



Industrial development of long chain paraffin ($n\text{-C}_{10}\text{--C}_{13}^0$) dehydrogenation catalysts and the deactivation characterization



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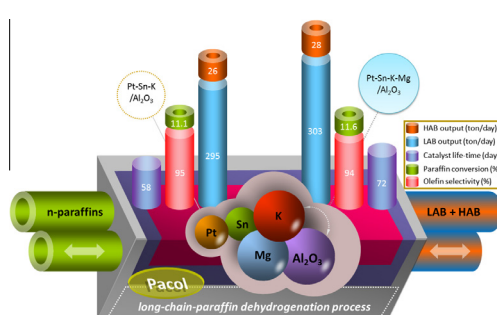
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HIGHLIGHTS

- A new type of long chain paraffin dehydrogenation catalysts was industrially developed.
- Pt–Sn–K–Mg/Al₂O₃ catalysts showed higher dehydrogenation activity.
- Pt–Sn–K–Mg/Al₂O₃ catalysts performed longer life time.
- Detailed characterization of the industrially deactivated dehydrogenation catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

Pt–Sn–K–Mg/Al₂O₃ catalysts for the dehydrogenation of long chain paraffins ($n\text{-C}_{10}\text{--C}_{13}^0$) were successfully developed and applied in the industry. The catalysts were tested on both the industrial side fixed bed reactor and the industrial PACOL dehydrogenation plant. The industrially deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts were characterized by TG–DTA, elemental analysis, UV Raman spectroscopy, TPO, SEM, XRD, BET, MIP and CO-chemisorption. The industrial 72-day-run data indicated that Pt–Sn–K–Mg/Al₂O₃ catalysts performed excellent dehydrogenation conversion of 11.6% and high mono-olefin selectivity of 94.1%. The daily output of alkylbenzene over Pt–Sn–K–Mg/Al₂O₃ catalysts was as high as 333.6 ton/day. The deactivated catalysts were deposited by the amorphous and graphitized coke, of which the weight percentage was 3.78% and the H/C mole ratio was 1.19. The coke covered parts of the Pt and support surface, while the pore and crystalline structure of the catalysts were not destroyed.

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1. Introduction

Dehydrogenation of long chain paraffins ($n\text{-C}_{10}\text{--C}_{13}^0$) to olefins is an important catalytic process of producing linear alkylbenzene sulfonates (LABS) for biodegradable detergents. By the late 1930s,

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UOP, USA successfully developed a paraffin dehydrogenation process called Universal and established the first set of paraffin dehydrogenation plant in Billingham, UK. Chromia-alumina catalysts were originally employed for the dehydrogenation of light hydrocarbons (e.g., $n\text{-C}_2$, C_3 , C_4 and $i\text{-C}_4$) [1]. In 1968, the PACOL dehydrogenation process was developed and industrialized by UOP [2,3] in which the noble metal Pt based Al₂O₃ catalysts were used. The DEH catalysts have been used widely in the dehydrogenation units all over the world and gradually updated by UOP Company. In 1969, DEH-4 catalysts were firstly used in the dehydrogenation industry. DEH-5 catalysts with Pt content of 0.375 wt.% and showed better

activity and stability were then developed successfully in 1972. Later on, the DEH-7 catalysts with Pt content of 0.41 wt.% have been put into use since 1983. The conversion of the catalysts was increased from 9% (over DEH-5 catalysts) to 12–13% (over DEH-7 catalysts). The reaction selectivity of the DEH-7 catalysts was almost the same as that of the DEH-5 catalysts, while the life time of the DEH-7 catalysts was 1.7 times to that of the DEH-5 catalysts. In 1990, the DEH-9 catalysts with higher selectivity were developed accompanied with the use of DEFINE and DETAL technology. The formation of by-products, such as, iso-paraffins, cyclo-paraffins, aromatics, etc., were then decreased greatly. The selectivity of the DEH-9 catalysts was improved 4% as that of the DEH-7 catalysts, and the production of LAB was increased about 3%. In 1999, the DEH-11 catalysts were invented and used in the new type of TCR reactor, whose conversion was 17–18%. The molten sodium was used as the heater in the TCR reactor. As the investment costs were high and the operating conditions were harsh, the DEH-11 catalysts were less in application. At present, the main dehydrogenation catalysts used in PACAL unit are still the DEH-7 catalysts. In 1979, China started to build the PACOL long chain paraffin dehydrogenation plant in Nanjing city and till now has three plants with LABS production capacity of 580,000 ton/year. The industrial research and application of the dehydrogenation catalysts in China was started by Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences in 1975 [4]. Pt–Sn–Li–S catalysts were successfully developed in 1980. Then with the cooperation of the industrial partners in China, DICP successfully developed NDC-2 dehydrogenation catalysts for Nanjing Alkylbenzene Plant in 1984 [5] and DF-1 catalysts for the Detergent Chemical Complex of PetroChina Fushun Petrochemical Company in 1991 [6]. The performance level of the NDC-2 and DF-1 catalysts reached to that of the DEH-7 catalysts. Later on Nanjing Alkylbenzene Plant developed the NDC-4 dehydrogenation catalysts in 1990. The stability of NDC-4 catalysts was better than that of DEH-7 catalysts. NDC-4 catalysts were also exported to some countries such as India and Iran, which broke the monopoly of the UOP dehydrogenation catalysts. DICP developed Pt–Sn–K/Al₂O₃ catalysts called DF-2 catalysts in 1997 [7] whose lifetime was better than that of DEH-7 catalysts and almost the same as that of the NDC-4 catalysts. In 2008, DICP developed Pt–Sn–K–Mg/Al₂O₃ catalysts which were called DF-3 catalysts and successfully industrialized [8] in PetroChina Fushun Petrochemical Company.

