Kinetics of propane dehydrogenation over
Pt–Sn/Al₂O₃[†]Cite this: *Catal. Sci. Technol.*, 2013,
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The kinetics of the gas-phase dehydrogenation of propane over Pt–Sn (1 : 1 mol ratio) supported on Al₂O₃ was investigated for the first time over the high range of reactant/products partial pressures (up to 0.875 atm). The Pt precursor was reduced to metallic form after a temperature-programmed reduction (TPR) at 873 K. X-ray photoelectron spectroscopy (XPS) analysis suggests that a Pt–Sn surface alloy forms, decreasing the H₂ adsorption on the Pt–Sn sites (5.6 nm in average size) relative to monometallic Pt (6.8 nm). We performed kinetic studies in the absence of mass/heat transfer limitations. The incorporation of Sn into Pt in Pt–Sn/Al₂O₃ enhanced the catalytic activity and stability when compared to Pt/Al₂O₃. We attribute this response to the surface electronic interaction between Pt and Sn. The initial propane consumption rate increases with the partial pressure of propane and decreases with the partial pressure of propene, while varying that of hydrogen has a negligible effect. Applying the Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach, the most likely kinetic model is non-dissociative adsorption of propane with simultaneous release of H₂, where surface reaction is the rate-limiting step. Our results of the kinetic aspects provide practical insights relevant to propane dehydrogenation.

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1. Introduction

Alkenes are essential building blocks in the bulk- and fine-chemicals industry with a large worldwide demand.¹ For example, propene is used for producing polypropylene (43 × 10⁶ tons in 2008), a key compound for making fibres and tubing.^{2,3} The main industrial routes to propene are steam cracking of naphtha and fluid catalytic cracking of (vacuum) gas oil. These processes are carried out at high temperatures (613–873 K)^{4,5} and deliver a low propene yield (≈17%) in a pool of hydrocarbons.⁶ The low propene selectivity forms a serious handicap to downstream processing, because the impurities affect the performance of the polymerization catalysts.⁷ Alternatively, the direct dehydrogenation of propane (see eqn (1)) represents an efficient route to propene:

There are many catalytic studies dealing with propane dehydrogenation, using Cr oxides,^{8,9} Ga oxides,^{10,11} as well as Ir and Pt supported on silica^{12,13} and alumina.^{14,15} In general, Pt/Al₂O₃ is reported as the most active catalyst, particularly in combination with Zn^{16,17} or Sn.^{18–22} These promoters enhance the selectivity to propene, as well as the stability against coking. Their role has been attributed to both electronic (*i.e.* electron transfer to Pt)^{23,24} and geometric effects (*i.e.* dilution in the Pt crystal structure),^{25,26} but a clear distinction has not been demonstrated.

The challenge is that, despite the large available scientific literature and patents, the kinetics of propane dehydrogenation are yet to be resolved, particularly at high partial pressures (> 0.5 atm). This is a major problem since this knowledge is the basis for the formulating rate expressions and models for chemical engineering and reactor design.²⁷ Notable exceptions include the works of Lyu *et al.*,²⁸ Larsson *et al.*,^{29,30} and Menéndez and co-workers,^{31,32} who have made significant efforts to elucidate the kinetics using power law and Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate expressions.

We report here a full investigation of the kinetics based on the best model associated with propane dehydrogenation using an in-house synthesized Pt–Sn/Al₂O₃ catalyst.³³ Steam is

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included to minimize deactivation and we analyse in full the thermodynamics and the (mass/heat) transport limitations. Our results have important implications: they enable comparison of the possible rate models, which are basic for process design.

2. Experimental

2.1. Materials and instrumentation

All gases in this study (Ar, C₃H₈, C₃H₆, H₂, H₂/N₂, N₂, O₂ and He $\geq 99.995\%$) were supplied by Praxair. The H₂ and Ar streams were further purified over molecular sieves and/or BTS columns kept at 353 K. Al₂O₃ pellets were purchased from Ketjen CK300 and the catalyst precursors (H₂PtCl₆·6H₂O and SnCl₂·2H₂O) from Sigma Aldrich ($\geq 99.5\%$).

TPR was performed using a TPDRO 1100 (Thermo Scientific) unit. The samples (100–300 mg) were loaded into a cylindrical quartz cell (197 × 10 mm i.d.), contacted with 5% v/v H₂/N₂ (40 N cm³ min^{−1}) and heated (5 K min^{−1}) to 873 K. They were then flushed in the same N₂ flow and room temperature. H₂ chemisorption (100 μ L pulses) was performed until surface saturation. Afterwards, passivation (in 5% v/v O₂/He, 40 N cm³ min^{−1}) was carried out for off-line analysis. Specific surface area/pore volume measurements were performed on a Surfer Instrument (Thermo Scientific) and evaluated using the BET/BJH equations, respectively; the samples were previously outgassed at 473 K to $<10^{-3}$ bar for one hour.

