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Influence of Calcium Addition on Catalytic Properties of PtSn/ZSM-5 Catalyst for Propane Dehydrogenation

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Abstract In this work the influence of the Ca addition to PtSn/ZSM-5 catalyst on its performance for propane dehydrogenation was investigated. The catalysts were characterized by X-ray diffraction, BET analysis, TEM, NH_3-TPD, TPO and TG. Results showed that the addition of calcium could not only modify the characteristics and properties of both acid and metal function but also suppress coke deposits on the catalyst. The addition of 0.9 wt% Ca to PtSn/ZSM-5 prompted catalytic activity. However, the incorporation of excessive Ca resulted in catalyst deactivation. TPR results implied that excessive Ca promoted the reduction of oxidized tin species to Sn^0. The Sn^0 probably could interact with Pt to produce a PtSn alloy which led to the diminution of catalytic activity.

Keywords Platinum–tin · Calcium · ZSM-5 · Propane dehydrogenation

1 Introduction

Propylene is one of the most important materials in the modern petrochemical industry, largely used as an important raw material in the production of polypropylene, polyacrylonitrile, acrolein, glycerine, isopropanol, refinery feed stock to improve the octane rating of gasoline [1] and other chemicals. In the last decade, the demand for propylene has increased significantly, outgrowing the quantity that can be mainly produced by the conventional sources, ethane steam crackers and FCCs (fluidized catalytic crackers). The dehydrogenation of propane has been proposed as an alternative to the process. Consequently, the catalytic dehydrogenation of propane has gained considerable interest. Yet catalytic dehydrogenation of propane to propylene shows relevant disadvantage. The transformation of propane into propylene is limited by thermodynamic constraints, because of the strong exothermic character of the reaction for propane. In order to overcome the obstacle of thermodynamic limitation, low pressure and high temperature are needed to obtain a high yield of propylene using platinum [2] or chromium [3] catalysts. Unfortunately, under the severe conditions, the deep side reactions are accelerated. The side reactions to lighter hydrocarbons and coke are favored. Coking leads to catalyst deactivation. Cracking and hydrogenolysis reactions decrease the propylene selectivity. As a consequence, a great deal of work has been carried out aiming to develop catalysts with high catalytic properties.

The platinum–tin catalysts have been widely used in reforming or dehydrogenation processes. The role of the Sn in Pt–Sn catalysts has been extensively investigated in several studies [4–10]. Both of geometric and electronic factors have been proposed to explain the tin modification effect [9, 10]. Bocanegra et al. [11] found that the Sn addition to $Pt/ZnAl_2O_4$ and $Pt/MgAl_2O_4$ catalysts led to an increase of the activity and selectivity in the *n*-butane dehydrogen reaction. Armendariz et al. [12] showed a good selectivity of $PtSn/MgAl_2O_4$ catalysts in the isopentane dehydrogenation to isoamilene. Llorca et al. [13] reported the performance of supported Pt–Sn catalysts in skeletal reaction of *n*-hexane; catalysts containing PtSn alloy were highly stable and selective to dehydrogenated products. However, the platinum–tin catalysts undergo fast

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deactivation on account of the carbon deposits. Thus, the continuous or frequent regeneration treatments are required to maintain activity, which makes energy and capital expensives.

The use of ZSM-5 Zeolite is attractive, because it possesses the specific pore structure and notable "selective shape" properties. Recently, ZSM-5 as a support has been used in the dehydrogenation reactions. Grasselli et al. [14, 15] combined the technologies of catalytic dehydrogenation with selective hydrogen combustion for the total dehydrogenation process on Pt–Sn/ZSM-5 catalyst and got good selectivity. In our previous works [16–20], we studied the effect of promoter, binder and reaction conditions on catalytic performance of PtSnNa/ZSM-5 catalyst in the propane dehydrogenation and found better results.

It is well established that improving catalytic performance and poisoning the acid sites of support can also be achieved by the addition of alkali or alkali earth metals to the catalyst formulation [21–25] for dehydrogenation catalysts. Tu and Chen [24] reported that the initial turnover frequencies were improved by adding alkaline earth metal ions to Cu/SiO_2 catalysts in the ethanol dehydrogenation, and the activity and stability of these systems varied according to the sequence: Mg > Ca > Sr > Ba. This behavior was explained in terms of the increase in the basicity of the alkaline earth metals. Dong et al. [25] investigated the effect of calcium promoter on catalytic properties of bimetallic $PtSn/MgAl_2O_4$ in the propane dehydrogenation diluted with N_2 and H_2O, respectively. Their data indicated that the promotional effect was strongly related to the calcium loading, and when the Ca content reached 0.5 wt%, highest activity and stability were achieved. However, the dispersive status of Ca species on Pt–Sn catalysts supported on different carrier may result in the variant behaviors, which may affect on the catalytic performance significantly.

