



## Rapid investigation of paraffin dehydrogenation catalyst by TPRn/SPI-TOF-MS technique for industrial application

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### ABSTRACT

Dehydrogenation of long chain paraffins over commercial Pt-Sn-K-Mg/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn-Na-Co/Al<sub>2</sub>O<sub>3</sub> catalysts were investigated using a temperature programmed reaction/single-photon ionization time-of-flight mass spectrometry (TPRn/SPI-TOF-MS) system under realistic reaction conditions using model compound C<sub>12</sub><sup>0</sup> and in the industrial PACOL dehydrogenation plant using n-C<sub>10</sub><sup>0</sup>-C<sub>13</sub><sup>0</sup> mixture. The catalysts were characterized by BET, mercury intrusion porosimetry, CO-chemisorption and NH<sub>3</sub>-TPD. Catalytic activity, selectivity to various components and stability were compared between TPRn/SPI-TOF-MS measurement and industrial plant run data to explore the reliability, predictability and application of TPRn/SPI-TOF-MS for rapid catalyst testing and screening. Characteristics of the catalysts, such as Pt dispersion and acidity, affected paraffin dehydrogenation conversion and mono-olefin selectivity. This was reflected in the catalyst performance data obtained on TPRn/SPI-TOF-MS system, which was in good agreement with the data from industrial runs. It is shown that use of TPRn/SPI-TOF-MS measurements allows to identify the reaction temperature range for maximum mono-olefin yield. Further it is possible to judge onset temperature for all the products and help identify operation temperature for industrial plant operation. Investigation of aromatics formation over the catalysts establishes the consecutive reaction pathways of long chain paraffin dehydrogenation over modified Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst.

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### 1. Introduction

Dehydrogenation of long chain, kerosene range, paraffins to produce mono-olefins, feedstock for linear alkylbenzene sulfonate (LAS), is a key process for industrial synthesis of biodegradable detergents. *n*-Paraffins conversion to *n*-olefins was first commercialized by UOP, USA (PACOL process) in the 1960s [1]. Paraffin dehydrogenation is an endothermic reaction limited by thermodynamic equilibrium. Higher temperatures and lower pressures favor higher paraffins conversions, but at the same time cause side reactions, such as deeper dehydrogenation to di-olefins and aromatics [2]. This also leads to extensive coke formation and the catalysts for long chain paraffin dehydrogenation have usually short life time of 40–60 days [3].

Lots of efforts have been reported on the modification of Pt-based dehydrogenation catalyst which was first applied by Bloch [4,5] in PACOL process. These include effect of supports [6–9] and promoters [9–12] on performance of the catalyst. There has been continuous research till to date resulting in the availability of newer generation of catalysts. The short life-time makes it vital to pre-test commercial catalyst of different batches before use in the PACOL plant. Thus an effective and proper testing method is very essential for the evaluation, comparison and improvements of the ever involving dehydrogenation catalyst. Normally a lab scale axial fixed bed reactor [8] run at the conditions in the PACOL plant for short times (1–2 h) is used for catalyst screening via initial activity/selectivity measurements. To obtain dehydrogenation activity at different temperatures, as reference for industrial operation, many tests are needed. In addition, to follow products selectivities, the gaseous dehydrogenation products need to be condensed, gas-liquid separated and collected to be analyzed off-line by titration [13] and chromatography [14]. All these procedures are time-consuming and labor-intensive. Further, a rapid method for

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the assessment of catalyst life-time for application in the industrial plant is also essential. This is because full life-time tests under realistic conditions [3] or even the so called “accelerated life-time test” by using harsh conditions, e.g., high temperature and low hydrogen to paraffin ratio [7] are time consuming. Importantly, design of such a rapid method for efficient catalyst evaluation must be reliable, and has high time and temperature resolution of the reactivity data.