In this contribution, the catalytic performance of Pt–Sn–K–Mg/Al₂O₃ catalysts for the long chain paraffin (n-C₁₀–C₁₃) dehydrogenation in both the industrial side fixed bed reactor and industrial PACOL plant was reported. As a reference, the catalytic performance of Pt–Sn–K/Al₂O₃ was also discussed. The characterization of industrially deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts being employed in PACOL unit was thoroughly studied by the combination of different characterization techniques.

2. Experimental

2.1. Fresh catalyst production

Commercial Pt_{0.5}–Sn_{1.5}–K_{0.5}–Mg₁/Al₂O₃ catalysts (hereafter denoted as Pt–Sn–K–Mg/Al₂O₃ catalysts) and Pt_{0.5}–Sn_{1.5}–K_{0.5}/Al₂O₃ catalysts (hereafter denoted as Pt–Sn–K/Al₂O₃ catalysts) were prepared by the vacuum complex co-impregnation method [8] and produced by PetroChina Fushun Petrochemical Company, China. The granular γ -alumina support material was commercially produced by Research Institute of Daily Chemical Industry (China) with the diameter of 1–2 mm and bulk density of 0.33 g cm⁻³. All the precursors, metal Pt, SnCl₂·2H₂O, HCl, KCl, MgCl₂ and ethanol are analytical grade. The aqueous solutions of platinum-

tin-potassium-magnesium precursors were sprayed onto alumina through a plastic nozzle. Then the mixture was gently stirred for 30 min at room temperature followed by being gently heated at 60–70 °C in order to evaporate the excess liquid, being dried at 120 °C for 3 h and calcined at 520 °C for 8 h. The final catalysts were reduced under H₂ at 490 °C for 8 h.

2.2. Industrial side life time testing of the catalysts

Catalytic dehydrogenation of n-C₁₀–C₁₃ was performed in an industrial side fixed bed reactor in the Detergent Chemical Complex of PetroChina Fushun Petrochemical Company, PR China. Long chain paraffins were from the Molex unit in No.3 Refinery of Fushun Petrochemical Company and the component of n-C₁₀–C₁₃ was: n-C₁₀ 11.67 wt.%, n-C₁₁ 29.37 wt.%, n-C₁₂ 32.29 wt.%, n-C₁₃ 26.25 wt.% and n-C₁₄ 0.07 wt.%. The recycle hydrogen was from the Detergent Chemical Complex of PetroChina Fushun Petrochemical Company and the component was: H₂ 93.13%, C₁ 1.1%, C₂ 3.21%, C₃ 1.36%, C₄ 0.41%, C₅ 0.13%, O₂ 0.05% and N₂ 0.62%. The weighted 10 ml of the catalysts were charged to the reactor. Prior to the dehydrogenation reaction, the catalysts were reduced at 470 °C in flowing H₂ for 4 h followed by cooling to the 380 °C to feed in the paraffins. Then the temperature was programmed up to 460 °C within 1 h and constant for 2 h to test the initial activity of the catalysts. The reaction conditions were: the liquid hourly space velocity (LHSV) of the n-paraffins 20 h⁻¹, the gas hourly space velocity (GHSV) of hydrogen 12,000 h⁻¹, and the reaction pressure 0.14 MPa. The temperature was stepwise from 460 °C to 500 °C. The dehydrogenation products were condensed and collected in the gas-liquid separator.

2.3. Industrial dehydrogenation process and deactivated catalysts

Industrial dehydrogenation of n-C₁₀–C₁₃ was performed on the industrial PACOL dehydrogenation plant (R101A/B) of the Detergent Chemical Complex of PetroChina Fushun Petrochemical Company, China. The weighted 2,050 kg of catalysts (about 6.2 m³) were charged into the stainless steel adiabatic fixed bed catalytic reactor. The dehydrogenation conditions were as follows: reaction pressure 0.15 MPa, initial reactor inlet temperature 478 °C, liquid hourly space velocity (LHSV) of the n-paraffins 20.5 h⁻¹ and gas hourly space velocity (GHSV) of hydrogen 12,000 h⁻¹. The reactor inlet temperature was increased stepwise up to 490 °C so as to maintain the conversion (12 ± 0.5%) in the specific stage of the reaction period.

After continuous run and being deactivated in the industrial plant, the catalysts were moved out under N₂ atmosphere and defined as deactivated catalysts. Part of the deactivated catalysts (about 12.5 ml) were then purged in Ar (99.99%, 500 ml/min) at 485 °C for 1 h to remove any hydrocarbon residue for the further coke characterization and analysis.

2.4. Product analysis

The product analysis was done in the analysis center of the Detergent Chemical Complex. The bromine number of the effluents was determined by the standard of ASTM D1159-98. The conversion of n-C₁₀–C₁₃ was calculated as the multiplication of 1.05 and bromine number. The liquid products were also analyzed on GC and HPLC by UOP method 411-75 to test the total non-normal paraffins (TNN), UOP method 688-68T to test carbon number distribution and total normal olefins (TNO), and UOP method 869-86 to test di-olefins. The selectivity was calculated by the following equation: selectivity (%) = TNO/conversion * 100%.

