Catalysis Letters 12 (1992) 267–276

Surface structure and catalytic performance of supported PtSn catalysts

Yang Weishen, Lin Liwu, Fan Yining and Zang Jingling

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian, P.R. China

The valence states of tin in supported PtSn catalysts after reduction were tracked by in situ Mössbauer spectroscopy. Combined with catalytic evaluation, it is suggested that only when tin is in oxidative states, the catalytic performance can be greatly improved. The changes of surface structure of $PtSn/Al_2O_3$ during repeated coking-regeneration-reduction (CRR) cycles were also studied.

Keywords: Supported PtSn catalysts; dehydrogenation; regeneration; Mössbauer spectroscopy

1. Introduction

Supported bimetallic catalysts consisting of an active metal (Pt, Rh, or Ru) and a second component (Re, Ge, Sn, Fe, Mn et al.) not only have a superior catalytic performance for hydrocarbon conversions [1,2] but also exhibit a high selectivity for F-T synthesis to oxygenates [3]. In order to elucidate the role of the second component, extensive fundamental work has been devoted to correlating the catalytic performance with the oxidation states of the second component [4] and the surface structure of the catalyst [5–7].

In early studies, due to the strong influence of catalytic theory by alloy [8] and the limitations of characterization techniques, the states of two highly dispersed catalytic components were usually considered to be presented as an alloy [1] or bimetallic cluster [6]. Recently, with the development of highly sensitive, and in situ physical techniques for characterization of catalysts, it has been reported that, for alumina supported bimetallic catalysts, due to the strong interaction between the catalytic components and support, only one of the components is in the metallic state, while the majority still remains in the oxidative states after reduction. For example, the components of Re, Ge and Sn in $PtRe/Al_2O_3$ [9,10], $PtGe/Al_2O_3$ [11], and $PtSn/Al_2O_3$ [12–15] could not be reduced to zero valence state after reduction at elevated temperature (< 823 K).

$PtSn/Al_2O_3$ catalysts have been widely used in the processes of naphtha reforming and normal paraffin dehydrogenation, and have been extensively studied by many research groups [12–19] by using different physical and/or chemical techniques, but the oxidation states of tin and the possibility of alloy formation between platinum and tin is still a point of controversy and seems to depend on the method of preparation, the nature of supports, and the loading of catalytic components. For example, some authors stressed that tin was not reduced to the zero valence state [12–15] while others emphasized that Sn^0 was formed and that it alloyed with Pt [16–19].

In this paper, in situ Mössbauer spectroscopy was used to explore the oxidation states of tin in supported PtSn catalysts after reduction, and the changes of surface structure of $PtSn/Al_2O_3$ catalyst after heat treatment. The catalytic dehydrogenation of normal light paraffins was carried out in a flow microreactor for correlating the catalytic performance and surface structure of supported PtSn system.

2. Experimental

2.1. CATALYST

Supported PtSn catalysts were prepared by coimpregnating the supports (as shown in table 1) with alcohol solutions of H_2PtCl_6 and $SnCl_2$. After impregnation, all the catalysts were dried for 4 h at 333 K, and 393 K separately, then the catalysts except PtSn/AC were calcined at 753 K for 4 h in air and in steam for chloride removal separately. For all the catalysts, the nominal platinum loading was held constant at 0.35 wt%, and the tin loading was varied from 0.21 wt% to 2.1 wt%. The chloride ions in the catalysts except PtSn/AC was less than 0.05 wt%.

2.2. MÖSSBAUER SPECTROSCOPY

Mössbauer spectra were recorded with a Cryophysics model MS-121 microprocessor-controlled Mössbauer spectrometer. γ-ray from 10 mCi $Ca^{119}SnO_3$

Table 1
Properties of supports

Supports	Specific surface area (m^2/g)	Packed density (g/cm^3)
AC	970	0.8
SiO_2	278	0.41
MgO	25	0.53
Al_2O_3	130–150	0.28–0.34

source was used and filtered by 0.05 mm thickness of Pd film. The spectrum of α-Fe was used to calibrate the velocity. All spectra were computer fitted. The chemical isomer shift (*IS*) data are quoted relative to SnO_2.

2.3. REACTION

All reactions were carried out in a flow microreactor with catalyst loading of 0.2 g at conditions of $GHSV = 2000\ h^{-1}$, 853 K, 40 KPa, and $N_2/C_3H_8 = 2$. Reaction products were analyzed by an on line gas chromatograph.