X-ray photoelectron spectroscopy (XPS) data were collected using a SSX-100 (Surface Science Instruments) spectrometer with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) operating at a base pressure of 5×10^{-10} mbar. The energy resolution was set to 1.16 eV to minimize measuring time and the photoelectron take off angle was 37°. Evaporated gold film Au(111) substrates were prepared by vacuum sublimation (10^{-7} mbar) of gold (99.99%, Umicore Materials AG) onto freshly cleaved mica sheets preheated at 648 K in a custom-built evaporator.³⁴ All catalysts (200 μ m) were dispersed in ethanol and after short stirring, drop cast onto the substrate and left to dry in air. The samples were then introduced into the spectrometer *via* a load lock. An electron flood gun in combination with a gold grid placed above the sample surface was used to compensate sample charging. Spectral analysis included a Shirley background subtraction and peak separation using mixed Gaussian–Lorentzian functions in a least-squares curve fitting program (Winspec) developed at the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium. Binding energies are ± 0.1 eV and were referenced to the Al 2s peak.³⁵ Quantitative analysis based on the photoemission peak areas was performed taking into account the sensitivity factors for each element, specific to the spectrometer used. Particle size/morphology was assessed by transmission electron microscopy (TEM) analysis: TEM, Zeiss EM922 Omega unit operating at 200 kV in combination with an ultra-microtome (Ultracut E Reichert Jung, thickness 50 nm) were applied to characterize the optical response, structure, and size of the nanoparticles. The surface area-weighted metal diameter (d_{TEM}) was

calculated using eqn (2), where n_i is the number of particles (*ca.* 200) of diameter d_i .

$$d_{\text{TEM}} = \frac{\sum_{i=1}^n (n_i d_i^3)}{\sum_{i=1}^n (n_i d_i^2)} \quad (2)$$

Numerical fitting of experimental rate data was done using the built-in non-linear regression function of *Wolfram Mathematica 8.0*.

2.2. General procedure for catalysts synthesis and activation

Alumina-supported Pt and Sn monometallic catalysts were prepared by impregnation where adequate volumes of H₂PtCl₆·6H₂O and (HCl acidified) SnCl₂·2H₂O solutions were added to the support.³⁶ A bimetallic Pt–Sn/Al₂O₃ was prepared by simultaneous addition of the precursor solutions (1 mol% loading of each metal). Example: 1 mol% Sn/Al₂O₃: 0.846 g of SnCl₂·2H₂O were added to 248.0 cm³ of deionized water (15 mM) and this was acidified with 2.0 cm³ of HCl (70 mM). Then, 98.0 cm³ of this acid-Sn solution was added to 15 g of the support and the volume was adjusted to 200 cm³. The slurries were heated (2 K min^{−1}) to 353 K at 600 rpm with an Ar purge. The solid residues were dried in 60 cm³ min^{−1} Ar at 383 K (2 K min^{−1}) overnight, cooled to room temperature and stored in a desiccator in the dark. Prior to catalysis, the samples were sieved to 150 μ m average particle size and activated in 80 cm³ min^{−1} 25% v/v H₂/Ar (5 K min^{−1}) at 873 K for 1 h.

2.3. Procedure for catalytic propane dehydrogenation

Reactions were carried out at 1 atm, over the temperature range 723 K $\leq T \leq$ 823 K, immediately after *in situ* catalyst activation, in a continuous flow fixed bed vertical quartz reactor (4 mm *i.d.*) which was controlled with an in-house built fully automated reactor system.^{37,38} The inlet partial pressures of propane (P_{A0}), propene (P_{E0}), H₂ (P_{H0}), Ar (P_{R0}) and steam (P_{W}) were set between 0–0.875 atm by means of Bronkhorst mass flow controllers and an evaporator (total flow: 80 N cm³ min^{−1}; GHSV = 4×10^4 h^{−1}). The ratio of catalyst mass (W) to the initial propane molar flow rate (F_{A0}) spanned the range (W/F_{A0}) = 0–0.49 g h mol^{−1}. A layer (≤ 3 mm) of quartz wool above the catalyst served as a preheating zone and isothermal conditions were kept by diluting with ground glass (typically 50% v/v); the reaction temperature was continuously monitored by a thermocouple at the catalyst bed. Example: 4 mg of Pt–Sn/Al₂O₃ were mixed with 155 mg of ground glass and placed inside the quartz reactor (10 mm catalyst bed height). The flow rates of propane and propene were fixed at 40 and 20 N cm³ min^{−1} (2.73×10^{-5} mol s^{−1} and 1.36×10^{-5} mol s^{−1}) and balanced with Ar at 80 N cm³ min^{−1} (5.45×10^{-5} mol s^{−1}), hence $P_{\text{A0}} = 0.50$ atm, $P_{\text{E0}} = 0.25$ atm, $P_{\text{R0}} = 0.25$ and (W/F_{A0}) = 0.04 g h mol^{−1}. The reactor effluent was passed through a liquid N₂ trap to avoid H₂O entering the GC. The samples were analysed on-line using a Interscience Compact GC equipped with two TCD detectors separating (a) Ar, H₂O, C₂ and C₃ hydrocarbons on a Porabond Q column (with He as the carrier gas) and (b) H₂ and CH₄ on a 5 Å molsieve column (with Ar as the

carrier gas). Analytical repeatability was better than $\pm 0.5\%$. The fractional conversion of propane is defined in this study as:

$$X_A = 1 - (F_A/F_{A0}) \quad (3)$$

where F_A represents the molar flow of propane at the reactor outlet. Repeated reactions with different samples from the same batch of catalyst delivered raw data that were reproducible within $\pm 7\%$.