2.5. Fresh and deactivated catalyst characterizations

The carbon content of the deactivated catalysts was measured on a thermogravimetry analysis (TG–DTA) instrument (SETSYS 16/18, France). The deactivated catalysts were heated from room temperature to 800 °C at a heating rate of 10 °C min⁻¹ in an air flow of 50 ml min⁻¹.

The H/C mole ratio of the coke deposition of the deactivated catalysts was determined on a Vario EL III universal CHNOS elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

The ultraviolet (UV) Raman spectra were collected at room temperature on a Jobin–Yvon T64000 triple-stage spectrograph (Paris, France) with spectral resolution of 2 cm⁻¹. A He–Cd laser with the laser line of 325 nm and the output of 25 mW was used as an excitation source.

Temperature-programmed oxidation (TPO) analysis of the deactivated catalysts was carried out on Micromeritics AutoChem II 2920 apparatus (USA). The samples were pretreated in He (99.99%, 20 ml/min) at 485 °C for 1 h followed by being cooled to room temperature in He. The gas flow was then switched to 2% O₂ in He and the samples were heated from room temperature to 800 °C with a temperature ramp of 10 °C min⁻¹. The O₂ consumption and CO₂ output were detected by an on-line quadrupole mass analyzer (Omnistar, Balzers, Vaduz, Liechtenstein).

Scanning electron microscopy (SEM) experiments were performed on a scanning electron microscope (Quanta 200F, FEI Co.). The accelerating voltage was 20 kV.

The crystallinity of the samples was analyzed by powder X-ray diffraction (XRD, Rigaku D/max-γB powder diffractometer, Japan) with Cu Kα radiation at 40 kV and 40 mA in the scan 2θ range of 10–80°.

The BET surface area of the catalysts was calculated from the adsorption isotherms of Nitrogen at 77 K on a volumetric adsorption system (Micromeritics ASAP 2010, American). The samples were degassed at 200 °C before BET measurements.

Mercury intrusion porosimetry (MIP) analysis was carried out with Micromeritics Autopore 9520, USA. Samples were outgassed in vacuum (0.01 torr) for 1 h at 95 °C.

Pulse chemisorption of CO (CO-chemisorption) experiment was performed on Micromeritics AutoChem II 2920 (American). The catalysts were reduced under H₂ (99.99%, 20 ml/min) at 500 °C for 1 h, followed by being purged in He (99.99%, 20 ml/min) at 520 °C for 1 h and cooled down to 50 °C in flowing He (20 ml/min). The 0.1 cm³ pulses of a mixture of 5% CO in He were sent to the reactor and the time between pulses was 4 min.

3. Results and discussion

3.1. Catalytic performance of Pt–Sn–K–Mg/Al₂O₃ and Pt–Sn–K/Al₂O₃ catalysts

In our previous paper [9–11] the effect of Mg addition of the Pt–Sn–K/Al₂O₃ catalysts on the catalyst physicochemical properties has been discussed. The catalysts were characterized by different technologies and results showed that adding Mg to the catalysts (i) slightly decreased the specific surface area of the catalysts and increased the pore volume and size; (ii) moderated the acidity and shifted the strong acidic sites to weak ones; (iii) inhibited the coke deposition on the catalysts; (iv) affected Pt dispersion and the interaction of Pt with the supports and (v) enhanced the mechanical strength and stability under high temperature. In this section, the effect of Mg addition on the catalytic dehydrogenation performance of long chain paraffins will be fully discussed by the life time test on the industrial side fixed bed reactor (lab scale) and industrial plant.

3.1.1. Catalytic performance of Pt–Sn–K–Mg/Al₂O₃ and Pt–Sn–K/Al₂O₃ catalysts in the industrial side fixed bed reactor

The conversion of n-C₁₀–C₁₃ and reaction temperature as a function of time-on-stream (TOS) during the life time test on the industrial side fixed bed reactor are depicted in Fig. 1. It can be seen that in the initial stage, the two catalysts exhibited almost same catalytic conversion (13.5%) when the dehydrogenation reaction started at 460 °C. This can be directly correlated to the same Pt dispersion of the two catalysts which was shown by CO pulse chemisorption of 70% for Pt–Sn–K–Mg/Al₂O₃ catalysts and 67% for Pt–Sn–K/Al₂O₃ catalysts. With the reaction continuously proceeding, the dehydrogenation catalysts were gradually deactivated. Temperature increase was often resorted to whenever the conversion fell below the desired level [12]. Comparatively, the temperature increasing frequency over Pt–Sn–K/Al₂O₃ catalysts was greatly faster than that over Pt–Sn–K–Mg/Al₂O₃ catalysts. After 800 h, the temperature over Pt–Sn–K/Al₂O₃ catalysts quickly reached 500 °C, and the drop of the conversion can be seen obviously when the temperature was kept constantly afterward. Over Pt–Sn–K–Mg/Al₂O₃ catalysts, the conversion was quite stable till 1650 h with the temperature being slowly ramped to 495 °C. Coke deposition has been considered as the main issue of the catalyst deactivation [13]. TG test results indicated that the coke formed on the spent Pt–Sn–K–Mg/Al₂O₃ and Pt–Sn–K/Al₂O₃ catalysts was 3.8% and 4.5%, over which the mean conversion was 14.2% and 12.5%. The difference of the coke formation is related to the acidity of the catalysts. Previous results have shown that Mg addition greatly reduced the acidity of the catalysts [10] which can also affect the production selectivity. The mono-olefin selectivity, TNO and di-olefin formation during the life time test on the industrial side fixed bed reactor are depicted in Fig. 2. Mg addition increased the selectivity to mono-olefins slightly but to normal olefins markedly, especially when the catalysts was run at high temperature. The di-olefin formation can be hydrogenated in the next 'DEFINE' process in PACOL plant. It can be somehow summarized that Pt–Sn–K–Mg/Al₂O₃ catalysts showed both higher paraffin conversion and higher mono-olefin selectivity than those of Pt–Sn–K/Al₂O₃ catalysts during the life-time test in the industrial side lab scale reactor.