3. Results and discussion

3.1. STATES OF TIN IN SUPPORTED PtSn CATALYSTS AND ITS EFFECT ON CATALYTIC PERFORMANCE

PtSn catalyst is one of the most important supported bimetallic catalysts in the petrochemical industry. In this section, four types of supports (active carbon AC, SiO_2, MgO, Al_2O_3) with same loading of platinum and tin were studied. In situ Mössbauer spectroscopy was used to monitor the valence changes of tin in the catalysts before and after reduction. A flow microreactor was employed to evaluate the performance of the catalysts for dehydrogenation of normal light paraffins.

The standard Mössbauer parameters of some tin compounds obtained at 298 K are listed in table 2 for a comparison with flowing experimental data. According to table 2, the *IS* is the most important Mössbauer parameter to monitor the valence changes of tin in the catalysts. For example, the *IS* values are usually less than 1 mm/s for Sn^{4+} species, larger than 2.6 mm/s for Sn^{2+} species, about 2.5 mm/s for metallic tin, and between 1 mm/s to 2.5 mm/s for PtSn alloys.

Fig. 1 shows the Mössbauer spectra recorded at 298 K from the supported PtSn catalysts before and after reduction in flowing H_2 (50 ml/min) at 753 K for

Table 2
Mössbauer parameters of standards

Standards	*IS* * (mm/s)	*QS* (mm/s)	Wdth (mm/s)
SnO_2	0.00	0.64	1.50
PtSn	1.84	0.00	0.92
Sn	2.53	0.00	0.83
SnO	2.64	1.32	1.15
$SnCl_2$	4.08	0.00	1.31

* With respect to SnO_2.

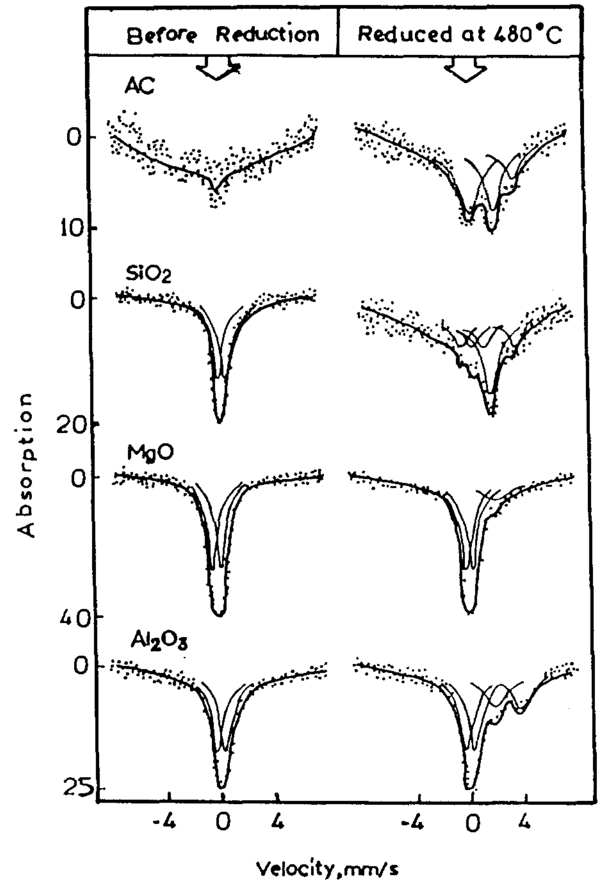

Fig. 1. Tin-119 Mössbauer spectroscopy of supported PtSn catalysts recorded at 298 K.

1 h, and their computer fitting parameters are reported in table 3. For the unreduced catalysts, it is obvious that the valence states of tin in the catalysts are similar, i.e. SnO_2-like compound, but the Mössbauer absorption intensities are quite different from each other. Since all of the catalysts have a same loading of tin (2.1 wt%), and the Mössbauer spectra were recorded with the same duration (24 h), it is pertinent to conclude that the Mössbauer absorption intensities of SnO_2-like compound on the different supports can reflect the strength of an interaction between Sn^{4+} and the supports, and the higher the Mössbauer absorption intensities, the stronger interaction between Sn^{4+} and the support [20]. From the Mössbauer spectra of the oxidized samples as shown in fig. 1 and the data in table 3, it is interesting to note that for the oxide supports the strength of the interaction between Sn^{4+} and the supports decreased with the increase of the reducibility of Sn^{4+} on supports, i.e.