3. Results and discussion

3.1. Catalysts synthesis and characterization

All three catalysts ($\text{Sn}/\text{Al}_2\text{O}_3$, $\text{Pt}/\text{Al}_2\text{O}_3$, and $\text{Pt-Sn}/\text{Al}_2\text{O}_3$) were prepared by impregnation and rigorously characterized. Table 1 gives the *post*-activation physicochemical properties of the catalysts. BET surface areas ($\approx 200 \text{ m}^2 \text{ g}^{-1}$) and pore volumes ($\approx 0.5 \text{ cm}^3 \text{ g}^{-1}$) are within the published range for $\gamma\text{-Al}_2\text{O}_3$.^{39,40}

Catalyst reducibility was examined by TPR (Fig. 1). The profile of $\text{Sn}/\text{Al}_2\text{O}_3$ (I) shows an ill-defined positive (*i.e.* H_2 consumption) peak at $T_{\text{max}} = 655 \text{ K}$.

The associated peak area matches within $\pm 5\%$ of the theoretical amount of H_2 required for the Sn precursor reduction. Indeed, Zgolicz *et al.*⁴¹ and Nava and Viveros⁴² independently linked H_2 consumption during TPR of $\text{Sn}/\text{Al}_2\text{O}_3$ (at 513–873 K and 573–873 K, respectively) to the complex reduction process of SnCl_2 . Conversely, the TPR of $\text{Pt}/\text{Al}_2\text{O}_3$ (Profile II) shows a main signal at $T_{\text{max}} = 467 \text{ K}$ with shoulders at higher temperatures. Since these temperatures are 90 K higher than those required for the reduction of bulk H_2PtCl_6 ,⁴³ we infer some degree of precursor-support interaction. Examining the studies on the reducibility of supported H_2PtCl_6 , one concludes that this interaction occurs over a large temperature range (340–740 K) depending on the support (Al_2O_3 ,^{15,44} SiO_2 ,^{45,46} or ZrO_2 ^{47,48}). The associated H_2 consumption for $\text{Pt}/\text{Al}_2\text{O}_3$ during TPR was twice as much as the theoretical amount needed for precursor reduction (see Table 1).

This over-consumption may reflect adsorption and dissociation of hydrogen as spillover.^{49,50} The TPR of $\text{Pt-Sn}/\text{Al}_2\text{O}_3$

Fig. 1 TPR profiles generated for $\text{Sn}/\text{Al}_2\text{O}_3$ (I), $\text{Pt}/\text{Al}_2\text{O}_3$ (II) and $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ (III).

(Profile III) is similar to that of monometallic $\text{Pt}/\text{Al}_2\text{O}_3$, but the dominant signal is shifted by 10 K lower ($T_{\text{max}} = 457 \text{ K}$). This response suggests a Pt-Sn synergy that lowers the reduction requirements.²² Indeed, Håkonsen and co-workers have reported a similar TPR shift.⁵¹ Note that $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ bears *ca.* 16% lower excess H_2 compared to $\text{Pt}/\text{Al}_2\text{O}_3$. Moreover, room temperature H_2 chemisorption over the bimetallic system ($77 \mu\text{mol g}^{-1}$) was 15% smaller than the theoretical sum of the independent contribution of the two metals. These results suggest a Pt-Sn interaction that affects the H_2 adsorption process.^{52,53}

XPS measurements were carried out to determine the oxidation state of the different metals in the monometallic and bimetallic *post*-TPR catalyst surfaces. The most intense photoemission lines of Pt were those arising from the 4f core levels. However, since this energy region was overshadowed by the presence of the very strong Al 2p peak, the Pt 4d lines were analysed instead.^{54,55}

$\text{Pt}/\text{Al}_2\text{O}_3$ showed two components at binding energies (BEs) of 313.0 eV and 315.1 eV in the Pt 4d_{5/2} core level region (see Fig. 2a, Profile I). The lower BE component, accounting for *ca.* 39%, originates from the presence of Pt⁰ in agreement with previous reports on Al_2O_3 -supported Pt.^{56–58}

