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Investigation of Pt-based Model Catalysts for Propane Dehydrogenation Reaction

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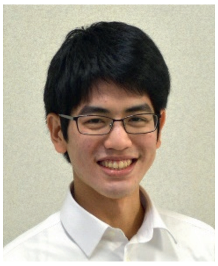
§SCS-dsm-firmenich Award for best poster presentation in Catalysis Sciences & Engineering

Abstract: Large scale exploitation of shale gas has stimulated the developments of on-purpose propane dehydrogenation (PDH) technologies. Pt-based PDH catalysts have been utilized in industry, *e.g.* Pt-Sn/Al_2O_3 and Pt-Ga/Al_2O_3, where the actual role of metal dopants is not fully understood. In this regard, the development of model systems possessing tailored surface sites is necessary in order to look into the structure-activity relationships. In that context, the surface organometallic chemistry (SOMC) approach has emerged as a powerful tool to yield PDH model catalysts, revealing that the formation of alloyed particles and residual unreduced metal sites are important for high productivity and stability.

Keywords: Heterogeneous catalyst · Platinum · Propane dehydrogenation



Kazutaka Sakamoto obtained his Bachelor's and Master's degree in Engineering Science from Osaka University, spending three years in the lab of Prof. Dr. Kazushi Mashima for his Master's thesis project, working on aerobic oxidation catalysed by Ce complexes. Since February 2022, he has been a doctoral candidate in the group of Prof. Dr. Christophe Copéret at ETH Zurich. His research focuses on the investigation of Pt-based catalysts for propane dehydrogenation reactions.

Christophe Copéret (CCH) obtained his PhD in 1996 with Prof. Dr. E. Negishi in Purdue University and was a postdoctoral fellow in the group of Prof. Dr. K. B. Sharpless in Scripps Research Institute. Afterwards, CCH joined CNRS in 1998 as a permanent research position and was promoted to research director in 2008. CCH became a Professor in the Department of Chemistry and Applied Bioscience at ETH Zurich in 2010. His research interests lie in bridging the gaps among molecular, surface and material chemistry based on the molecular-level understanding of complicated surface speciation. In order to achieve this goal, his group focuses on surface organometallic chemistry approaches combined with spectroscopic and microscopic techniques, such as XAS, solid-state NMR and STEM.

1. Introduction

The demand for light olefins has been increasing since the 1930s. These are typically utilized as the building blocks in the petrochemical industry to produce chemical intermediates and polymers. For light olefins, propylene conversion is one of the biggest markets, mainly directed towards the production of polypropylene, propylene oxide and acrylonitrile. As a result of the broad applications, the gap between propylene supply and demand, the so-called 'Propylene Gap', has been increasing.[1] Initially, propylene production relied on naphtha-based cracking processes, yielding a variety of paraffins and olefins as well as aromatics. In recent years, the exploration of shale gas significantly influenced the availability of light alkanes as feedstocks, resulting in a switch for propylene production from the traditional cracking process into the on-purpose dehydrogenation process.

The non-oxidative propane dehydrogenation (PDH) reaction to propylene has thus become a key technology for the petrochemical industry. This reaction is highly endothermic, requiring +124.3 kJ mol^{-1} to proceed, resulting in the use of relatively high operation temperatures, typically 500–700 °C, in order to achieve reasonable propylene productivity (Fig. 1A). In fact, the highest productivity of the PDH reaction is limited by its equilibrium. For instance, the equilibrium conversion of propane at 550 °C under atmospheric pressure (1 bar) is thermodynamically calculated to be *ca.* 30% without feed dilution (Fig. 1B).[2] Such high reaction temperatures often cause undesired side reactions, such as thermal cracking and coke formation. In addition to the product selectivity, PDH catalysts also undergo rapid deactivation by coking and sintering under the harsh conditions (Fig. 1C). For these reasons, constant catalyst regeneration, including calcination to remove cokes and reactivation of the catalysts, is necessary in order to obtain constant propylene production. This necessity stimulates the further development of selective and stable PDH catalysts.

The primary industrial catalysts for the on-purpose PDH reaction were developed in the 1970s, known as the Lummus Catofin process (Cr_2O_3/Al_2O_3)[3] (Fig. 2A) and UOP Oleflex process (Pt-Sn/Al_2O_3)[4] (Fig. 2B) for the two major working catalysts. Moreover, the recent development announced by Dow utilizes Pt-Ga/Al_2O_3 as a PDH catalyst.[5] For Pt-based catalysts, dopants (promoters), such as Sn and Ga, play an essential role in improving the catalyst productivity and selectivity as well as stability. These catalysts are, prepared by conventional impregnation procedures, resulting in complicated catalyst surfaces. Due to this complexity