No literature data have been found on the use of calcium as a promoter for dehydrogenation reaction on the PtSn based catalyst supported on ZSM-5. In principle, calcium should have some similar behaviors as other alkaline metals, but its unique physicochemical and acid–base characteristics may result in different properties as compared to alkali metals. The goal here is to investigate the modifying effect of Ca addition to ZSM-5 supported PtSn catalysts on the physicochemical characteristics and the catalytic behavior in the propane dehydrogenation.

2 Experimental

2.1 Catalyst Preparation

PtSnCa/ZSM-5 catalysts with different Ca contents were prepared by successive impregnation. The powder H-ZSM-5 was impregnated in an aqueous solution of 0.458 M $Ca(NO_3)_2$ at 80 °C for 4 h to obtain 0, 0.9, 1.7 and 2.5 wt% Ca, then dried at 80 °C for 3 h. Afterwards, the samples were impregnated at 80 °C for 4 h in solutions mixture of 0.033 M H_2PtCl_6 and 0.153 M $SnCl_4$. Finally the prepared catalysts were dried at 80 °C for 3 h. The nominal compositions of the each sample were 0.5 wt% for Pt, and 1.0 wt% for Sn, respectively.

Monometallic Pt/ZSM-5, Sn/ZSM and Ca/ZSM-5 catalysts were also prepared as references by impregnation of H-ZSM-5 with the corresponding metallic precursor. The loading of Pt, Sn and Ca were 0.5, 1.0 and 0.9 wt%, respectively.

Afterwards, the prepared samples were fully agglomerated with 5.0 wt% alumina during the process of pelletization. After totally dried, the catalysts were calcined at 500 °C in flowing air for 4 h, then dechlorinated at 500 °C for 4 h in air containing steam and finally reduced in flowing H_2 at 500 °C for 8 h. Catalysts used during this investigation were abbreviated as PtSnCa(x)/ZSM-5, where x represented the weight percentage of Ca in the catalysts (wt%).

2.2 Catalyst Characterization

The BET surface area and pore volume of the catalysts were measured using a Micromeritics ASAP 2000 adsorptive and desorptive apparatus. The samples were pretreated in vacuum at 350 °C for 15 h before the measurement. The specific surface area was obtained using the BET method. The microporous volume was calculated from the *t*-plot method.

X-ray diffraction (XRD) patterns of the different samples were obtained on a XD-3A X-ray powder diffractometer coupled to a copper anode tube. The Cu-Kα radiation was selected with a diffracted beam monochromator. An angular range 2θ from 5° to 40° and long counting times were used to determine the positions of the ZSM-5 peaks.

Transmission electron microscopy (TEM) was carried out on a JEM-2010 at 200 kV. Samples were prepared by grinding, suspending and sonicating them in ethanol and placing a drop of the suspension on a copper grid with a perforated carbon film.

Surface acidity was measured by NH_3-TPD in TP-5000 apparatus at ambient pressure. The sample (150 mg) was preheated at 500 °C for 1 h, and then cooled to room temperature in flowing He. At this temperature, sufficient pulses of NH_3 were injected until adsorption saturation, TPD was carried out from 100 to 550 °C with a heating rate of 10 °C/min and with helium (30 ml/min) as the carrier gas.

Temperature-programmed reduction (TPR) was measured in the TP-5000 apparatus. Prior to the TPR experiments, 0.15 g catalyst was dried in flowing N_2 at 100 °C for 1 h. 5% H_2/N_2 was used as the reducing gas at a flow rate of 40 ml/min. The rate of temperature rise was 10 °C/min up to 800 °C.

Temperature-programmed oxidation (TPO) was also measured in the TP-5000 apparatus. About 0.05 g of coked sample was placed in a quartz reactor at room temperature, and then heated up to 700 °C at a rate of 10 °C/min in a 5% O_2/He mixture (50 ml/min).

The amount of coke deposited on the catalyst was measured by using a LCT thermogravimetric analyzer (Beijing optical instrument factory, China).The samples, ca. 15 mg, were placed in a Pt cell and heated from room temperature to 800 °C at a heating rate of 10 °C/min with a gas feed (air) of 50 ml/min.

2.3 Catalytic Activity

The activity of the catalyst samples for dehydrogenation of propane was tested in a stainless fixed bed tubular reactor, at 590 °C and atmospheric pressure using a catalyst charge of 1.5 g. The propane weight hourly space velocity (WHSV) was 3 h^{-1} and the mole ratio of H_2/C_3H_8 was 0.25. The reaction products were analyzed with an online GC-14C gas chromatograph equipped with an activated alumina packed column and a flame ionization detector (FID). The conversion of propane and selectivity were expressed as mole percent and were calculated as follows:

$$\text{conversion(mol\%)} = \frac{\text{moles of } C_3 \text{ reacted}}{\text{moles of } C_3 \text{ fed}} \times 100;$$

$$\text{selectivity(mol\%)} = \frac{\text{moles of product } i \text{ formed}}{\text{moles of } C_3 \text{ fed}} \times \frac{N_i}{N_{C_3}} \times 100,$$

where i = propylene, ethylene, ethane, and methane and N_i and N_{C_3} are number of carbon atoms in the product and propane, respectively.