Temperature Programmed Reaction (TPRn) under realistic reaction conditions, using mass spectrometry (TPRn/MS) for analysis, has been demonstrated as a powerful, rapid and reliable technique in catalysis research for catalyst screening, optimisation of reaction temperature, reaction mechanisms, kinetics and energetics. However, this is mostly applied in simplified catalytic reaction systems involving low molecular weight and permanent gas reactions on solid catalysts. Examples are dry reforming of CH<sub>4</sub> with CO<sub>2</sub> [14], 3-way catalysis with CO, NO and C<sub>2</sub>H<sub>2</sub> [15], oxidative dehydrogenation of C<sub>2</sub>H<sub>6</sub> [16,17] and partial oxidation of CH<sub>4</sub> [18–20].

The limitations of TPRn/MS in reactions involving complex molecules are the use of hard ionization sources (e.g., resulting in high fragmentation and complex spectra) and type of mass analyzers (e.g., low practical m/z range and limited resolution). Recently, Single Photon Ionization – Time of Flight – MS (SPI-TOF-MS) has emerged and shown to be promising for both off-line and [21,22] on-line analyses [8,23,24]. SPI-TOF-MS, which combines the advantages of soft ionization (e.g., high yield of parent ions and low fragmentations [25]) and TOF-MS (e.g., high resolution, accuracy and practical m/z range [26]), could be one solution for the bottleneck of the current TPRn/MS technique. We recently demonstrated the suitability of the TPRn/SPI-TOF-MS system for rapid investigation of heterogeneous catalytic reactions under realistic reaction conditions [27]. For example, TPRn/SPI-TOF-MS showed excellent time and temperature resolution of data for paraffin dehydrogenation [27]. The system could be used to identify product distribution, onset of reaction temperature, conversion/selectivity, activation energies, and reaction pathways.

This work describes the use of newly developed TPRn/SPI-TOF-MS technique to compare data and establish correlations with long chain paraffin (n-C<sub>10</sub><sup>0</sup>-C<sub>13</sub><sup>0</sup>) dehydrogenation in the industrial PACOL plant over two commercial catalysts. Results obtained are used (i) together with catalyst characteristics to draw structure-performance relationships for academic practice; and (ii) to compare data from a conventional industrial run in the PACOL plant [3] in order to explore reliability of the technique to rapidly evaluate and screen catalyst for industrial reference.

## 2. Experimental

### 2.1. Catalysts and characterization techniques

Commercial Pt-Sn-K-Mg/Al<sub>2</sub>O<sub>3</sub> catalyst denoted as Cat-D and Pt-Sn-Na-Co/Al<sub>2</sub>O<sub>3</sub> catalyst named as Cat-N were supplied by Fushun Petrochemical Company Research Institute, China. Details of the catalysts are given in Table 1.

BET surface areas of the catalysts were calculated from N<sub>2</sub> adsorption isotherms at 77 K measured on a volumetric adsorption system (Micromeritics ASAP 2010, USA). Catalysts were degassed at 300 °C prior to measurements.

Total pore volumes of the catalysts were measured using mercury intrusion porosimetry (Micromeritics Autopore 9520, USA). Catalysts were outgassed in vacuum (0.01 torr) for 1 h at 95 °C beforehand.

Pt dispersion of the catalysts was determined by CO pulse chemisorption on Micromeritics AutoChem II 2920 (USA). Catalysts were reduced under pure H<sub>2</sub> at 500 °C for 1 h, purged with helium

at 520 °C for 1 h and then cooled down to 50 °C in He. 100 μL pulses of 5% CO/He were sent to the reactor and the time between pulses was 4 min.

Acidity of the catalysts was measured using NH<sub>3</sub>-TPD on Micromeritics AutoChem II 2920 (USA). The samples were pre-treated at 550 °C for 1 h in helium and then cooled to 100 °C to be saturated with pure NH<sub>3</sub>. NH<sub>3</sub>-TPD was carried out in helium at 10 °C min<sup>-1</sup> up to 500 °C. The desorbed products were detected by a thermal conductivity detector (TCD).