3.1.2. Catalytic performance of Pt–Sn–K–Mg/Al₂O₃ and Pt–Sn–K/Al₂O₃ catalysts in the industrial PACOL plant

The two catalysts were further tested in the industrial PACOL dehydrogenation plant. The daily industrial run data (temperature, conversion, selectivity, paraffin and benzene consumption, LAB

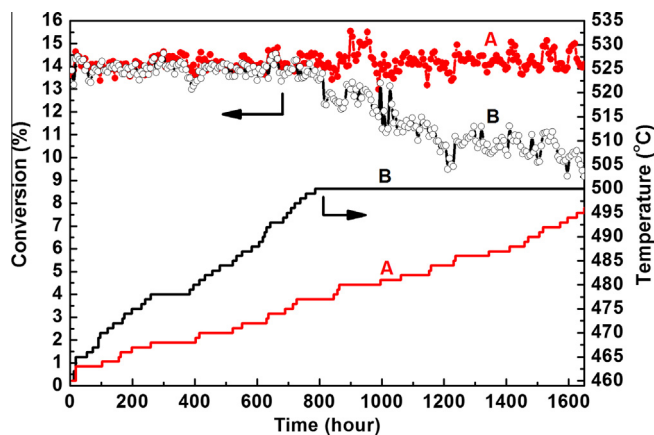


Fig. 1. Dependence of the conversion of n-C₁₀–C₁₃ and the reaction temperature on the reaction time during the industrial side life time test of (A) Pt–Sn–K–Mg/Al₂O₃ and (B) Pt–Sn–K/Al₂O₃ catalysts.

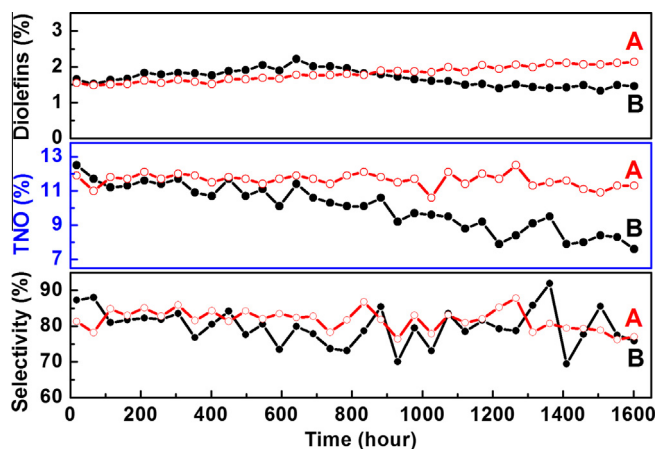


Fig. 2. Dependence of the mono-olefin selectivity, TNO of the products and di-olefin formation on the reaction time during the industrial side life time test of (A) Pt-Sn-K-Mg/Al₂O₃ and (B) Pt-Sn-K/Al₂O₃ catalysts.

and HAB output) over the two catalysts are depicted in Fig. 3. The statistical data are listed in Table 1. The reaction conditions of the two catalysts were almost same; the initial reaction temperature

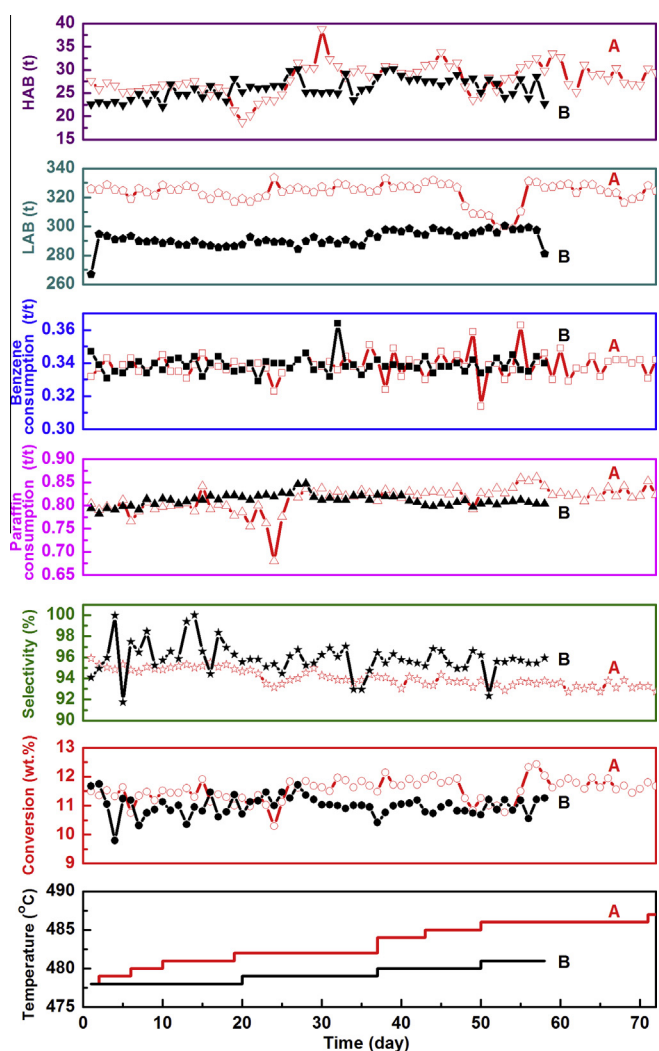


Fig. 3. Dependence of the reaction temperature, conversion of n-C₁₀–C₁₃, mono-olefin selectivity, paraffin consumption, benzene consumption, daily output of LAB and HAB on the reaction time during the industrial run of (A) Pt-Sn-K-Mg/Al₂O₃ and (B) Pt-Sn-K/Al₂O₃ catalysts.

