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Temperature programmed reaction/single-photon ionization time-of-flight mass spectrometry system for rapid investigation of gas-solid heterogeneous catalytic reactions under realistic reaction conditions

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A Temperature Programmed Reaction (TPRn)/ Single-Photon Ionization Time-of-Flight Mass Spectrometry (SPI-TOF-MS) system is described. TPRn/SPI-TOF-MS system allows rapid characterizations of the heterogeneous catalytic reactions under realistic reaction conditions and at the same time allows for description of the reaction schemes.

Catalysis plays a vital role in chemical, pharmaceutical, automobile and petrochemical industry and is being applied in emerging areas such as fuel cells and bio-refinery/bio-technology[1]. In the design of efficient catalysts a proper understanding of the catalysed reaction pathways is essential. In order to do this, general analysis techniques (titration, chromatography, *etc*.) have been adopted for off-line analysis of the catalytic reaction effluents. Low time-resolution[2] or loss of temperature-resolution[3] of data in such off-line analysis bears the risk of missing vital clues for the performance of the catalysts. On-line analysis techniques (infrared spectroscopy, mass spectrometry, etc.) which offer real-time detection could be one of the solutions. Mass spectrometry (MS) has been coupled with chromatography, *e.g.,* gas (GC-MS) or liquid (LC-MS) for off-line analysis. With its high analysis speed and sensitivity, MS is also used for on-line monitoring of catalytic reactions[4]. Combined temperature-programmed (TP) techniques, *e.g.,* reduction (TPR)[5], oxidation (TPO)[6], desorption (TPD)[7, 8], surface reaction (TPSR)[9], etc., TP-MS has been developed as a very powerful characterization technique in investigating the physico-chemical properties of solid catalysts. Furthermore, usefulness of temperature-programmed reaction (TPRn/MS) systems for the evaluation of the catalytic reactions; dry reforming[10], three-way catalysis[11], oxidative dehydrogenation[12] and partial oxidation of methane[13] under realistic reaction conditions has also been reported.

It has been demonstrated that TPRn/MS is a powerful, rapid and reliable technique for catalysis research in terms of catalyst selection, optimisation of reaction conditions, reaction kinetics/mechanisms, and energetics. However, at present, this is more often applied in simplified catalytic reaction systems involving low molecular weight, permanent gases and on solid catalysts.

Conventionally, quadrupole or magnetic sector mass spectrometers with hard ionization sources such as electron ionization (EI) are utilized for the TPRn/MS or on-line MS monitoring systems. Hard ionization methods give in addition to molecular ions also a high degree of ion fragmentation. This results in a very complex spectrum, which increases the difficulty of precise spectral identification of reaction effluents. Further, quadrupole mass analyzers used often have limited resolution, m/z range and can hardly analyze heavy ions which cannot pass through. These factors limit a comprehensive application of TPRn/MS in catalysis research and have led to a demand for robust, fragmentation-free soft ionization methods for MS with higher resolution, m/z range and accuracy.

Nowadays, time of flight mass spectrometry (TOF-MS) is attracts much more attention. Comparatively, TOF is the fastest MS analyzer with high (i) ion transmission, (ii) sensitivity, and provides accurate mass measurement for practical m/z range[14]. More recently, Single Photon Ionization (SPI) has emerged as an important soft ionization method. SPI with vacuum ultraviolet (VUV) radiation is suitable for ionization of organic components including saturated alkanes[15]. In contrast to the hard ionization methods, SPI is characterized by a high yield of parent ions and drastically reduced fragmentation. It can thus eliminate spectral congestion and improve the sensitivity in complex matrices[16].

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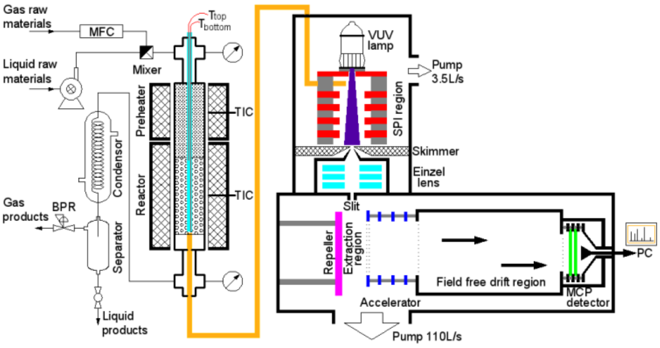

Fig. 1 Pneumatics of TPRn/SPI-TOF-MS system.