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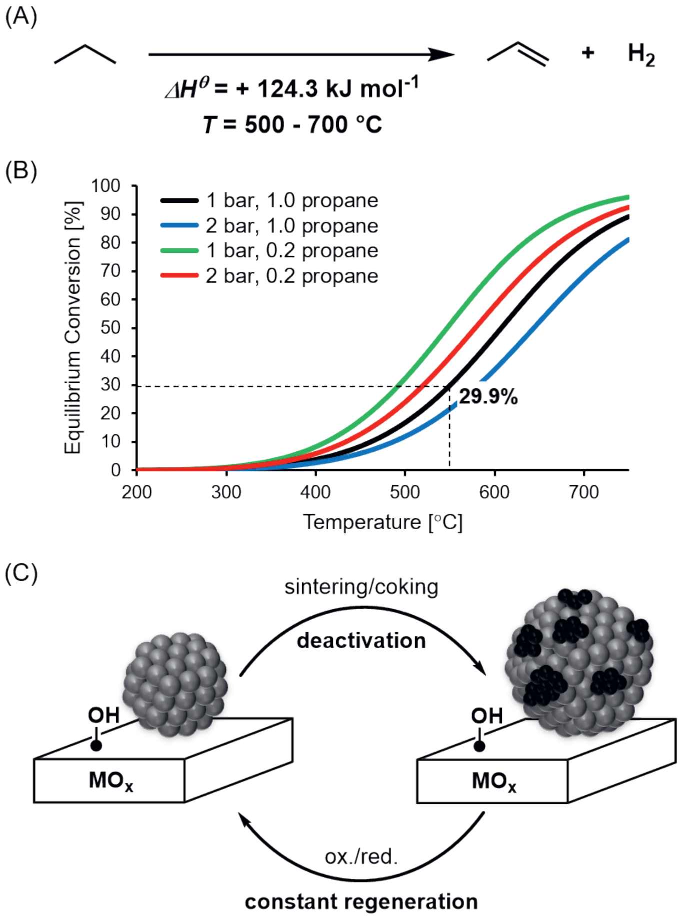

Fig. 1. (A) Dehydrogenation of propane, requiring 500–700 °C due to its high reaction enthalpy, +124.3 kJ mol^{-1}. (B) Equilibrium conversion of propane to propylene at different total and partial pressures. (C) Deactivation of PDH catalysts typically due to sintering and coking necessitate constant regeneration by calcination and reduction.

in the working catalysts, the roles of the dopants and deactivation processes (*i.e.* coking and sintering) are not fully understood.

Additionally, recent research on PDH catalysts has focused on the various dopants (M) for Pt-M bimetallic systems in order to enhance the catalysts productivity and stability under not only PDH conditions but also regeneration conditions (M = Sn,[6] Ga,[7] Zn,[8] Mn[9] *etc.*). The primary synthetic procedures for Pt-M bimetallic systems also typically rely on the impregnation techniques, followed by a reduction step to yield active surface sites. Contrary to such a simple scheme, this preparation leads to complex materials containing significant amounts of spectator sites, making it difficult to obtain accurate structure-activity relationships through detailed spectroscopic investigations. In this regard, the development of model systems is needed to obtain insights into the nature of active site(s) and the roles of dopants/promoters, which could ultimately lead to further catalyst improvements.

2. Exploration of PDH Model Catalysts

The control of the surface sites as well as the interfacial sites between the metal oxide and nanoparticles is necessary to investigate the model systems for PDH catalysts. The surface organometallic chemistry (SOMC) approach is a powerful technique, which allows us to add metal dopants sequentially through grafting the proper metal precursors following a thermal treatment.[10] These preparation approaches lead to the formation of well-dispersed metal sites and/or nanoparticles with narrow particle size distributions. Moreover, such tailored surface sites enable the evaluation of the active sites though the *in situ* or *operando* spectroscopic characterization, resulting in a deeper understanding of structure-activity relationships. In this context, Pt-based PDH catalysts prepared *via* the SOMC approach have been explored, supported on silica with various dopants, such as Ga,[7b] Zn[8a,d] and Mn.[9]

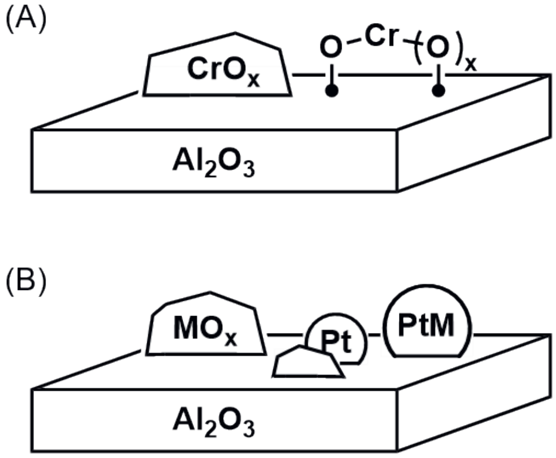

Fig. 2. (A) General structure of Cr-based PDH catalysts, such as the Catofin catalyst. (B) General structure of Pt-based PDH catalysts (M = Sn, Ga *etc.*).