was 478 °C and the pressure is 0.15 MPa. But as compared with Pt-Sn-K/Al₂O₃ catalysts, the lifetime of Pt-Sn-K-Mg/Al₂O₃ catalysts was longer and the ending temperature was higher. The reaction over Pt-Sn-K-Mg/Al₂O₃ catalysts in the higher temperature zone was prolonged, which indicated that the activity and stability of Pt-Sn-K-Mg/Al₂O₃ catalysts was better than those of Pt-Sn-K/Al₂O₃ catalysts. The output data of alkylbenzene showed that the daily output of LAB and HAB over Pt-Sn-K-Mg/Al₂O₃ catalysts were 9.91 tons and 2.18 tons higher than those over Pt-Sn-K/Al₂O₃ catalysts. And the increased percentage of LAB and HAB were 3.35% and 8.38%. It can also be found from the data of the paraffin and benzene consumption showed in Table 1 that the paraffin consumption per ton LAB of Pt-Sn-K-Mg/Al₂O₃ catalysts was 0.001 higher than that of Pt-Sn-K/Al₂O₃ catalysts, which is due to the more production of the HAB. And the paraffin consumption per ton LAB and HAB of Pt-Sn-K-Mg/Al₂O₃ catalysts was 0.001 lower than that of Pt-Sn-K/Al₂O₃ catalysts. The benzene consumption per ton LAB of the two catalysts were same, while the benzene consumption per ton LAB and HAB of Pt-Sn-K-Mg/Al₂O₃ catalysts was 0.001 lower than that of Pt-Sn-K/Al₂O₃ catalysts. The average conversion of Pt-Sn-K-Mg/Al₂O₃ catalysts was 0.43% higher than that of Pt-Sn-K/Al₂O₃ catalysts. The selectivity of Pt-Sn-K-Mg/Al₂O₃ catalysts was 0.81% lower than that of Pt-Sn-K/Al₂O₃ catalysts, which may be affected by more production of the HAB and caused by the high operation temperature. But from the other parameter – paraffin consumption, the selectivity of Pt-Sn-K-Mg/Al₂O₃ catalysts was acceptable. During the whole lifetime of the catalysts, the total output of LAB and HAB over Pt-Sn-K-Mg/Al₂O₃ catalysts was 27% and 34% higher than those over Pt-Sn-K/Al₂O₃ catalysts. The calculated catalyst consumption of Pt-Sn-K-Mg/Al₂O₃ catalysts was 21% lower than that of Pt-Sn-K/Al₂O₃ catalysts. The catalyst lifetime, alkylbenzene output and catalyst consumption indicated that the development of Pt-Sn-K-Mg/Al₂O₃ catalysts was a big breakthrough of Pt-Sn-K/Al₂O₃ catalysts.

3.2. Characterization of the fresh and deactivated Pt-Sn-K-Mg/Al₂O₃ catalysts

As was shown and discussed above, the lifetime of the industrial dehydrogenation catalysts was relatively short. In industrial, the spent catalysts deactivated by coking need be unloaded followed by being discharged after the recovery of Pt, which is inconvenient, noneconomic and environmentally contaminated. Thus it is very important to understand the catalyst deactivation

Table 1

The industrial data of Pt-Sn-K-Mg/Al₂O₃ and Pt-Sn-K/Al₂O₃ catalysts.

	Pt-Sn-K/ Al ₂ O ₃	Pt-Sn-K-Mg/ Al ₂ O ₃
Run duration (days)	58	72
Reaction temperature (°C)	478–481	478–490
Reaction pressure (MPa)	0.15	0.15
Ratio of H ₂ to paraffins (mol/mol)	5.4	5.3
LHSV (h ⁻¹)	20.5	20.6
LAB output	(ton) (ton/day)	17,137 295.5
HAB output	(ton) (ton/day)	1509 26.0
LAB + HAB (ton/day)		321.5
Paraffin consumption (t/t)	LAB	0.811
	LAB + HAB	0.745
Benzene consumption (t/t)	LAB	0.339
	LAB + HAB	0.311
Conversion (%)		11.1
Selectivity (%)		94.9
Life time (ton LAB/ton catalysts)		8.5
Catalyst consumption (ton catalysts/ton LAB)		0.118
		0.093

characteristics. The chemistry and structural characterization of the coke deposits on the catalysts after industrial dehydrogenation of $n\text{-C}_{10}\text{--C}_{13}$ were discussed by Afonso et al. [14] and Sahoo et al. [15] very earlier. In this section, the deactivation of Pt-Sn-K-Mg/ Al_2O_3 catalysts will be comprehended by different characterization techniques.