The SPI-TOF-MS, which combines the advantages of SPI and TOF-MS, is being developed as an effective, rapid analysis (GC/SPI-TOF-MS[17]) and on-line monitoring (TG/SPI-TOF-MS[3]) technique. We have shown earlier the promise of SPI-TOF-MS[18-22] for analysis of complex organic species[19, 20] and long-term real-time monitoring of catalytic reactions[2, 23].

This communication focuses to establish the unique combination of TPRn and SPI-TOF-MS as a versatile technique suitable for a rapid investigation of complex catalytic reactions under realistic reaction conditions.

To demonstrate validity, dehydrogenation of long chain paraffins selectively to mono-olefins, which is industrially operated at high temperature (475-485 °C) and mild pressure (0-1.5 bar) conditions[24, 25], was performed as the model reaction. Conventional catalyst studies for this system have been reported in our former papers[24-27]. The reactant used was n-dodecane (98.7 wt.%[23], boiling point 216 °C) with a flow of 50 ml/hr and hydrogen (30 L/hr, 99.99% pure). n-Dodecane was vaporized at 380 °C before passing through the fixed catalyst bed. The catalysts used were γ-Al_2O_3 and Mg-Al-O oxides supported $Pt_{0.3}$-$Sn_{0.9}$[23]. Details of the catalysts can be seen in Table 1. The catalysts were pre-reduced at 470 °C and stabilized at 0.7 bar, 380 °C for 1 hour. Five minutes after n-dodecane flow was started, the reactor was heated from 380 to 490 °C at 1.5 °C/min to carry out TPRn.

Details of the TPRn/SPI-TOF-MS system are shown in Fig. 1. The SPI-TOF-MS was operated in linear mode and consisted of an ion source, an ion transmission system and a TOF analyzer. The VUV light source for SPI was a commercial krypton discharge lamp (PKS106, Heraeus Noblelight Gmbh) with photon energy of 10.6 eV and a photon flux of 1×10^{11} photons/s. The ion source was pumped by a 3.5 L/s dry scroll vacuum pump (Agilent Technologies Inc.). The ions were transferred from the ion source through the sample center hole and skimmer orifice into the einzel lens where the ion beam was collimated to be guided through the slit into the extraction region. The TOF analyzer was pumped by a 110 L/s turbo molecular pump (KYKY Technology Development Ltd.). The ions were collected by the microchannel plate (MCP) detectors[28] and the signals were recorded with 2 minutes for a single analysis by using a time-to-digital converter (TDC, model P7888-1E, FAST ComTec Gmbh) with a repetition rate of 1GHz. Time-resolution of 2 minutes used here ensured sufficient MS response of all the products. To avoid collisions of ions and gas molecules and also to control the ions trajectories effectively, the TOF analyzer must be operated under vacuum lower than 1.0×10^{-3} Pa. In this work, a stainless steel tube connected to the SPI source was used for sampling and to combine TPRn and SPI-TOF-MS. To keep the high vacuum of TOF-MS and to avoid any condensation, the size of the sampling tube (1/16 inch×3m) and interface temperature (250 °C) were optimized.

Table 1 Characterizations of Al_2O_3 and Mg-Al-O supported $Pt_{0.3}$-$Sn_{0.9}$ catalysts

Catalysts	Mg/Al mole ratio	S_{BET} (m^2 g^{-1})[a]	Pt dispersion (%)[b]	Acidity (a.u.)[c]
Pt-Sn/Al_2O_3	0:1	186.3	99.3	11.3
Pt-Sn/Mg-Al-O	1:2	142.2	41.8	5.5

* measured by [a] BET, [b] CO chemisorption and [c] NH_3-TPD.