$$\begin{aligned} &\text{PtSn/MgO}(85\%\ Sn^{4+}) > \text{PtSn/Al}_2\text{O}_3\ (68.4\%\ Sn^{4+}) \\ &\qquad > \text{PtSn/SiO}_2\ (23.6\%\ Sn^{4+}). \end{aligned}$$

Table 3
Mössbauer parameters of supported PtSn catalysts on different supports after reduction at 480°C for 1 h

Catalysts	*IS* * (mm/s)	*QS* (mm/s)	Wdth (mm/s)	States of tin	Contribution of spectra (%)
PtSn/AC	0.72	0.00	2.21	$SnCl_4$	56.8
	2.53	0.00	1.21	Sn^0	32.4
	4.05	0.00	0.99	$SnCl_2$	10.7
$PtSn/SiO_2$	0.05	0.77	0.90	SnO_2	23.6
	1.94	0.00	1.15	SnPt	52.1
	2.61	2.43	0.86	SnO	24.2
PtSn/MgO	−0.01	0.50	0.94	SnO_2	85.2
	2.07	0.00	1.88	SnPt	14.8
$PtSn/Al_2O_3$	−0.04	0.65	1.02	SnO_2	68.4
	2.83	1.88	1.22	SnO	31.6

* With respect to SnO_2.

For the reduced catalysts, it can be seen from table 3 that a substantial amount of metallic tin with $IS = 2.53$ mm/s and $QS = 0$ appeared on the active carbon (AC) supported PtSn catalyst after reduction at 753 K for 1 h. According to table 2, it is assigned to β-phase-like tin, and considered to have a very weak interaction with platinum due to the high surface area (970 m^2) and highly heterogeneous characteristic of AC support. As for the $PtSn/SiO_2$ catalyst, the SnO_2-like species on SiO_2 is very easy to be reduced to zero valence tin (52%) with $IS = 1.94$ mm/s and $QS = 0$. Compared with table 2, the zero valence tin, in this case, is assigned to PtSn alloy. This result implies that the interactions between tin and platinum are more significant than the tin oxides with SiO_2 support. After reduction of PtSn/MgO catalyst, only a small amount of SnO_2-like species on MgO is reduced to metallic tin which alloyed with platinum ($IS = 2.06$ mm/s, $QS = 0$ mm/s), the remainder of tin is still in Sn^{4+} state. It is also confirmed that there exists a very strong interaction between Sn^{4+} and MgO support, as mentioned above. When $PtSn/Al_2O_3$ catalyst was reduced at same conditions, no metallic tin can be detected by Mössbauer spectroscopy due to a very strong stabilization of Sn^{2+} by Al_2O_3 support [12–15]. It can be concluded that the nature of supports plays a significant role in controlling the type of interactions that occur between tin and platinum and between tin and the support.

Fig. 2 shows the reaction results of propane dehydrogenation on supported PtSn catalysts with different Sn/Pt atomic ratios. It is observed that the catalytic activities of four kinds of PtSn catalysts with different supports could be arranged in the following order:

$$PtSn/Al_2O_3 > PtSn/MgO > PtSn/AC,\ PtSn/SiO_2.$$

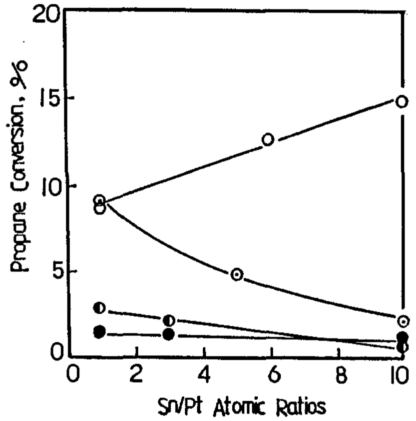

Fig. 2. Dehydrogenation of propane on supported PtSn catalysts with different Sn/Pt atomic ratios ○ $PtSn/Al_2O_3$; ⊙ PtSn/MgO; ◐ $PtSn/SiO_2$; ● PtSn/AC.

