H_8 in N_2 ; total flow rate: 10 sccm; Temperature: 600 °C; catalyst amount: 0.3g.

Figure 6. Temperature effect on C_3H_8 conversion (a) and C_3H_6 selectivity (b) using a IG2-98 catalyst. Reaction condition: 5 vol% C_3H_8 in N_2 ; total flow rate: 20 sccm; Temperature: 600 °C; catalyst amount: 0.1g.

Figure 7. XRD patterns of In_2O_3 - Ga_2O_3 mixed oxides before (pre) / after (post) reaction, and for the IG10-90 catalyst after the re-oxidation step (after regen).

Figure 8. Propane dehydrogenation time on stream study with the IG10-90 catalyst with intermediate oxidation steps. Reaction condition: 5 vol% C₃H₈ in N₂; total flow rate: 20 sccm; Temperature: 600 °C. Regeneration conditions: re-oxidation step with air flow rate of 30 sccm, N₂ purge before and after re-oxidation step with flow rate of 30 sccm.

Figure 9. Propane dehydrogenation time on stream study of the IG10-90 catalyst with intermediate reduction steps. Reaction condition: 5 vol% C₃H₈ in N₂; total flow rate: 20 sccm; Temperature: 600 °C. Pretreatment and regeneration conditions: reduction step is 2.5 vol% H₂ in N₂ with total flow rate of 20 sccm, N₂ purge before and after re-oxidation step with flow rate of 30 sccm.

Figure 10. Raman spectra of coke deposits formed on the surface of the IG catalysts. Open circles: raw data; Red curve: overall fitting; Blue dashed line: deconvoluted individual peaks.

Figure 1. XRD patterns of bulk In_2O_3 , Ga_2O_3 , and various In_2O_3 - Ga_2O_3 mixed oxides.

Figure 2. H₂-TPR profiles of bulk In₂O₃, Ga₂O₃, and various In₂O₃-Ga₂O₃ mixed oxides.

Figure 3. C_3H_8 conversion (a) and C_3H_6 selectivity (b) of various In_2O_3 - Ga_2O_3 mixed oxides at low conversions. Reaction condition: 5 vol% C_3H_8 in N_2 ; total flow rate: 20 sccm; Temperature: 600 °C; catalyst amount: IG2-98 0.1g, IG5-95 0.15g, IG10-90 0.2g.

Figure 4. C₃H₈ conversion (a) and C₃H₆ selectivity (b) of various In₂O₃-Ga₂O₃ mixed oxides at a fixed catalyst loading. Reaction condition: 3 vol% C₃H₈ in N₂; total flow rate: 10 sccm; Temperature: 600 °C; catalyst amount: 0.3g.

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Figure 9. Propane dehydrogenation time on stream study of the IG10-90 catalyst with intermediate reduction steps. Reaction condition: 5 vol% C₃H₈ in N₂; total flow rate: 20 sccm; Temperature: 600 °C. Pretreatment and regeneration conditions: reduction step is 2.5 vol% H₂ in N₂ with total flow rate of 20 sccm, N₂ purge before and after re-oxidation step with flow rate of 30 sccm.

Figure 10. Raman spectra of coke deposits formed on the surface of the IG catalysts. Open circles: raw data; Red curve: overall fitting; Blue dashed line: deconvoluted individual peaks.