The second component is ascribed to oxidized Pt species (still present at the surface of Al_2O_3 probably due to strong platinum-support interactions that hinder reduction⁵⁹). The XPS of $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ (Profile III) shows two components in the Pt 4d_{5/2} core level region but the component due to metallic Pt (at 313 eV) accounts in this case for up to 52%. Moreover, the higher component (*i.e.* oxidized Pt) appears at lower BE than that for $\text{Pt}/\text{Al}_2\text{O}_3$. A similar trend has been reported for Pt-based bimetallic catalysts supported on Al_2O_3 ⁵⁹ and is indicative of alloy formation between Pt and Sn. The XPS spectrum of $\text{Sn}/\text{Al}_2\text{O}_3$ (Fig. 2b, Profile II) also revealed two components in the Sn 3d_{5/2} core level region: a lower BE component at 484.8 eV attributed to Sn⁰ (*ca.* 72%) and a BE component at 486.7 eV from oxidized Sn (2+ and/or 4+) species.⁶⁰ In the case of $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ (Fig. 2b, Profile III), the spectroscopic signature of Sn⁰ was found at 485.1 eV, *i.e.* at a higher BE than the corresponding value for $\text{Sn}/\text{Al}_2\text{O}_3$. This result supports the formation of a (surface) Pt-Sn alloy with charge transfer from Sn to Pt.⁶¹ Moreover, this is also demonstrated by the lower relative

Table 1 Catalyst properties and performance

		$\text{Sn}/\text{Al}_2\text{O}_3$	$\text{Pt}/\text{Al}_2\text{O}_3$	$\text{Pt-Sn}/\text{Al}_2\text{O}_3$
Loading (wt%)	Sn	1.2	—	1.2
	Pt	—	1.9	1.9
TPR T_{max} (K)		655	467	457
TPR H_2 consumption ($\times 10^4 \text{ mol g}^{-1}$)		0.9 ^a	4.4 ^b	3.8 ^{a,b}
H_2 chemisorption ($\mu\text{mol g}^{-1}$)		2	89	77 ^c
N_2 BET surface area ($\text{m}^2 \text{ g}^{-1}$)		193	205	188
Pore volume ($\text{cm}^3 \text{ g}^{-1}$)		0.46	0.49	0.50
d_{TEM} (nm)		—	6.8	5.6
XPS BE ^d (eV)	Sn 3d _{5/2}	484.8	—	485.1
	Pt 4d _{5/2}	—	313.1	312.9
m		−0.83	−1.08	−0.10
r_0^e ($\text{mol h}^{-1} \text{ g}^{-1}$)		0.5	1.5	1.7

^a Theoretical TPR H_2 consumption: $1.0 \times 10^{-4} \text{ mol g}^{-1}$. ^b Theoretical TPR H_2 consumption: $1.9 \times 10^{-4} \text{ mol g}^{-1}$. ^c Theoretical additive contribution of Pt and Sn = $91 \mu\text{mol g}^{-1}$. ^d BE associated with the second (weaker) signal in the doublet. ^e $P_{A0} = 0.5$, $P_{E0} = P_{H0} = 0$; $P_W = 4 \times 10^{-4} \text{ atm}$; $T = 823 \text{ K}$.

Fig. 2 XPS of the (a) Pt 4d_{5/2} and (b) Sn 3d_{5/2} regions for reduced/passivated Pt/Al₂O₃ (I, □), Sn/Al₂O₃ (II, ○) and Pt-Sn/Al₂O₃ (III, △). Solid (envelope), dashed (baseline) and dotted (deconvolution) lines represent fitted data.

percentage (*ca.* 64%) of zero-valent Sn in Pt-Sn/Al₂O₃.⁴⁸ TEM analyses were performed to confirm the average size of the metal clusters. A representative Pt/Al₂O₃ micrograph is shown in Fig. 3aI, with evidence of globular particles with slight faceting.

Similar morphologies were observed elsewhere for oxide supported-Pt and taken as a feature of metal-support interactions.⁶² Fig. 3aII shows the bimodal particle size distribution of Pt/Al₂O₃ with a mean size of $d_{\text{TEM}} = 6.8$ nm. Comparatively, Pt-Sn/Al₂O₃ showed smaller clusters ($d_{\text{TEM}} = 5.6$ nm, see Fig. 3bI) and a narrower particle size distribution (see Fig. 3bII). A similar unimodal distribution was reported for Pt-Sn supported on ZSM-5⁶³ and SBA-15 and attributed to alloy formation.²² Moreover, Liu *et al.* suggested a “sandwich-like” structure for supported Pt-Sn where the support is covered by Sn particles and these are decorated by Pt nanoparticles, *i.e.* Pt migrates to support surfaces where Sn is available.⁶⁴ Our results suggest the reduction of the metallic precursor(s) *post*-TPR at 873 K for all three catalysts with the formation of small metal clusters. The alumina crystal structure is unchanged. Moreover, the XPS shows a Pt-Sn electronic interaction (surface alloy) that changes the dynamics of hydrogen adsorption.