3 Result and Discussion

3.1 Catalysts Characterization

XRD patterns of the investigated catalysts are shown in Fig. 1. It can be observed that the XRD patterns between the pure ZSM-5 and the different catalysts are very similar, which implies that the zeolite structure is preserved very well during the process of impregnation. Based on our previous work [8], the platinum species were well dispersed on the external surface of the catalyst, and part of tin species could enter the main channels of ZSM-5 zeolite. The peaks of Platinum and tin are not observed due to the low metals concentration. Taking into account that the average diameter of Ca^{2+} (0.204 nm) is less than that of the ZSM-5 average mouth, therefore part of Ca^{2+} cations may enter the main channels of ZSM-5 zeolite during the process of impregnation. Moreover, XRD patterns did not show any characteristic peak of calcium-related crystalline phases, indicating that they were highly dispersed on the external surface of ZSM-5 or were incorporated in the channels of ZSM-5 zeolite as well. This shows that calcium additives have no effect on the phase compositions of support. It must be noted that when the calcium content was increased, the intensities of corresponding peaks of angle $2\theta = 23 - 24°$ decreased slowly, thus implying that the addition of Ca degrades the crystallinity of ZSM-5 zeolite.

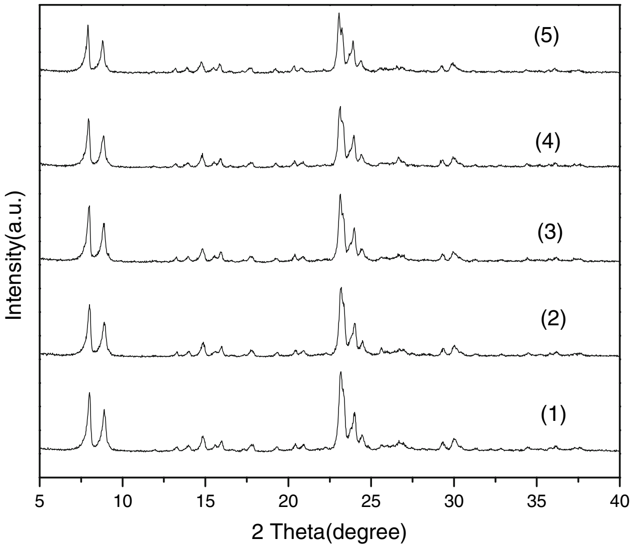

Fig. 1 XRD patterns of the different samples. (*1*) ZSM-5; (*2*) PtSn/ZSM-5; (*3*) PtSnCa(0.9%)/ZSM-5; (*4*) PtSnCa(1.7%)/ZSM-5; (*5*)PtSnCa (2.5%)/ZSM-5

To assess the influence of the presence of Ca on the catalyst surface, the BET surface area (S_{BET}) and the pore volume (V_p) of selected Pt–Sn–Ca containing samples were compared to those of PtSn/ZSM-5 catalysts. Besides, ZSM-5 is also included. Table 1 shows that the surface area and pore volume decreased after impregnation of Pt and Sn in ZSM-5 zeolite. Moreover, when Ca was added, the surface area and pore volume were further reduced, and these

Table 1 Characterization data for the prepared catalysts

Catalyst	S_{BET}(m^2/g)	V_p(cm^3/g)
ZSM-5	352	0.2357
PtSn/ZSM-5	340	0.2124
PtSnCa(0.9%)/ZSM-5	324	0.2017
PtSnCa(1.7%)/ZSM-5	319	0.1986
PtSnCa(2.5%)/ZSM-5	315	0.1973