### 2.2. Paraffin dehydrogenation on the TPRn/SPI-TOF-MS system

Dehydrogenation of n-C<sub>12</sub><sup>0</sup> (98.7 wt.%, industrial grade) was performed on a tubular fixed bed laboratory catalytic reactor with an on-line SPI-TOF-MS [27]. Two grams of catalyst was first pre-reduced under pure H<sub>2</sub> at 470 °C for 2 h. The catalytic reactor was then conditioned at 380 °C for 1 h in hydrogen followed by feeding n-C<sub>12</sub><sup>0</sup>-n-C<sub>12</sub><sup>0</sup> flow (50 ml hr<sup>-1</sup>) was controlled by a HPLC pump and hydrogen flow (30 L h<sup>-1</sup>) by a mass flow controller. The reaction system was operated at 0.07 MPa overpressure using a back pressure regulator. The catalyst bed temperature was then programmed from 380 to 490 °C with a low heating rate (1.5 °C min<sup>-1</sup>) to achieve thermal equilibrium between the catalyst and the furnace. Product samples from the bottom of the catalyst bed were sent to the ionizer of the TOF-MS system, which was continuously calibrated with 100 ppm benzene in N<sub>2</sub>. The conversion of n-C<sub>12</sub><sup>0</sup> was derived from MS peak signal (P) ratio as  $X_T = (1 - P_T/P_{380}) \times 100\%$ . The selectivity is expressed using MS peak ratios, e.g., di-olefins or aromatics to mono-olefins. Further, liquid products were also collected simultaneously and analysed by GC method [7] in order to be able to validate conversion measured by TPRn/SPI-TOF-MS method.

### 2.3. Paraffins dehydrogenation in industrial PACOL plant

Dehydrogenation of n-C<sub>10</sub><sup>0</sup>-C<sub>13</sub><sup>0</sup> mixture was run on the industrial PACOL dehydrogenation plant in the Detergent Chemical Complex of PetroChina Fushun Petrochemical Company, China [3]. The composition of n-C<sub>10</sub><sup>0</sup>-C<sub>13</sub><sup>0</sup> (denoted as n-paraffins) was: n-C<sub>10</sub><sup>0</sup> 11.67 wt.%, n-C<sub>11</sub><sup>0</sup> 29.37 wt.%, n-C<sub>12</sub><sup>0</sup> 32.29 wt.%, n-C<sub>13</sub><sup>0</sup> 26.25 wt.% and n-C<sub>14</sub><sup>0</sup> 0.07 wt.%. Re-circulation Hydrogen stream consisted of H<sub>2</sub> 93.13%, C<sub>1</sub> 1.1%, C<sub>2</sub> 3.21%, C<sub>3</sub> 1.36%, C<sub>4</sub> 0.41%, C<sub>5</sub> 0.13%, O<sub>2</sub> 0.05% and N<sub>2</sub> 0.62%. In the plant, 2050 kg catalyst was charged into the adiabatic radial fixed bed reactor. The dehydrogenation conditions were: reaction pressure 0.15 MPa, initial reactor inlet temperatures 478 °C for Cat-D and 477 °C for Cat-N, LHSV of n-paraffins 20.5 h<sup>-1</sup> and GHSV of hydrogen 12,000 h<sup>-1</sup>. The reactor inlet temperature was increased stepwise so as to maintain conversion at the desired level. Dehydrogenation products were analyzed at the Detergent Chemical Complex. The conversion (X<sub>n</sub>) of n-paraffins was calculated as 1.05 times bromine number as per the standard ASTM D1159-98 method [13]. The selectivities to mono-olefins were calculated as TNO/X<sub>n</sub> × 100%, where TNO (Total Normal Olefins) was measured by GC according to ASTM UOP688-09 method [28].

## 3. Results and discussions

### 3.1. Characterizations of catalysts

Alumina supported Pt-Sn catalysts have been widely investigated and used for long chain paraffin dehydrogenation. It has been reported that the acidity of the catalyst needs to be neutralized to inhibit side reactions such as dehydrocyclization and aromatization [2]. Several additives, e.g., alkaline [11,29], alkaline earth [7,8] and transition metals [30], have been investigated and some of

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