3.2. Catalytic propane dehydrogenation

Prior to the comparative kinetics study we ensured the absence of external/internal mass/heat transfer limitations.⁶⁵ This was

Fig. 3 (a) Representative TEM micrographs and (b) particle size distributions associated with reduced/passivated Pt/Al₂O₃ (I) and Pt-Sn/Al₂O₃ (II).

done using experimental^{66–68} and theoretical^{69,70} methods (see Appendix A, Fig. A1, ESI†). Moreover, we also studied the maximum equilibrium propane conversion and its response to the presence of the propene and/or hydrogen products (see Appendix B, Fig. B2, ESI†). In this way, we ensured that the experiments were carried out in the proper kinetically-controlled regime.

3.2.1. Alumina supported Sn, Pt, and Pt-Sn. The processing of propane over all catalysts generated mainly propene and hydrogen under all conditions in this study (*i.e.* selectivity towards propane dehydrogenation: 90–95%).

Fig. 4 shows the time-on-stream fractional conversion of propane (X_A). All three systems deactivate at extended reaction times, probably reflecting coke deposition which has been shown to proceed *via* acetate/carboxylate⁷¹ and aromatic⁷² species. This deactivation is ubiquitous, regardless of the active

Fig. 4 Time-on-stream variation of propane fractional conversion (X_A) for reaction over Sn/Al₂O₃ (●), Pt/Al₂O₃ (■) and Pt-Sn/Al₂O₃ (▲); (W/F_{A0}) = 0.12 g h mol⁻¹; P_{A0} = 0.5, P_{E0} = P_{H0} = 0; T = 823 K; lines represent fit to eqn (4). Inset: pseudo-first order kinetic plot for propane dehydrogenation; lines represent fit to eqn (5).

phase (Pt^{14,73}/Pt-Sn^{18,74} metals or Cr^{8,9,75}/Ga¹⁰ oxides) or support (Al₂O₃,^{8,14,74} SiO₂,^{9,10,18,73} ZrO₂⁷⁵) used. Moreover, it also applies to ethane,⁷⁶ *n*-butane⁵⁸ and isobutane dehydrogenation.⁷⁷ To measure catalyst performance under minimal influence of coking, the initial fractional conversion (X_{A0}) was calculated by applying the empirical relationship shown in eqn (4), where Δt is the integral time-on-stream and m a measure of deactivation. The dotted curves show the quality of data fit ($R^2 \geq 0.98$).

$$X_A = X_{A0}(\Delta t)^m \quad (4)$$

Pt/Al₂O₃ was the most sensitive catalyst to deactivation (highest m value, see Table 1). Sn/Al₂O₃ showed less deactivation (*ca.* 20% lower m) and Pt-Sn/Al₂O₃ was the most robust.^{78,79} Wang *et al.* suggested that Sn weakens the bonding between Pt and the hydrocarbon, thus preventing coke formation.²⁶ Kogan and co-workers⁵³ called for an ensemble/diluent effect of Sn on Pt as responsible for less coking. In contrast, Holmen *et al.*²² reported a higher coke formation over Pt-Sn and attributed this to the small size and high surface roughness. Catalyst performance was compared by applying the mass balance for a plug-flow reactor (eqn (5)), where r_0 is the initial propane consumption rate in mol h⁻¹ g⁻¹. The results are shown in the inset to Fig. 4.

$$r_0 = \frac{dX_{A0}}{d(W/F_{A0})} \quad (5)$$

The linear relationship between X_{A0} and (W/F_{A0}) demonstrates operation under differential conditions,⁸⁰ and r_0 follows the sequence of decreasing rate: Pt-Sn/Al₂O₃ (1.7) > Pt/Al₂O₃ (1.5) > Sn/Al₂O₃ (0.5). Larsson *et al.*⁸¹ also found that Sn/Al₂O₃ was inactive under the same reaction conditions where Pt/Al₂O₃ and Pt-Sn/Al₂O₃ delivered complete conversion to the thermodynamic equilibrium. Marginal improvements in the activity of Pt-Sn relative to Pt were also reported by Assabumrungrat *et al.*⁸² and attributed to the ensemble effect where Pt dispersion was increased (*i.e.*, a greater number of available active sites). Our results suggest that this increase in the reaction rate and robustness is due to the presence of a Pt-Sn electronic interaction *via* the formation of a surface alloy. These conclusions find agreement with the work of Kumar *et al.*,²² Praserttham *et al.*,²³ Yarusov *et al.*²⁴ and Wang *et al.*,²⁶ all of whom suggested an *electronic* rather than a *geometric* effect of Sn on Pt.