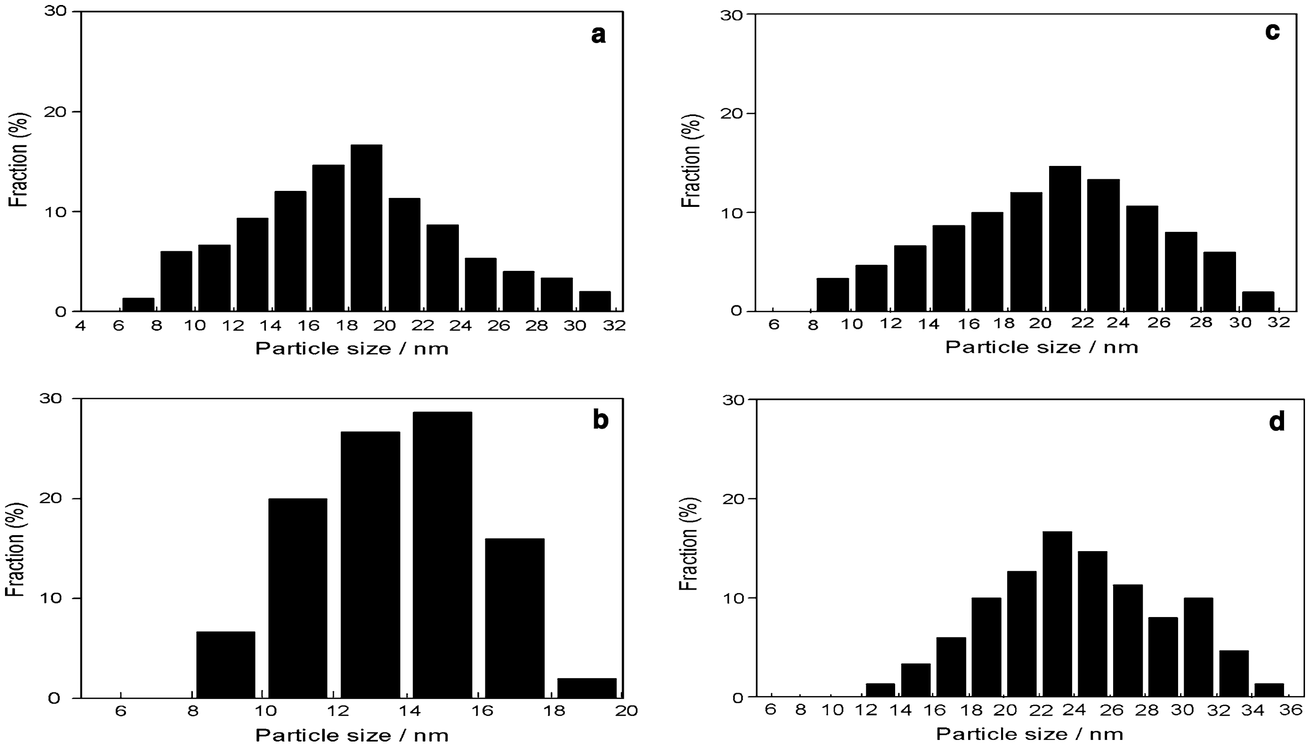

Fig. 2 Particle size distribution obtained by TEM: **a** PtSn/ZSM-5; **b** PtSnCa(0.9%)/ZSM-5; **c** PtSnCa(1.7%)/ZSM-5; **d** PtSnCa(2.5%)/ZSM-5

trends became evident as Ca loading was increased. This phenomenon indicates that in the impregnation process, the presence of Ca and Sn could enter into the channels plugging some of pores of the ZSM5 support, which caused a decrease in pore volume with a concomitant loss of surface area.

The mean particle sizes of different catalysts were obtained by direct observation by TEM. The mean particle sizes for PtSn/ZSM-5, PtSnCa(0.9%), PtSnCa(1.7%) and PtSnCa(2.5%) were 18.1, 13.6, 22.3 and 25.4 nm, respectively. Figure 2 shows the particle size distributions of the different catalysts. It can be seen that the Ca addition to the PtSn/ZSM-5 catalyst had a marked influence on particle size distributions.

The desorption of ammonia is used to characterize the acidic properties of the surface. This technique can provide information on the amount and strength of acid sites. Generally, the peak area of a TPD profile represents the amount of desorbed NH_3, whereas the peak position corresponds to the strength of acidity. The profiles of NH_3-TPD over different samples are presented in Fig. 3. In ZSM-5 zeolite, the profile exhibited two desorption peaks: the first desorption peak around 240 °C represented weak acid sites, and the second peak near 450 °C was ascribed to the strong acid sites, as it has been reported in the literature [26]. By contrast, after the impregnation of Pt and Sn, the acidity decreased. As known, Platinum did not change the number of acid sites [27], whereas, tin could reduce the acidity on the support, which is consistent with the results of prior research as summarized earlier in the literatures [28–30]. Moreover, the ammonia desorption temperature moved toward the lower range, indicating that the acid strength became weak. When the Ca content reached 0.9 wt%, the acidity of catalyst continuously decreased,