It is also observed that with the increasing of Sn/Pt atomic ratios, the catalytic activity was nearly unchanged for PtSn/AC catalysts, decreased for $PtSn/SiO_2$ and PtSn/MgO catalysts, and enhanced significantly for $PtSn/Al_2O_3$ catalysts. Correlating the activity with the results of Mössbauer spectroscopy, we can draw some conclusions as follows: unreduced tin oxides on alumina support exhibit a beneficial effect on the catalytic performance of $PtSn/Al_2O_3$ catalyst; while reduced metallic tin on the surface of SiO_2 and MgO supports inhibits the catalytic activities of the catalysts through the formation of PtSn alloys on which the inactive metallic tin is surface enriched [4]; but the metallic tin formed on AC support has little influence on the catalytic activity of PtSn/AC catalyst because the formed metallic tin is free from platinum and support.

3.2. CHANGES OF SURFACE STRUCTURE OF $PtSn/Al_2O_3$ CATALYST AND ITS EFFECT ON CATALYTIC PERFORMANCE

In order to clarify the roles of Sn^{2+} and Sn^0 alloyed with Pt in the $PtSn/Al_2O_3$ catalyst the changes of surface structure and catalytic performance of the $PtSn/Al_2O_3$ after repeated coking-regeneration-reduction (CRR) cycles were studied via in situ Mössbauer spectroscopy, H_2 chemisorption technique and catalytic evaluation. In our previous papers, it has been reported that the substable bulk SnO by disproportionation, at high temperature, is easy to form SnO_2 and Sn^0 [12], and the Sn^0 produced inhibits the catalytic activity of supported PtSn catalysts through the enrichment of inactive metallic tin on the catalytic surface [4,21]. Therefore, the stabilization of Sn^{2+} in the supported PtSn catalysts is very important for controlling the catalytic stability. Lin et al. [12] and many other researchers [13–15] noted that $PtSn/Al_2O_3$ after reduction, the formed Sn^{2+} can strongly interact with the surface of Al_2O_3 to form a layer

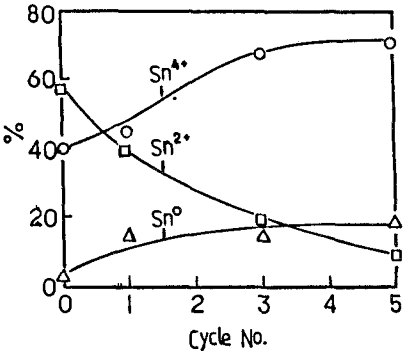

Fig. 3. Changes of valence states of tin in $PtSn/Al_2O_3$ catalyst with CRR cycles.

of stable tin(II)-aluminate. The interaction of Pt with this Sn^{2+}-Al_2O_3 layer enhanced the stability of the catalyst for hydrocarbon conversions [2].

Fig. 3 shows the changes of valence states of tin in $PtSn/Al_2O_3$ catalyst with the proceeding of CRR cycles. The reduction procedure was performed in flowing H_2 (50 ml/min) at 853 K. It can be seen that Sn^{2+} species, with the increasing of CRR cycles, is decreased; while Sn^{4+} and Sn^0 (alloyed with Pt) species are increased simultaneously. These results suggest that the stable tin(II)-aluminate layer formed between Sn^{2+} and Al_2O_3 support is gradually destroyed by repeated CRR cycles, and more Sn^{2+} species disproportionate to Sn^{4+} and Sn^0 (alloyed with Pt). The degradation of surface structure of $PtSn/Al_2O_3$ catalyst after CRR cycles is also confirmed by HREM images of $PtSn/Al_2O_3$ catalyst before and after 5 CRR cycles [22]. It is reported that only highly dispersed Pt with crystallite of 20 Å, for fresh $PtSn/Al_2O_3$ catalyst, is found to locate on the top of SnO. SnO_2-Al_2O_3 matrix; and a large PtSn alloy particle with crystallite of 80 Å, after 5 CRR cycles, is clearly observed. Combining the data of Mössbauer spectroscopy with the results of HREM, we know that the burning of coke located on the interface of Sn^{2+} and Al_2O_3 support during the process of regeneration, may cause a tremendous temperature rise in the local area, and the interaction between Sn^{2+} and Al_2O_3 support would be remarkably weakened. As a result, the Sn^{2+} in the tin(II)-aluminate is easier to disproportionate, at high temperature, to Sn^{4+} bonded to Al_2O_3 support and Sn^0 alloyed with Pt. The destruction of the stable surface structure, i.e. tin(II)-aluminate complex on $PtSn/Al_2O_3$ catalyst, cause the decreasing of H_2 adsorption on Pt and the deactivation of $PtSn/Al_2O_3$ catalyst for dehydrogenation of butane due to the enrichment of inactive metallic tin on the catalytic surface, as shown in fig. 4. Therefore, it is very important to stabilize Sn^{2+} and/or Sn^{4+} in oxidative states in order to prolong the life of $PtSn/Al_2O_3$ catalyst. The work in this respect has been published elsewhere [23].