In order to create model systems for Pt-Ga based catalysts, which are among the principal working catalysts, a Pt-Ga bimetallic material was prepared *via* the SOMC approach using $Ga[OSi(OtBu)_3]_3(THF)$ and $(cod)Pt[OSi(OtBu)_3]_2$ as grafting precursors.[7b] Ga(III) isolated sites supported on silica, Ga(III)/SiO_2, were obtained by grafting of a Ga precursor onto dehydroxylated silica with subsequent thermal treatment under high vacuum. Subsequently, a Pt precursor was grafted onto Ga(III)/SiO_2 followed by thermal treatment under a flow of hydrogen to yield nanoparticles with a narrow size distribution (1.0 ± 0.2 nm), PtGa/SiO_2 (Fig. 3A). The monometallic Pt catalyst, Pt/SiO_2, gave larger particle sizes and a broader distribution (2.0 ± 0.8 nm). The obtained Pt-Ga catalyst was tested for PDH reactions, showing higher productivity and stability with almost perfect selectivity compared to Pt/SiO_2 (Table 1). The detailed characterization, including chemisorption studies, X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS), revealed the formation of Pt-Ga alloys along with 10% of residual Ga(III) sites. EXAFS analysis indicated the absence of Ga_2O_3 domains on the silica surface. These observations combined with *meta*-dynamics (MTD) simulations[11] suggested that the formation of Pt-Ga alloys enabled the Pt sites to be isolated on the surface of the nanoparticles, preventing deep-dehydrogenation to generate cokes. Additionally, the residual Ga(III) sites worked as Lewis acidic sites to suppress sintering of Pt-Ga nanoparticles under PDH conditions.

Similarly, silica-supported Pt-Zn and Pt-Mn were prepared starting from Zn(II) isolated sites and Mn(II) isolated sites on silica, respectively (Figs. 3B and 3C).[8a,9] Both bimetallic systems yielded small nanoparticles with narrow distributions (0.8 ± 0.2 nm and 1.0 ± 0.3 nm, respectively), which is one of the key features of the SOMC approach. Notably, bimetallic systems always show enhanced productivity, selectivity and stability compared to monometallic systems (Table 1). It is also noteworthy that Pt-Mn systems show the highest productivity and stability over long PDH tests. Similarly to the Pt-Ga bimetallic system, detailed spectroscopic characterization clarified the formation of Pt-Zn alloys and Pt-Mn alloys with the residual Zn(II) and Mn(II) sites, respectively, after the reduction of the Pt-grafted materials. STEM images of the spent catalysts revealed that the Pt-Zn