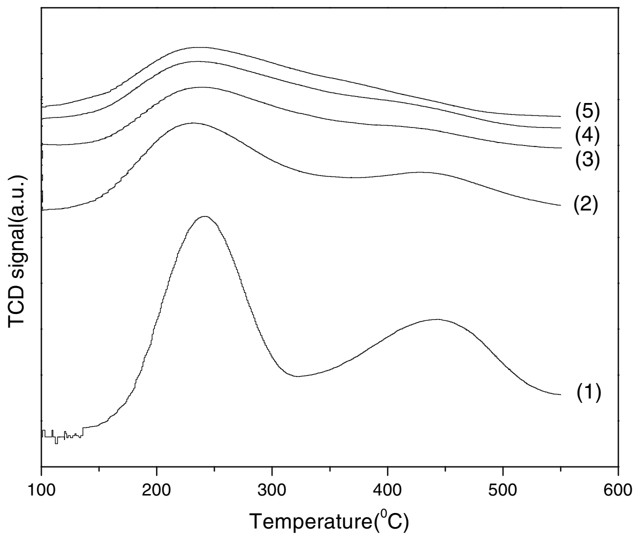

Fig. 3 NH_3-TPD profiles of the different samples: (*1*) ZSM-5; (*2*) PtSn/ZSM-5; (*3*) PtSnCa(0.9%)/ZSM-5; (*4*) PtSnCa(1.7%)/ZSM-5; (*5*)PtSnCa(2.5%)/ZSM-5

whereas ammonia desorption at high temperature was still observed. It is interesting to note that increasing Ca content to values higher than 0.9 wt%, the amounts of low acid sites slightly increased, whereas the amount of strong acid sites was almost unchanged. The above results suggest that the Ca loading and Sn addition could partially neutralize the strong acid sites.

3.2 H_2-TPR

TPR is a useful technique for characterizing the reduction behavior of the surface species on a catalyst. In our experiments, TPR measurements were carried out to characterize the reducibility of the platinum and tin species as well as the interaction between the metals and the carrier. The TPR profiles of different catalysts are shown in Fig. 4. The Pt/ZSM-5, Sn/ZSM-5 and Ca/ZSM-5 monometallic catalysts as references are also included in the figure. The TPR profile of the Pt/ZSM-5 showed two reduction peaks: one with maximum temperature at around 260 °C and the other peak at about 440 °C, which are in consistent with the literature data for Pt/ZSM-5 [31]. The presence of two reduction peaks was explained by the different ratios of Pt species interacting with the zeolite. The TPR profile of the fresh Sn/ZSM-5 also represented two reduction peaks: one with maximum temperature at around 430 °C and the other peak at about 625 °C. The former may correspond to the partial formation of Sn^{2+} species from the reduction of Sn^{4+}, while the latter could be associated with the reduction of Sn^{2+} species to form Sn^0 species [8]. The TPR profile of Ca/ZSM-5 represented no reduction peaks, thus indicating that the Ca additives were not reduced in the reduction process. The appearance of three reduction peaks in the TPR profiles for PtSn/ZSM-5 is in good agreement with the literature [16]. The first reduction zone at temperature around 260 °C could be assigned to the reduction of PtO_2 particles on the support surface,the second reduction zone displays a maximum at around 380 °C which could be the result of the reduction of Sn^{4+} to Sn^{2+}, and the third reduction zone at temperature around 620 °C, which could be related to the reduction of Sn^{4+} and Sn^{2+} to Sn^0. Comparing to the TPR profiles of these catalysts, it can be observed that the first reduction peak was gradually shifted to lower temperatures with increasing Ca loading. This effect could be attributed to a modification of Pt-support interaction by the Ca addition. That is, Ca promoted the reduction of Pt oxide species. Meanwhile, the presence of calcium also affected the reducibility of Sn^{4+} and Sn^{2+} to Sn^0: the third reduction peak shifted to lower temperature and at the same time its area increased as the amount of Ca increased,especially in the case of the catalyst with the highest calcium content. This phenomenon can account for the facts: the presence of Ca could lead to a lower interaction of the support with tin oxides, which notably assisted the reduction of tin species. It must be emphasized that the third reduction peak area for PtSnCa(0.9%)/ZSM-5 catalyst increased slightly, whereas for PtSnCa(1.7%)/ZSM-5 catalyst the increase was higher, in comparison to that of PtSn/ZSM-5 catalyst. Thus, with the Ca content exceeding 0.9 wt%, a high amount of zero valence state of tin could be formed and the possibility of PtSn alloy increased greatly. In this sense, a probable formation of intermetallic PtSn alloy could take place after reduction. Furthermore, Fig. 5 shows the relationship between the Ca content and the H_2 consumption. It is interesting to note when Ca content was more than 0.9% the trimetallic catalyst produced a marked increase of the