3.2.1. TG measurement

TG results showed that the coke amount of the industrially deactivated Pt-Sn-K-Mg/ Al_2O_3 catalysts was 3.78 wt.%. Sahoo et al. [15] reported that TG analysis data of the coke on the deactivated long chain paraffin ($n\text{-C}_{10}\text{--C}_{13}$) dehydrogenation catalysts was 7–9 wt.% under the following reaction conditions: the catalysts Pt-Sn-In-Li-Fe/ Al_2O_3 , the days-on-stream (DOS) 30–40 days, the average conversion 10.7–12.3 wt.%, the reaction pressure 0.14 MPa, the reaction temperature range 470–485 °C, the LHSV of the n -paraffins 20 h^{-1} and the mole ratio of hydrogen and paraffins 5.5. Afonso et al. [14] reported that the coke on the deactivated long chain paraffin ($n\text{-C}_{10}\text{--C}_{13}$) dehydrogenation catalysts was 5 wt.% according to the elemental analysis. The reaction conditions were: the catalysts Pt-Sn-Li-Cl/ Al_2O_3 , the DOS 30 days, the average conversion 8 wt.%, the reaction pressure 0.25 MPa, the reaction temperature range 460–480 °C, the LHSV of the n -paraffins 15 h^{-1} and the mole ratio of hydrogen and paraffins 8. It is apparent that the dehydrogenation operation conditions affect coke deposition on the catalysts. Further the coke deposition amount of the deactivated catalysts in this paper is somewhat small although the catalyst life and catalytic conversion are comparatively high. The character of the catalyst itself is a vital factor for the coke deposition on the dehydrogenation catalysts.

3.2.2. Elemental analysis

The elemental analysis data of the deactivated Pt-Sn-K-Mg/ Al_2O_3 catalysts showed that H/C mole ratio of the coke on the deactivated catalysts was 1.19, which was greatly higher than that of the coke on the deactivated catalysts (0.86) which was successively run in the dehydrogenation of $n\text{-C}_{16}\text{--C}_{19}$ for only 40 days [13]. Thus it can be deduced here that with the increase of carbon number of the influent paraffins, the degree of polymerization and graphitization of the coke deposited on the deactivated catalysts was getting higher.

3.2.3. UV Raman spectra analysis

The UV Raman spectra of the deactivated Pt-Sn-K-Mg/ Al_2O_3 catalysts are shown in Fig. 4. Several Raman bands appeared at 1390, 1505, 1605 and 1720 cm^{-1} in Fig. 4. Generally, the bands at 1390 and 1605 cm^{-1} are assigned to the D (distorted) band and G (graphite) band. These two peaks are considered to be

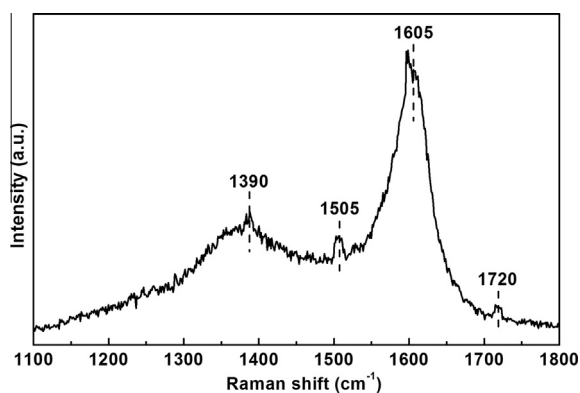


Fig. 4. UV Raman spectra of the deactivated Pt-Sn-K-Mg/ Al_2O_3 catalysts.

disordered, amorphous and graphite-like carbon species [16]. Both bands were relatively broad which indicates that the coke was highly inhomogeneous in nature [17]. Sahoo et al. [15] and Afonso et al. [14] divided the coke into soluble and insoluble coke species by the extraction treatment of the deactivated long-chain-paraffin dehydrogenation catalysts in a Soxhlet apparatus. By combination of different analytical techniques such as Gas Chromatography-Mass Spectrometry (GC-MS), High Performance Liquid Chromatography (HPLC), Infrared Absorption Spectroscopy (IR) and ^{13}C solid-state nuclear magnetic resonance (NMR), they reported that the H/C mole ratio of the soluble coke was far higher than that of the insoluble coke. It was also reported that some of the soluble coke was aliphatic paraffins and olefins with longer chain length ($>\text{C}_{15}$), while most of the insoluble coke was polyaromatics such as alkylbenzenes, alkyl-naphthalenes, phenanthrene, triphenylene, chrysene, pyrene and coronene. And the predominant insoluble coke was polyaromatic in structure. Thus, it can be deduced that the coke on the deactivated long chain paraffin dehydrogenation catalysts is the deep-dehydrogenated carbonaceous compounds, which includes longer chain paraffins, conjugated olefinic species and polycyclic aromatic hydrocarbons (PAHs).

3.2.4. TPO analysis

In terms of location of coke deposits on the catalyst surface, the results of TPO analysis seem to be of special reference significance in distinguishing between coke deposited on the metallic surface and on the support. The deactivated Pt-Sn-K-Mg/ Al_2O_3 catalysts were then subjected to TPO analysis and the TPO profiles are given in Fig. 5. The presence of two distinct peaks with the maximum temperature at about 430 °C and 500 °C for the industrially deactivated catalysts, which indicated the burning of two type of coke with different degrees of graphitization, was similar with the reports in [14,18–20]. The CO_2 formation curve was multi-peak fitted and the fitted peaks are dotted in Fig. 5. It is generally accepted that Peak I in the lower temperature region is attributed to the burning of the coke deposited on or in contact with the metal. In this oxidation zone, the H/C mole ratio of the coke is relatively high [14], and the coke is existing in a less organized and amorphous form [21]. Peak II in the higher temperature region is ascribed as the burning of the coke on the support, which is more polymerized, poorer in hydrogen [22] and more graphitic-like coke [23].