We then focused the kinetic study solely on Pt-Sn/Al₂O₃ as the best formulation. Fig. 5 shows clearly that co-feeding of steam served to minimize the loss of activity. Low steam partial pressures ($P_W \approx 0.001$ atm) were sufficient to maintain catalytic activity at extended time-on-stream (*i.e.* $m \rightarrow 0$ with increasing P_W). These results are in line with the recent thermodynamic study of Voronetskii *et al.*, who demonstrated that the presence of steam at 700 K $\leq T \leq$ 1000 K reduces three-fold the formation of carbonaceous deposits.⁷² Moreover, adding steam had only a minor effect on the rate, as equivalent r_0 were obtained independent of the steam pressure (see the inset to Fig. 5). We then set the inlet steam pressure at $P_W = 6 \times 10^{-4}$ atm for the remainder of the study, to decouple the deactivation kinetics, which are out of our scope.

Fig. 5 (a) Temporal variation of propane fractional conversion (X_A) at different steam partial pressures (P_W) = 0 atm (∇), 4×10^{-4} atm ($\blacktriangledown$) and 8×10^{-4} atm ($\bullet$); (b) deactivation coefficient (m) and initial rate (r_0 , inset) variations with P_W ; (W/F_{A0}) = 0.04 g h mol⁻¹; P_{A0} = 0.5, P_{E0} = P_{H0} = 0; T = 823 K. Note: lines in (a) represent fit to eqn (3).

3.2.2. Langmuir–Hinshelwood–Hougen–Watson (LHHW) model over Pt-Sn/Al₂O₃. Fig. 6 shows the variation of r_0 with the inlet partial pressures of propane (P_{A0} , I), propene (P_{E0} , II) and hydrogen (P_{H0} , III).

The rate increases following a power-law mode with P_{A0} where a change in slope at $P_{A0} > 0.3$ is evident. This trend suggests some degree of catalyst surface saturation.²⁸ We studied the effect of propene in the inlet propane stream by varying P_{E0} at a constant P_{A0} = 0.125 atm (see Fig. 6II). The presence of propene slowed down the reaction, particularly at $P_{E0} > 0.4$. This result may reflect competitive adsorption where the interaction of propene with the catalyst surface has to be stronger than that of propane. Lower rates when increasing the partial pressure of propene (0.12–0.53 atm) were also noted elsewhere.²⁸ Moreover, DFT calculations also showed that the adsorption of propene on Pt-Sn surfaces is stronger than that of propane.⁸³

Fig. 6III shows a small minimum in r_0 with P_{H0} ; nonetheless, this effect was statistically negligible accounting for relative standard deviations of $\pm 5\%$ for r_0 . This means that hydrogen does not significantly compete with propane on the catalyst surface and is in line with our characterization measurements where a lower H₂ chemisorption was observed over Pt-Sn/Al₂O₃.

Fig. 6 Variation of the initial rate (r_0) with the initial partial pressures of (I) propane ($\square$, $\blacksquare$, $P_{H_0} = P_{E_0} = 0$), (II) propene ($\circ$, $\bullet$, $P_{A_0} = 0.125$, $P_{H_0} = 0$) and (III) hydrogen (Δ , $\blacktriangle$, $P_{A_0} = 0.125$, $P_{E_0} = 0$) at $T = 723$ K (open symbols) and 823 K (solid symbols).

The kinetic modelling of propane dehydrogenation was done using the LHHW approach.^{69,70,84} This method assumes that reactivity towards (reversible) adsorption, reaction and desorption is independent of the surface coverage (*i.e.* uniform surface energetics). A rate-determining step is chosen and all other steps are in quasi-equilibrium to eliminate the coverage-dependent terms.⁸⁵ Fig. 7 shows all the possible steps in our reaction: propane adsorption (steps 1 and 2), surface reaction (steps 3–8), and desorption of propene (step 9) and hydrogen (steps 10–12). We considered the following elementary steps in the various models:

- Dissociative (1) and non-dissociative (2) propane adsorption;
- Surface reaction with release of hydrogen (4) and propene (7 and 8);

- Stepwise desorption of hydrogen with (10 and 11) and without (12) surface recombination.

For example, model IX involves non-dissociative propane adsorption (step 2), surface reaction with release of propene gas (step 8) and desorption of surface-recombined hydrogen (step 12). All kinetic expressions in each model considering all possible rate-determining steps were derived accordingly (see Appendix C, ESI† for a detailed example).

We discarded those models predicting “ $r_0 = \text{constant}$ ” or “ $r_0 \propto P_{A_0}$ ” at $P_{E_0} = P_{H_0} = 0$ because r_0 increased following a power-law with P_{A_0} (see Fig. 5a). Table 2 gives the corresponding rate expressions that are consistent with the experimental observations. The rate expressions were fitted to the experimental data using non-linear regression analysis of

Fig. 7 Schematic of LHHW models for propane dehydrogenation.