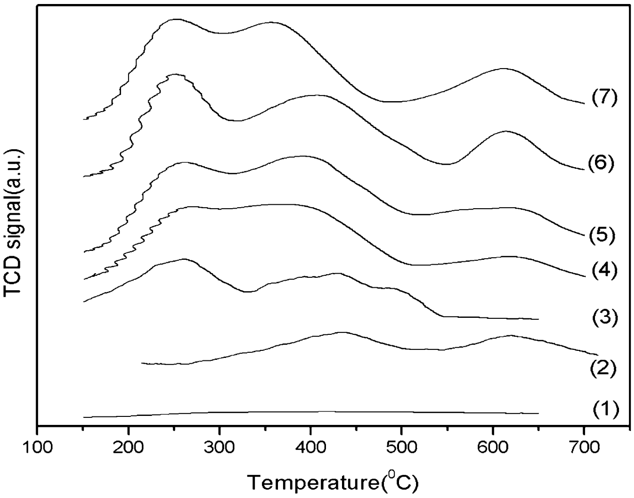

Fig. 4 H_2-TPR profiles of the different samples: (*1*) Ca/ZSM-5; (*2*)Sn/ZSM-5; (*3*) Pt/ZSM-5; (*4*) PtSn/ZSM-5; (*5*) PtSnCa(0.9%)/ZSM-5; (*6*) PtSnCa(1.7%)/ZSM-5; (*7*) PtSnCa(2.5%)/ZSM-5

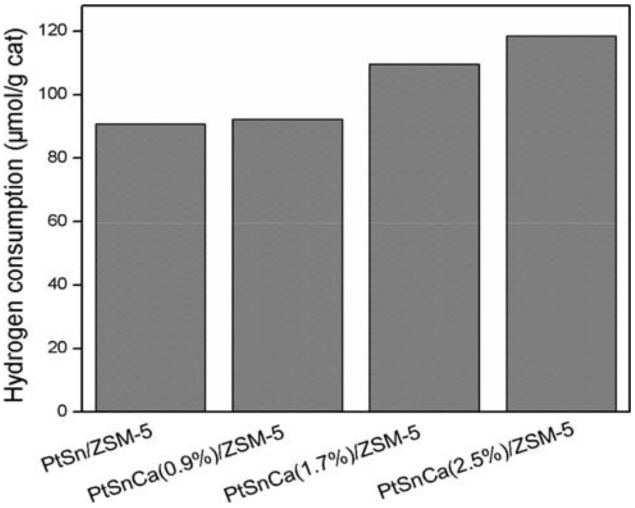

Fig. 5 H_2 consumption values in TPR experiments for bimetallic and trimetallic catalysts

H_2 consumption in the TPR experiments, which could be related to a high Sn reducibility. Dong et al. [25] investigated the effect of Ca addition on PtSn/$MgAl_2O_4$ catalyst for propane dehydrogenation, and similar results were also obtained. It has been reported that part of the tin species are reduced to the metal state and this Sn^0 becomes alloyed to Pt, which may affect its catalytic properties [32, 33]. Generally, keeping the oxidized state of Sn species on Pt–Sn catalysts is vital for the dehydrogenation reaction.

3.3 Catalyst Activity

The catalytic behavior of PtSn/ZSM-5 catalytic systems, unmodified and modified by the Ca addition, was investigated for propane dehydrogenation reaction at 590 °C. Figure 6 plots the propane conversion as a function of time on stream for the catalysts containing different Ca loadings. For all catalysts, the propane conversion decreased gradually with reaction time due to coke deactivation. It is noteworthy that the calcium content influenced both the stability and catalytic activity. The PtSn/ZSM-5 showed higher initial activity and underwent fast deactivation. The initial propane conversion was 35.1%, after 8 h reaction, propane conversion decreased to 22%. The poor stability is possibly related to a high amount of strong acidity sites, which makes cracking reaction occurring easy. Under this situation, the produced coke could cover the active sites fully, resulting in a rapid deactivation. On the other hand, when 0.9 wt% calcium was added, the PtSn/ZSM-5 catalyst showed high catalytic activity and relative stability. With increasing Ca loading, the activity decreased. This effect could probably be attributed to a gradual decrease in platinum dispersion and/or the formation of PtSn alloys. The reduced Sn atoms were alloyed to Pt and modified the metal function. Upon the formation of the Pt–Sn alloy, the amount of adsorbed propane decreased, due to the overall decrease in the Pt surface concentration. Thus, the propane dehydrogenation reactivity studies have shown that the activity of the supported bimetallic PtSn/ZSM-5 catalyst must be related to the calcium loading.