3.2.5. SEM imaging and XRD spectra

The morphology of the coke on the deactivated Pt-Sn-K-Mg/ Al_2O_3 catalysts was characterized by SEM. Since the deactivated catalysts are visually black in color, the images observed in the SEM can be regarded as the morphology of the coke deposited on

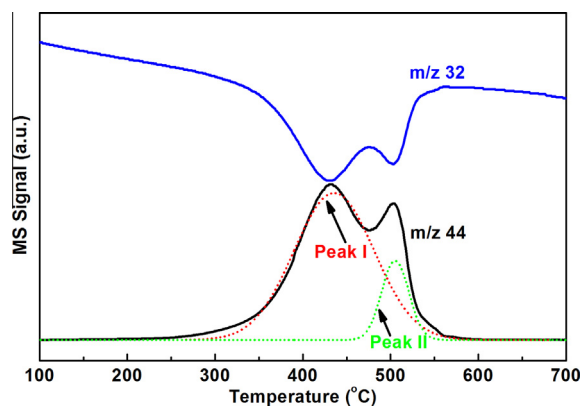


Fig. 5. TPO profiles of the deactivated Pt-Sn-K-Mg/ Al_2O_3 catalysts.

the deactivated catalysts [24]. The SEM images are presented in Fig. 6. For comparison, the SEM images of alumina supports and the fresh Pt–Sn–K–Mg/Al₂O₃ catalysts are also shown in Fig. 6. It can be observed from Fig. 4C and D that the coke on the deactivated catalysts is large flocculent structure. The XRD patterns of the fresh and deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts are shown in Fig. 7. The diffraction peaks of the fresh and deactivated catalysts are similar and the patterns only show the diffraction peaks corresponding to the alumina supports. XRD results indicated that the crystal structure of the catalysts was not destroyed during the dehydrogenation process. The SEM morphology of the coke could be related to the amorphous coke structure. Zhang et al. [23,25] successfully observed the graphitic layer of coke after the partial oxidation of the coke on the deactivated long chain paraffin dehydrogenation catalysts. Thus the coke on the deactivated catalysts is amorphous and graphitized structure, and the graphitization degree is less as compared to the coke on the deactivated catalysts after the dehydrogenation of higher paraffin (n-C₁₆–C₁₉) [13].

3.2.6. BET measurements and MIP analysis

The BET surface area of the fresh and deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts is 149.0 m² g⁻¹ and 139.4 m² g⁻¹. The surface area of catalysts was slightly decreased after the coke deposition. Nitrogen adsorption/desorption isotherms of the fresh and deactivated catalysts are shown in Fig. 8 and type IV [26]. The hysteresis loop of fresh catalysts (Fig. 8A) was type of H1 which was often associated with mesoporous or macroporous materials that have cylindrical pore structures [27]. The BET isotherms and hysteresis loop of the deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts (Fig. 8B) were almost same with those of the fresh catalysts. The Barrett–Joyner–Halenda (BJH) pore size distribution (PSD) of the fresh and deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts calculated from the desorption branches of the isotherms according to the BJH method are inset in Fig. 8. It can be found that the PSD of the deactivated catalysts was slightly shifted to lower pore diameters as compared with that of the fresh catalysts, and some of the new pores with the diameter of 3–5 nm were formed. Since there were some pores bigger than 100 nm in the long chain paraffin dehydrogenation catalysts [12], BET analysis was insufficient. MIP analysis was also performed and the MIP PSD curves of the catalysts are depicted in Fig. 9. The PSD of the fresh Pt–Sn–K–Mg/Al₂O₃ catalysts (Fig. 9A) exhibits an obvious bimodal distribution with one centered in the

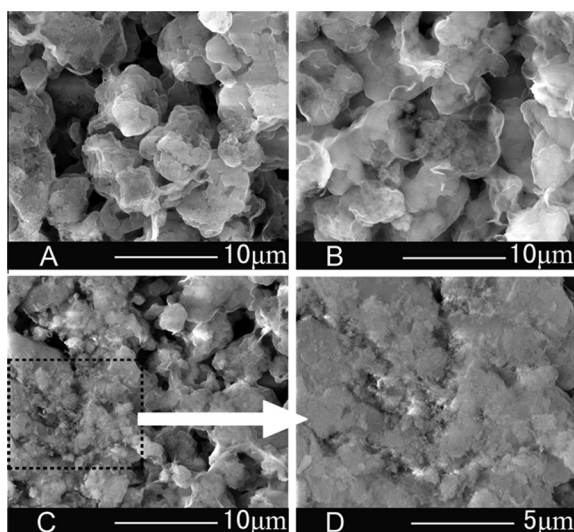


Fig. 6. SEM morphologies of (A) Al₂O₃, (B) fresh catalysts, (C) and (D) deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts.