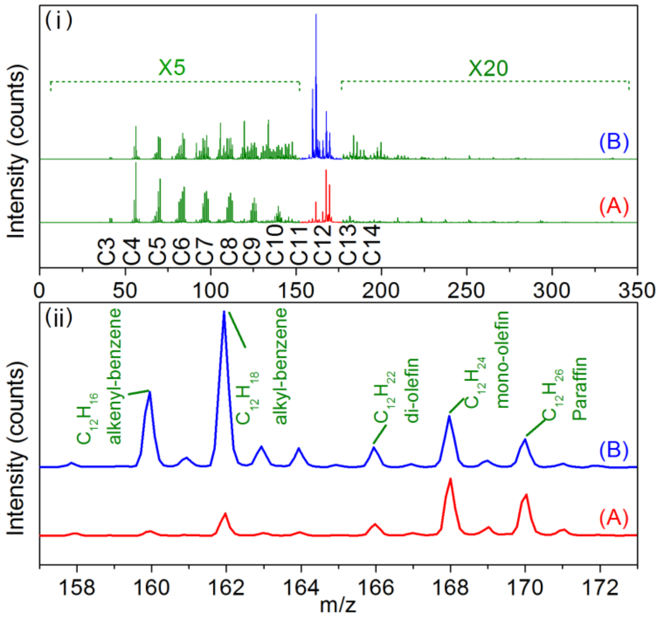

Fig. 2 Product distribution of n-C_{12}^0 dehydrogenation over (A) Pt-Sn/Mg-Al-O and (B) Pt-Sn/Al_2O_3 catalysts at 490 °C: (i) full, and (ii) zoomed range spectra. (×5 and ×20 imply 5 and 20 times of the original MS intensity.)

The product distributions of n-C_{12}^0 dehydrogenation over two catalysts are shown in Fig. 2. The SPI-TOF-MS spectrum (Fig. 2-i) indicates that small amount of n-C_{12}^0 was converted to C_3-C_{11} hydrocarbons. The ion source used (10.6 eV) is not capable to ionize H_2, CH_4, C_2H_6 and C_2H_4 which, thus did not appear in the spectrum. It can be seen from Fig. 2-ii that

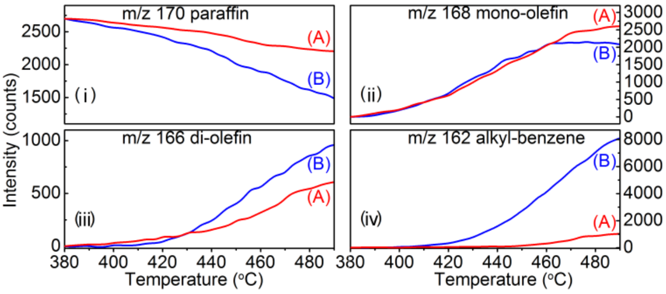

Fig. 3 Monitoring results of n-C_{12}^0 dehydrogenation products over (A) Pt-Sn/Mg-Al-O and (B) Pt-Sn/Al_2O_3: (i) paraffin, (ii) mono-olefin, (iii) di-olefin and (iv) alkylbenzene.

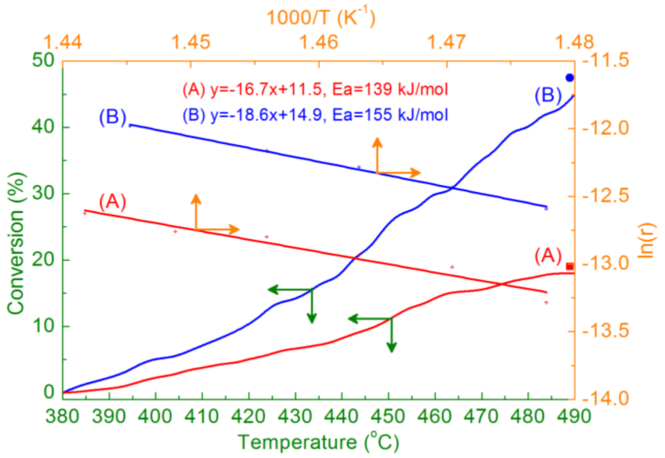

Fig. 4 Conversion and Arrhenius plot of n-C_{12}^{0} dehydrogenation over (A) Pt-Sn/Mg-Al-O and (B) Pt-Sn/Al_2O_3.

mono-olefin (m/z 168), di-olefin (m/z 166), alkyl-benzene (m/z 162) and alkenyl-benzene (m/z 160) are the main products.

The online monitoring of n-C_{12}^{0} and the dehydrogenation products over two catalysts are presented in Fig. 3. The unreacted paraffin is compared in Fig. 3-i. The conversion of n-C_{12}^{0} at any temperature was derived from the peak signal (P) ratios as $X_T = (1-P_T/P_{380})\times100\%$. The conversion *vs.* reaction temperature is shown in Fig. 4. Two dots indicate conversion as obtained during separate steady-state dehydrogenation at 490 °C using offline GC analysis[23]. Excellent agreement between the conversion data from conventional steady-state experiment GC analysis and from TPRn/SPI-TOF-MS indicates the reliability of this technique.