In the case of propane dehydrogenation process, side reactions like hydrogenolysis, cracking and coke formation compete with dehydrogenation reaction. Propylene is the major product of the reaction, whereas methane, ethane and ethylene are by-products. Platinum is the only active metal and propylene is only formed on the metal by dehydrogenation. Methane is generated by cracking of propane (acid sites) or by hydrogenolysis of propane on Pt sites. Ethylene is mainly formed from cracking on the carrier. Ethane is the product of propane hydrogenolysis and ethylene hydrogenation on Pt sites. As can be observed in Fig. 7, the selectivity to propylene followed the same trend for all catalysts. That is, the selectivity to propylene increased as time on stream. This is most likely due to the rapid coking occurring in the metallic sites that were active for hydrogenolysis and cracking reactions in the beginning of the reaction, which caused a gradual blocking of the active sites by carbon deposition. This means that coke acts as a promoter to improve the selectivity by deactivating those sites that are active for C–C bond activation. It is worthwhile to mention that the selectivity to propylene was enhanced with the increase of Ca loading, which could be due to the modification of the acidity properties and the metallic phase by Ca addition. The selectivity to propylene was low, indicating that the side reactions of cracking and hydrogenolysis were more important for propane dehydrogenation.

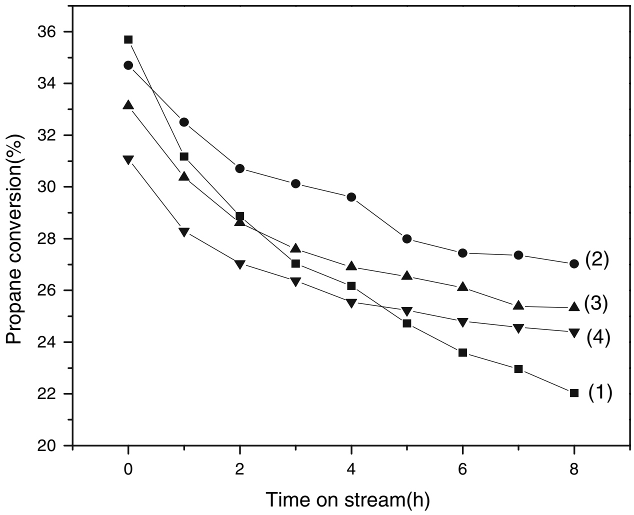

Fig. 6 Propane conversion vs. reaction time of the different catalysts: (*1*) PtSn/ZSM-5; (*2*) PtSnCa(0.9%)/ZSM-5; (*3*) PtSnCa(1.7%)/ZSM-5; (*4*) PtSnCa(2.5%)/ZSM-5

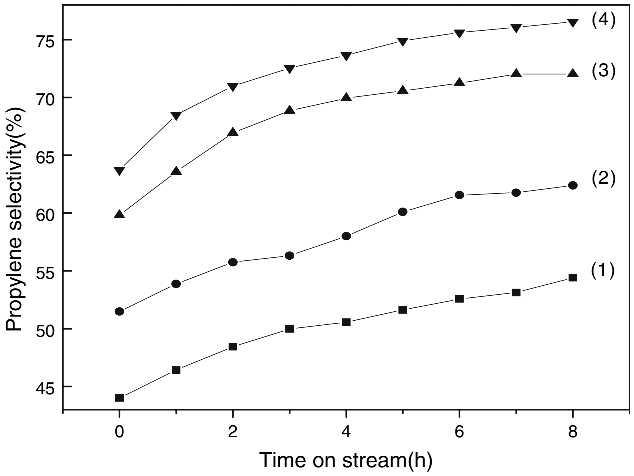

Fig. 7 Propylene selectivity versus reaction time of the different catalysts: (*1*) PtSn/ZSM-5; (*2*) PtSnCa(0.9%)/ZSM-5; (*3*) PtSnCa(1.7%)/ZSM-5; (*4*) PtSnCa(2.5%)/ZSM-5

3.4 Coke Formation

Coke on some used catalysts was characterized by TPO and thermogravimetric experiments. Thermogravimetic analysis can be used for quantitative analysis of coke. Figure 8 shows the relationship between the Ca content in the PtSnCa/ZSM-5 catalyst and the amount of coke deposited on the catalyst after reaction for 8 h. The coke content over PtSn/ZSM-5 catalyst was 12.8%, whereas over PtSnCa(0.9%)/ZSM-5 catalyst was 5.9%. This implies that the addition of 0.9 wt% Ca to catalyst could greatly reduce coke deposit. With the increase of Ca, the tendency became slower. Hence, from the above-mentioned results, it is clear that presence of calcium could remarkably inhibit the carbonaceous deposits on catalysts. As known, the carbonaceous deposit is mainly produced by the polymerization of olefins formed during the dehydrogenation process. The polymerization is catalyzed both by acid and metallic sites. According to the results of NH_3-TPD, for Ca catalysts, the strong acid sites were partially poisoned by calcium, which resulted in the diminution of acidity. Our TPR results showed that part of Sn species could be reduced to metallic Sn, which may be alloyed with platinum. The formation of PtSn alloy resulted in an increase in the electronic density of surface Pt [34], which would weaken the strength of the Pt–(C=C) bond and repulse the coke precursors. These important modifications in the catalyst structure by the Ca addition would cause the pronounced diminution of the deactivation by the carbon deposition.