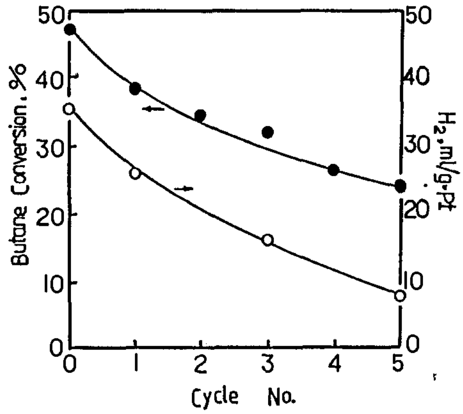

Fig. 4. n-butane conversion and H_2 chemisorption with CRR cycles.

Acknowledgments

We thank Dr. F.J. Berry very much for his help in the determination of the Mössbauer spectroscopic data of PtSn on different supports in Birmingham University, UK.

References

[1] M.E. Kluksdahl, U.S. Patent, 3, 415, 737 (1968).
[2] Lin Liwu, Zang Jingling, Wu Rongan and Jiang Bingnan, in: *Proc. 7th Int. Congr. Catal.*, E_3 (Tokyo, Japan, 1980) 1466.
[3] M. Ichikawa, T. Fukushima and K. Shikakuya, in: *Proc. 8th Int. Congr. Catal.*, Vol. 2 (Dechema Frankfurt, W. Germany, 1984) 69.
[4] Yang Weishen, Wu Rongan and Lin Liwu, Cuihua Xuebao 8 (1987) 345.
[5] H. Verbeek and W.M.H. Sachtler, J. Catal. 42 (1976) 257.
[6] J.H. Sinfelt, *Bimetallic Catalysis* (John-Wiley & Sons Inc., 1983).
[7] S.R. Adkins and B.H. Davis, J. Catal. 87 (1984) 371.
[8] G.M. Schwab, Disc. Faraday Soc. 8 (1950) 166.
[9] O.R. Short, S.M. Halid and J.R. Katzer, J. Catal. 72 (1981) 288.
[10] M.F.L. Johnson and V.M. Leroy, J. Catal. 35 (1974) 434.
[11] R. Bouwman and P. Biloen, J. Catal. 48 (1977) 209.
[12] Yang Weishen, Lin Liwu, PhD Thesis of Dalian Institute of Chemical Physics, Chinese Academy of Sciences 1989.
[13] K. Balakrishnan and J. Shwank, J. Catal. 127 (1991) 287.
[14] R. Burch, J. Catal. 71 (1981) 348.
[15] B.A. Sexton, A.E. Hughes and K. Foger, J. Catal. 88 (1984) 466.
[16] Y.X. Li, K.J. Klabunde and B.H. Davis, J. Catal. 128 (1991) 1.
[17] Zhang Su, Xie Bingyan, Zang Jingling, Wang Guanghou and Zhang Jian, Cuihua Xuebao 1 (1980) 253.
[18] R. Bacaud, P. Bussere and F. Figueras, J. Catal. 69 (1981) 399.
[19] R.M. Dautzenberg, J.N. Helle, P. Biloen and W.M.H. Sachtler, J. Catal. 63 (1980) 119.

[20] D.A. Shirley, M. Kaplam and P. Axel, Phys. Rev. 123 (1961) 816.

[21] Yang Weishen, Wu Rongan and Lin Liwu, Petrochemical Technology (China) 20 (6) (1991) 375.

[22] Fan Yining, Lin Liwu, PhD Thesis of Dalian Institute of Chemical Physics, Chinese Academy of Sciences 1991.

[23] Fan Yining, Xu Zusheng, Zang Jingling and Lin Liwu, in: *Study in Surface Science and Catalysis: Catalyst Deactivation*, eds. J.B. Butt and C.H. Bartholomew (Elsevier, Amsterdam, 1991) 683.