It can further be seen that n-dodecane conversion over Pt-Sn/Al_2O_3 is always higher than over Pt-Sn/Mg-Al-O catalysts. The Arrhenius plots from the TPRn-TOF-SPI data in the temperature range of 400-420 °C (Fig. 4) give apparent activation energy (Ea) of n-C_{12}^{0} dehydrogenation over Pt-Sn/Mg-Al-O and Pt-Sn/Al_2O_3 catalysts to be 139 KJ/mol and 155 KJ/mol. Ea over Pt-Sn-K-Mg/Al_2O_3 catalysts is in good agreement with that (136 KJ/mol) obtained during the kinetic research[29].

The mono-olefin formation (Fig. 3-ii) over the two catalysts is almost same till 460 °C. At temperatures higher than 460 °C, mono-olefin formation over Pt-Sn/Al_2O_3 catalysts remained constant but that over Pt-Sn/Mg-Al-O increased.

Di-olefin formation (Fig. 3-iii) over Pt-Sn/Mg-Al-O catalysts started from the beginning when mono-olefin was formed. The onset temperature of di-olefin formation over Pt-Sn/Al_2O_3 catalysts is roughly 410°C. Di-olefin formation over Pt-Sn/Al_2O_3 catalysts increased greatly and exceeded that over Pt-Sn/Mg-Al-O catalysts when the temperature is above 430 °C. With increasing temperatures, this difference is getting higher.

Table 2 Onset temperature of dehydrogenation products formation over two catalysts

Catalysts	$C_{12}H_{24}$ mono-olefin	$C_{12}H_{22}$ di-olefin	$C_{12}H_{18}$ Aromatics
Pt-Sn/Al_2O_3	380 °C	410 °C	420 °C
Pt-Sn/Mg-Al-O	380 °C	380 °C	445 °C

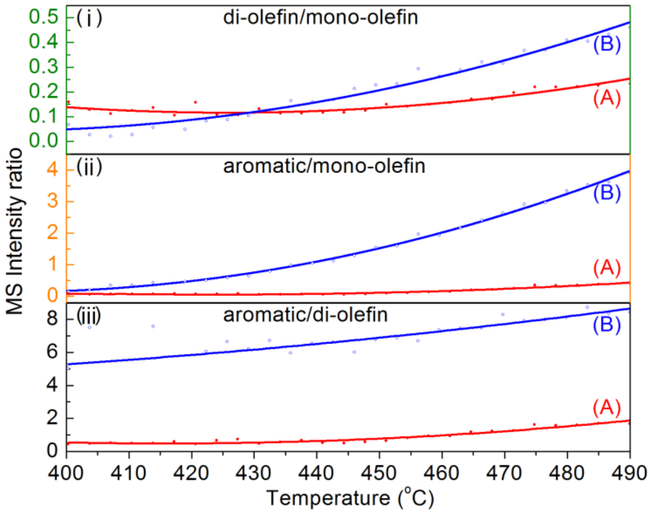

Fig. 5 Product ratio of n-C_{12}^{0} dehydrogenation over (A) Pt-Sn/Mg-Al-O and (B) Pt-Sn/Al_2O_3: (i) di-olefin/mono-olefin, (ii) aromatic/mono-olefin and (iii) aromatic/di-olefin.

Typically, di-olefin formation is not a big problem commercially as it can be selectively hydrogenated later (*e.g.,* UOP DeFine^{TM} process). However, formation of aromatics is a dead end and affects mono-olefin product yields. Alkyl-benzene formation (Fig. 3-iv) is higher for Pt-Sn/Al_2O_3 catalysts. The onset temperatures of alkyl-benzene over two catalysts are tabulated in Table 3. With the increase of temperature, Pt-Sn/Al_2O_3 catalysts produced higher amounts of aromatics than Pt-Sn/Mg-Al-O catalysts. The higher amount of aromatics over Pt-Sn/Al_2O_3 catalysts at elevated temperature causes not only lower olefin selectivity but also contribution to coke formation and catalyst instability.

The selectivity for the two catalysts can be visually expressed by the ratio of di-olefins or aromatics to mono-olefins (Fig. 5). Comparatively, Pt-Sn/Mg-Al-O catalysts show much lower di-olefin/mono-olefin and aromatic/mono-olefin ratio, especially when the temperature is higher than 430 °C.

Dehydrogenation is favoured on the Pt sites and smaller Pt particles (see Table 1) and hence the enhanced conversion observed over Pt-Sn/Al_2O_3 (Fig. 4). Correspondingly, the catalysts also show a higher extent of di-olefin formation (Fig. 3-iii). Di-olefin/mono-olefin ratio (Fig. 5-i) implies that deeper dehydrogenation is very sensitive to temperature increase especially over small Pt particle size catalysts.