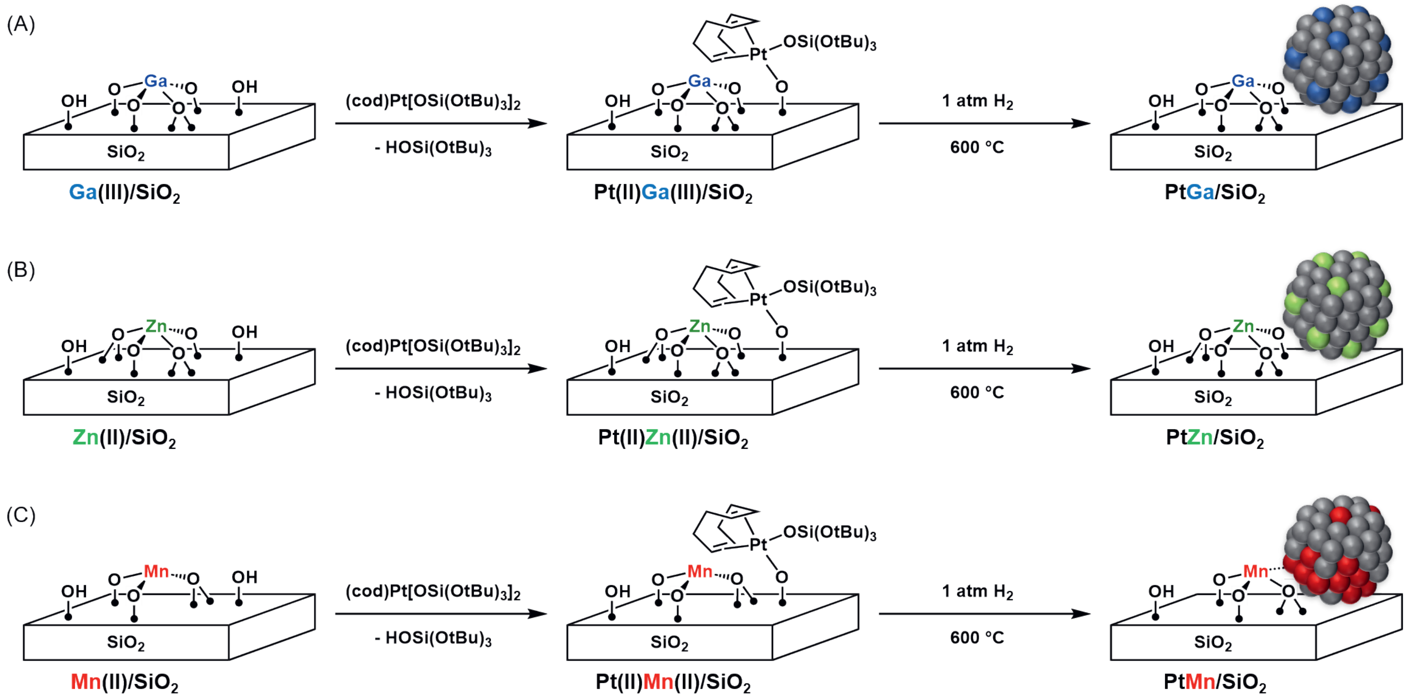

Fig. 3. Synthetic approach for (A) PtGa/SiO_2, (B) PtZn/SiO_2 and (C) PtMn/SiO_2. Pt precursor, (cod)Pt[Osi(OtBu)$_3$]$_2$, is grafted onto M/SiO_2, followed by thermal treatment under a flow of H_2 to yield alloyed nanoparticles with the remaining M sites (M = Ga[7b], Zn[8a] and Mn[9]).

system (0.8 ± 0.2 to 1.2 ± 0.3 nm, after 30 hours PDH) showed more sintering than the Pt-Mn system (1.0 ± 0.3 to 1.2 ± 0.3 nm, after 66 hours PDH), consistent with a stronger interaction of Pt with Mn. Towards the further understanding of improved stability of the Pt-Mn bimetallic system, EXAFS analysis and MTD simulation indicated the segregation of reduced Mn in the Pt-Mn alloys toward the surface of the support together with the presence of interfacial sites between Pt-Mn alloys and the surface Mn(II) sites. The segregated and interfacial nature could lead to the further stabilization of the Pt-based alloyed nanoparticles under PDH conditions, correlating with the enhanced catalyst productivity and stability.

3. Conclusions

The SOMC approach has shown the preparation of Pt-based bimetallic PDH catalysts with different dopants possessing well-defined surface sites. Such tailored PDH catalysts enable further understanding of the structure-activity relationships of Pt-M systems (M = Ga, Zn and Mn) combined with spectroscopic and microscopic techniques as well as computational studies, which gives more insights into the catalyst deactivation mechanisms. The isolation of Pt sites in the alloyed particles can suppress the coking processes, while the residual M sites plays an essential role in the stabilization of the nanoparticles to prevent sintering under PDH conditions. Overall, the tailored PDH catalysts prepared *via* the SOMC approach can work as model catalysts for further understanding of the working catalysts. We are currently working on further developments for the modelling of actual catalysts.

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Table 1. Catalytic properties of Pt-based PDH catalysts prepared *via* the SOMC approach[a]

Material	Pt [wt%]	Particle Size [nm]	Time [h]	WHSV [$g_{C_3H_8}$ g_{Pt}^{-1} h^{-1}]	Productivity [$g_{C_3H_6}$ g_{Pt}^{-1} h^{-1}]	Select. [%]	k_d[b] [h^{-1}]
Pt/SiO_2[9]	3.96	2.0 ± 0.8	0.1	817	109	81.5	
			2		6.67	77.8	1.46
PtGa/SiO_2[7b]	4.82	1.0 ± 0.2	0.3	2220	668	> 99	
			20		381	> 99	0.042
PtZn/SiO_2[8a]	3.05	0.8 ± 0.2	0.1	2450	692	98.1	
			30		357	95.0	0.027
PtMn/SiO_2[9]	2.97	1.0 ± 0.3	0.1	2250	822	96.1	
			60		378	97.3	0.018

[a] Catalytic tests are carried out with 50 mL/min, 20% C_3H_8 in Ar at 1 bar(g). [b] Deactivation constant: $k_d = (\ln(1 - conv_{end}/conv_{end}) - \ln(1 - conv_{int}/conv_{int}))/t$. WHSV, productivity and k_d are recalculated based on the reported conversion and selectivity.

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