In terms of location of coke deposits on catalyst surface, results of TPO analysis seem to be of special interest. The TPO profiles of all different samples after reaction for 8 h are shown in Fig. 9. The TPO profile of PtSn/ZSM-5catalyst presents two peaks: one with maximum temperature at ca. 480 °C and the other at ca. 580 °C. The first peak at low temperature has been assigned to coke deposited on metallic centers, which is more reactive to oxygen. The second peak appears at higher temperature and corresponds to coke deposited on the support [17, 35]. These results imply that the nature of coke could be different on metal and support sites in all catalysts. In all catalysts, the TPO profiles also exhibited some differences in the temperature and shape of peaks. The combustion peak area both in low and high temperature decreased with the Ca loading. This suggests that Ca addition to PtSn/ZSM-5 catalyst inhibits the formation of both types of coke.

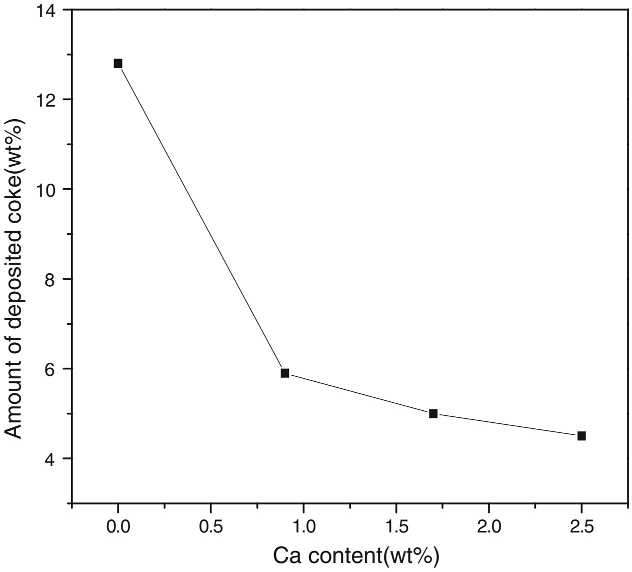

Fig. 8 Effect of Ca content on amount of coke deposited on PtSnCa/ZSM-5 catalyst

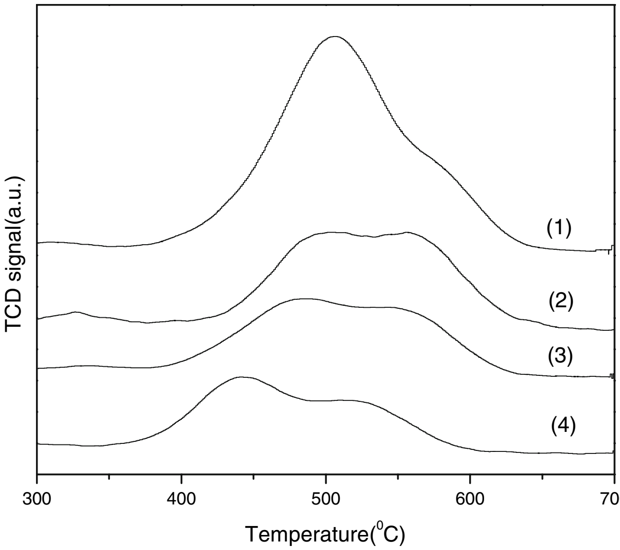

Fig. 9 Temperature programmed oxidation (TPO) profiles of the different catalysts: (*1*) PtSn/ZSM-5; (*2*) PtSnCa(0.9%)/ZSM-5; (*3*) PtSnCa(1.7%)/ZSM-5; (*4*) PtSnCa(2.5%)/ZSM-5

4 Conclusion

The presence of calcium in the catalysts improved the selectivity to propylene but also decreased the amount of carbon deposits on catalyst. The addition of 0.9 wt% Ca to PtSn/ZSM-5 catalyst exhibited better catalytic activity. However an excessive Ca loading caused that a large amount of oxidized tin species were reduced to metallic state, which could interact with Pt to produce high percentage of PtSn alloy, leading to a decrease in catalytic activity. It was observed that Ca is basic in character and could reduce the number of strong acid sites, as the Ca content was no more than 0.9 wt%. With increasing Ca loading, the amount of strong acid sites remained constant. Therefore, side reaction of cracking couldn't be suppressed to some extent. TPO analysis has shown that two different types of coke were deposited on the ZSM-5: a fraction deposited on the metallic surface, and another one adsorbed on the support. The Ca addition to PtSn/ZSM-5 catalyst inhibited the formation of both types of coke.

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