Table 2 Rate expressions for various kinetic models and rate-limiting steps in propane dehydrogenation (see Fig. 7), excluding those that predict “ $r_0 = \text{constant}$ ” or “ $r_0 \propto P_{A0}$ ” at $P_{E0} = P_{H0} = 0$

Model	Limiting step	$r_0 = \text{Kinetic} \times (P_{A0} - P_{E0}P_{H0}/K_{eq})/\text{Resistance}$	
		Kinetic	Resistance
I	3	$sC_T k_3 K_1 / \sqrt{K_{10}}$	$[P_{H0}^{-1/4}(P_{E0}K_9/\sqrt{K_{10}}) + P_{H0}^{1/4}(1 + P_{E0}K_9) + P_{H0}^{3/4}\sqrt{K_{10}}]^2$
	10	$C_T k_{10} K_{10} K_{eq}$	$[\sqrt{P_{A0}P_{E0}K_{eq}/K_{10}} + P_{E0}\sqrt{P_{A0}K_1K_9/K_3} + P_{E0}^2 + P_{E0}^3K_9]^2$
II	3	$sC_T k_3 K_1 / \sqrt{K_{11}K_{12}}$	$[P_{H0}^{-1/4}(P_{A0}K_1/\sqrt{K_{11}K_{12}}) + P_{H0}^{1/4}(1 + P_{E0}K_9) + P_{H0}^{3/4}\sqrt{K_{11}K_{12}} + P_{H0}^{5/4}K_{12}]^2$
	9	$C_T k_9 K_9 K_{eq}$	$[P_{A0}K_9K_{eq} + \sqrt{P_{H0}}(P_{A0}K_1/\sqrt{K_{11}K_{12}}) + P_{H0} + P_{H0}^{3/2}\sqrt{K_{11}K_{12}} + P_{H0}^2K_{12}]^2$
	11	$C_T k_{11} K_{11} K_{12} K_{eq}$	$[P_{E0}^{3/2}\sqrt{P_{A0}K_1}(P_{E0}\sqrt{K_9/K_3} + \sqrt{K_3/K_9}) + P_{E0}^2(1 + P_{H0}K_{12}) + P_{E0}^3K_9]^2$
III	4	$C_T k_4 K_2$	$[1 + P_{A0}K_2 + P_{E0}K_9]^2$
IV	5	$sC_T k_5 K_2$	$[1 + P_{A0}K_2 + P_{E0}K_9 + P_{H0}K_{12}]^2$
V	6	$s^2C_T k_6 K_2$	$[1 + P_{A0}K_2 + P_{E0}K_9 + \sqrt{P_{H0}K_{10}}]^3$
	10	$sC_T k_{10} K_{10} K_{eq}$	$[P_{A0}P_{E0}K_{10}K_{eq} + P_{E0}^2(1 + P_{A0}K_2) + P_{E0}^3K_9]^2$
VI	6	$s^2C_T k_6 K_2$	$[1 + P_{A0}K_2 + P_{E0}K_9 + P_{H0}K_{12} + \sqrt{P_{H0}K_{11}K_{12}}]^3$
	9	$C_T k_9 K_9 K_{eq}$	$[P_{A0}K_9K_{eq} + P_{H0}(1 + P_{A0}K_2) + P_{H0}^{3/2}\sqrt{K_{11}K_{12}} + P_{H0}^2K_{12}]^2$
	11	$sC_T k_{11} K_{11} K_{12} K_{eq}$	$[(P_{E0}^{3/2})\sqrt{P_{A0}K_{11}K_{12}K_{eq}} + P_{E0}^2(1 + K_2P_{A0} + P_{H0}K_{12}) + P_{E0}^3K_9]^2$
VII	7	$sC_T k_7 K_2$	$[1 + P_{A0}K_2 + \sqrt{P_{H0}K_{12}}]^2$
	10	$sC_T k_{10} K_{10} K_{eq}$	$[(P_{E0}^{3/2})\sqrt{P_{A0}K_{10}K_{eq}} + P_{E0}^2(1 + K_2P_{A0})]^2$
VIII	7	$sC_T k_7 K_2$	$[1 + P_{A0}K_2 + P_{H0}K_{12} + \sqrt{P_{H0}K_{11}K_{12}}]^2$
	11	$sC_T k_{11} K_{11} K_{12} K_{eq}$	$[(P_{E0}^{3/2})\sqrt{P_{A0}K_{11}K_{12}K_{eq}} + P_{E0}^2(1 + K_2P_{A0} + P_{H0}K_{12})]^2$
IX	8	$C_T k_8 K_2$	$[1 + P_{A0}K_2 + P_{H0}K_{12}]^2$

Mathematica 8.0 and by calculating the temperature dependencies using a temperature-centred approach (at 773 K).

Indeed, Kapteijn and Moulijn have shown that this methodology avoids strong parameter correlations.^{69,70} The equilibrium constant was calculated as a function of temperature from thermochemical data (see Appendix B, Fig. B1, ESI†)

$$K_{eq}[\text{atm}] = (1.48 \times 10^7) \exp(-15403/T) \quad (6)$$

where the temperature is always expressed in Kelvin.