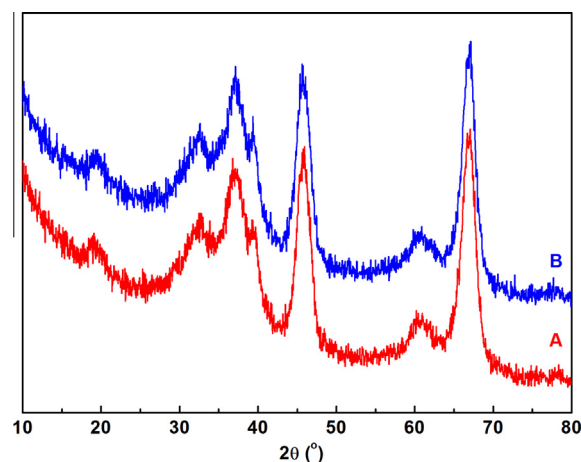


Fig. 7. XRD patterns of (A) fresh and (B) deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts.

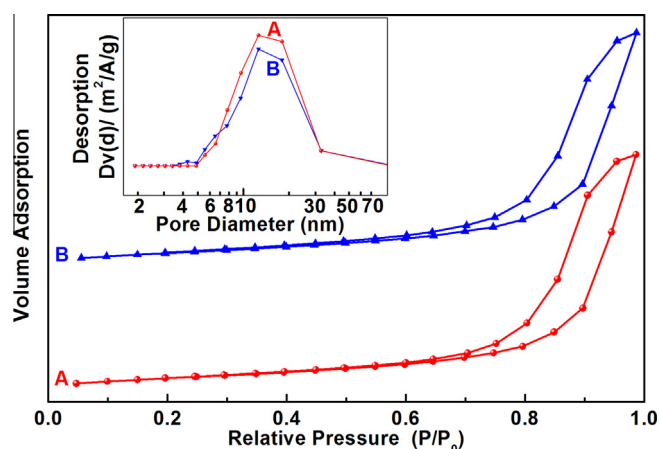


Fig. 8. Nitrogen adsorption/desorption isotherms and BJH PSD of (A) fresh and (B) deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts.

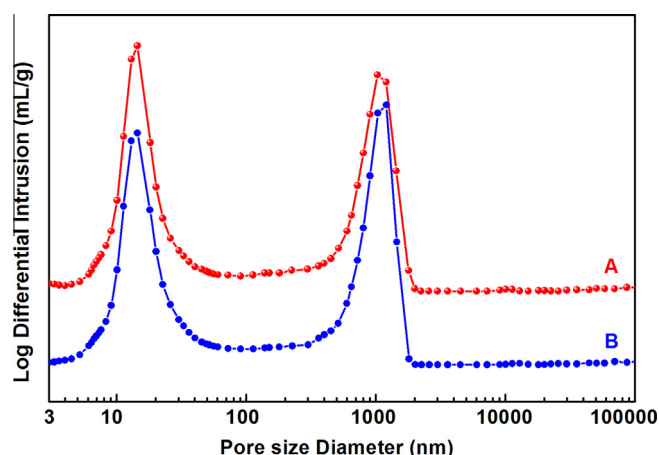


Fig. 9. MIP PSD of (A) fresh and (B) deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts.

mesoporous range (14.6 nm) and the other centered in the macroporous range (1300 nm). The total pore volume of the fresh and deactivated Pt–Sn–K–Mg/Al₂O₃ catalysts analyzed by MIP method is 1.64 cm³ g⁻¹ and 1.52 cm³ g⁻¹. After the coke deposition, the total pore volume of the deactivated catalysts is decreased slightly and the PSD is appreciably shifted to smaller pore diameters. BET

measurements and MIP analysis indicated that no or slight changes in the pore structure of the catalysts were taken place during the long-term run of the dehydrogenation of n-C₁₀–C₁₃. The coke does not fill the pores completely; it slightly decreases the surface area and the total pore volume of the catalysts, and narrows the pore size to smaller values.

3.2.7. CO pulse chemisorption

The Pt dispersion of the fresh catalysts was 70%. After the long term operation of the dehydrogenation of n-C₁₀–C₁₃, the Pt dispersion of the deactivated catalysts was 47.6%. As compared to the dehydrogenation of higher paraffins (n-C₁₆–C₁₉) [13], it is more difficult to cause the deactivation of the active sites by the coke deposition during the dehydrogenation of shorter chain normal paraffins. The decrease of Pt dispersion of the deactivated catalysts might be caused by the coke deposition covering the Pt surface. Pt sintering might be another factor which was reported in other literature [28] and its effect cannot be excluded completely here.

4. Conclusions

Pt–Sn–K–Mg/Al₂O₃ catalysts were successfully developed for the dehydrogenation of long chain paraffins (n-C₁₀–C₁₃). Compared with Pt–Sn–K/Al₂O₃ catalysts, Pt–Sn–K–Mg/Al₂O₃ catalysts showed a big breakthrough of the dehydrogenation performance: the catalysts continuously run 72 days in the PACOL plant with the average conversion of n-C₁₀–C₁₃ of 11.6 wt.%. The output of linear alkylbenzene (LAB) was 21,822 tons (303.1 ton LAB/day) and the output of heavy alkylbenzene (HAB) was 2,020 tons (28.1 ton HAB/day). The paraffin consumption was 0.81 ton/ton LAB and the benzene consumption was 0.34 ton/ton LAB. After the continuous 72-day run, Pt–Sn–K–Mg/Al₂O₃ catalysts were deactivated by the coke deposition with the amount of 3.78 wt.% and the H/C mole ratio of 1.19. The coke was deep dehydrogenated carbonaceous compounds in amorphous and graphitized structure. Some of the coke covered parts of Pt surface which resulted in the 30% decrease of Pt dispersion, and other of the coke deposited on the support surface which decreased the BET surface area and PSD slightly. While the crystalline structure of the catalysts was remained.

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