The higher selectivity to aromatics over Pt-Sn/Al_2O_3 catalysts is logically caused by its very strong acidity (Table 1) which catalyzes dehydrocyclization to aromatics. This is also as expected. As explained earlier, aromatics formation is detrimental to mono-olefin formation and catalyst stability *via* coke formation. It is therefore critical to minimize aromatics formation. From the TPRn, the onset temperature for aromatic formation can be seen and this provides the clue for optimal operating temperature (OOT) for the catalysts. The MgO modified catalysts with lower acidity can be operated at a higher temperature (Fig. 3-iv, Table 2) while keeping the aromatic contents lower.

Industrial operation usually runs from 475 °C to reach the maximum mono-olefin yield (Fig. 3-ii), which suggests that modification of the acidic Pt-Sn/Al_2O_3 catalysts (*e.g.,* MgO addiction) is essential to decrease the production of aromatics. Similar Ea over the two catalysts indicates that the rate determining step is same. This is generally accepted as the first dehydrogenation and mono-olefin formation. However, different ratios of di-olefins or aromatics to mono-olefins over the two catalysts also suggest that different dehydrogenation mechanisms operate over modified and unmodified Pt-Sn/Al_2O_3. This has indeed been proposed before[30]. It is accepted that cyclization and aromatization take place on the acid sites through the following Route 1:

Paraffins→olefins→dienes→trienes→aromatics (Route 1)

However, the increase of aromatic/mono-olefin ratio along with the di-olefin/mono-olefin ratio over Pt-Sn/Al_2O_3 catalysts supports the additional parallel route for aromatics formation proposed over the very acidic catalysts, *viz*.

Paraffins→cyclo-paraffins→aromatics (Route 2)

Route 2 only can be observed for paraffins with long chain length. Dehydrocyclization to make cyclo-paraffins from paraffins also requires a dehydrogenation step. Strong acidity is also necessary for Route 2 and aromatization. Thus neutralizing the acidity of the Pt-Sn/Al_2O_3 catalysts is an effective way to reduce the aromatics formation and coke as well via both routes.

In summary, this communication demonstrates a high-throughput TPRn/SPI-TOF-MS technique to rapidly and reliably establish key issues of heterogeneously catalysed reactions. These include product distribution; the onset formation temperature; conversion/selectivity with good temperature-resolution; Arrhenius plots and activation energies. In principle, the current TPRn/SPI-TOF-MS system described has the capability to follow gas phase catalytic conversions of most organic molecules with the exception of those with the ionization energy higher than the photo energy of SPI (7.5-11.8 eV). Combined with other catalyst characterization techniques, TPRn/SPI-TOF-MS can effectively investigate the reactivity, obtain the reaction mechanism and accelerate the catalyst testing and screening.

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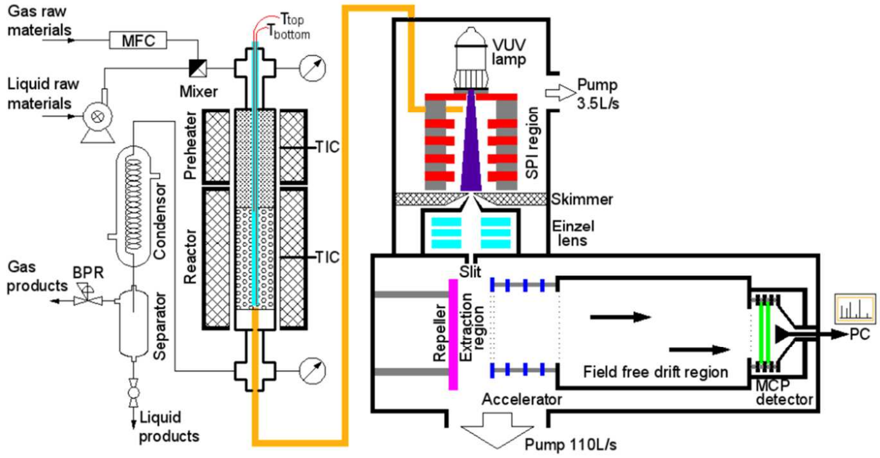
Graphical and textual abstract



A new TPRn/ SPI-TOF-MS system for rapid investigation of gas-solid heterogeneous catalytic reactions under realistic reaction conditions