Finally, the models were compared on the basis of the adjusted regression coefficient R_{adj}^2 (see eqn (6)) which takes into account the differences in terms of the number of observations (N) and parameters (P) and the ratio between the model-to-total sum of squares (R^2).

$$R_{adj}^2 = 1 - R^2 \times \left(1 - \frac{N-1}{N-P}\right) \quad (7)$$

Fig. 8 displays the values of R_{adj}^2 for those models that yielded positive values for the kinetic (k_j) and adsorption constants (K_j). For example, the R_{adj}^2 values for models II and VI having step 9 (propene desorption) as the limiting step are not displayed in Fig. 8 for this reason. All models fit reasonably well at 723 K, while model III4 is the best at 823 K. Fig. 9(a) shows that the distribution of model III4 residuals did not show any trend (*i.e.* is not biased) as a function of P_{A0} , P_{E0} , P_{H0} , nor with temperature. Fig. 9(b) confirms the good fit between the experimental (r_0) and predicted (r_{Calc}) rates. The mathematical expression that fits the experimental data corresponds

then to model III4:

$$r_0 = \frac{C_T k_4 K_2 [P_{A0} - P_{E0}P_{H0}/K_{eq}]}{[1 + P_{A0}K_2 + P_{E0}K_9]} \quad (8)$$

It should be noted that eqn (8) does predict a change in slope of r_0 with P_{A0} , as the dependency shifts from linear at low P_{A0} to quasi-rational at higher P_{A0} values (see Fig. 6). The extracted temperature-dependency of the constants is given in eqn (9)–(11):

$$(C_T k_4) [\text{mol g}^{-1} \text{ h}^{-1}] = (5.09 \pm 0.5) \exp \left[(1593 \pm 164) \left(\frac{1}{T} - \frac{1}{773} \right) \right] \quad (9)$$

$$K_2 [\text{atm}^{-1}] = (1.93 \pm 0.3) \exp \left[(-6566 \pm 308) \left(\frac{1}{T} - \frac{1}{773} \right) \right] \quad (10)$$

$$K_9 [\text{atm}^{-1}] = (2.36 \pm 0.7) \exp \left[(-2162 \pm 78) \left(\frac{1}{T} - \frac{1}{773} \right) \right] \quad (11)$$

Our experimental results and kinetic analysis suggest that the most probable reaction model (III-4, see Table 2) for propane dehydrogenation over Pt-Sn/Al₂O₃ is the following:

- Non-dissociative adsorption of propane on the catalyst (step 2).
- Dehydrogenation yielding propene (which remains adsorbed on the catalyst surface) and simultaneous desorption of hydrogen (step 4).
- Propene desorption from the catalyst surface (step 9).

Menéndez *et al.* also reported a better fit of combined dehydrogenation and deactivation data when using this LHHW-type model but in their case, propene desorption was

Fig. 8 Adjusted correlation coefficients (R_{adj}^2) for the different LHHW models in agreement with the experimental data (see Table 1 and Fig. 5) at (a) 723 K and (b) 823 K.

Fig. 9 (a) Variation of model residuals (Δr_0) with the initial partial pressures of propane ($\square$, $\blacksquare$), propene ($\circ$, $\bullet$) and hydrogen (Δ , $\blacktriangle$) and (b) parity plots of experimental (r_0) and calculated (r_{Calc}) rates (slope = 0.98 ± 0.02); (W/F_{A0}) = $0\text{--}0.49\text{ g h mol}^{-1}$; $0 \leq P_{i0} \leq 0.9$; $T = 723\text{ K}$ (open symbols) and 823 K (solid symbols).

chosen as the rate-determining step.³¹ Our results also agree with the work of Larsson *et al.*, who rejected LHHW models based on dissociative propane adsorption and propene

desorption as limiting steps.³⁰ Lyu and co-workers suggested a different model (dissociative adsorption of propane with desorption of surface-recombined H_2), but did not incorporate experimental evidence for variations of r_0 with P_{H_2} .²⁸ We demonstrate here, for the first time, the results of systematic research of the kinetics for propane dehydrogenation over Pt-Sn/ Al_2O_3 , which are valid over $723\text{ K} \leq T \leq 823\text{ K}$ and a whole range of reactant/product(s) partial pressures.

4. Conclusions

We present a novel kinetic study of propane dehydrogenation over Pt-Sn/ Al_2O_3 . Catalyst characterization reveals the existence of a Pt-Sn surface alloy (5.6 nm in average particle size), which has an impact on H_2 adsorption. Moreover, Pt-Sn/ Al_2O_3 shows a greater catalytic activity and stability when compared to that of Pt/ Al_2O_3 . The presence of low steam partial pressures minimises catalyst deactivation during propane dehydrogenation. Under our reaction conditions, the system is free from both mass-transport and heat-transport limitations. The initial propane consumption rate varies directly/inversely with an increase in the partial pressures of propane/propene, respectively. Changes in the hydrogen partial pressure had no measurable effect on the rate. The kinetic and statistical analysis of rival LHHW models led to the selection of a preferred kinetic model based on non-dissociative adsorption of propane, followed by a surface reaction as the rate-limiting step with simultaneous release of H_2 .

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