Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 723–729

TEMPERATURE PROGRAMMED REDUCTION STUDIES OF SPILLOVER EFFECT IN Pd IMPREGNATED METAL OXIDE CATALYSTS

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Abstract

Temperature programmed hydrogen reduction studies have been carried out for SnO_2 and Ce–Sn mixed oxides with and without Pd metal impregnation, to demonstrate the existence of spillover of hydrogen from Pd metal centers to support oxides. TPR pattern of SnO_2 showed a main peak at ~973 K indicating the bulk reduction of this sample. In Pd metal impregnated sample, the bulk reduction peak shifts to lower temperature (~923 K) due to the spillover of activated hydrogen from Pd metal to SnO_2 at relatively lower temperatures and its subsequent reaction with SnO_2. For Pd impregnated Ce–Sn mixed oxide samples also, a similar effect or an enhanced reduction was observed indicating the spillover effect of hydrogen. These results have been further confirmed from ^{119}Sn Mössbauer spectroscopic measurements carried out for some representative samples of SnO_2 and Pd/SnO_2 heated in hydrogen flow up to a temperature of 473 K. The value of $Sn^{2+}/(Sn^{4+}+Sn^{2+})$ ratio was found to be significantly higher for Pd impregnated sample. Both these observations provide direct evidence for the existence of spillover effect of hydrogen taking place in the metal impregnated samples.

Keywords: mixed oxide, Mössbauer spectra, Pd impregnated oxides, temperature programmed reduction, tin oxide

Introduction

Metal oxide or mixed metal oxide catalysts are widely employed for oxidation/selective oxidation of hydrocarbons and also in automobile threeway catalysis [1–4]. For these reactions, low temperature reducibility of oxides is desired and it can often be achieved by the metal impregnation of these oxides. In order to have an idea about the catalytic oxidation activity, the reduction behaviour of these oxides has to be studied and different thermal techniques have been employed for this purpose [5, 6]. Temperature programmed reduction (TPR) technique is widely employed to study the reduction behaviour of oxides. The TPR profiles thus obtained can give an idea about the different types of reducible species and the catalytic oxidation activity of these oxides [7, 8].

Pd/SnO_2 is a well-studied oxidation catalyst and a synergistic effect has been reported in this system for CO oxidation reaction [9]. The existence of synergistic ef-

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

fect has been explained on the basis of a spillover effect [10], which is the migration of reactant species from the metal sites to support after getting activated at metal sites. The interaction of the activated CO with SnO_2 leads to its reduction at relatively lower temperature. TPR profiles of such samples should exhibit a shifting of reduction peak to low temperature as compared to that of oxides without metal because of the activation of reactant species on metal sites at relatively lower temperatures. In the case of partially reducible oxides as support, an enhanced reduction should take place due to spillover effect. With this aim, the TPR studies have been carried out for SnO_2 and Ce–Sn mixed oxides with and without metal impregnation using hydrogen. In order to get supplementary evidence for spillover effect, the ^{119}Sn Mössbauer spectra of some samples were also recorded after reduction in hydrogen and the extent of reduction was evaluated by calculating the fraction of Sn^{2+} in these samples.

Experimental

SnO_2 was prepared by the precipitation of tin chloride solution using ammonia. Sn–Ce mixed oxides ($(1–x)SnO_2+xCeO_2$, where x=0.3 and 0.5 referred to as C30S and C50S, respectively) were prepared by coprecipitation method from the chloride and nitrate solutions of Sn and Ce respectively using NH_4OH at pH ~9. The oven-dried precipitates after washing thoroughly were calcined at 773 K in air for 2 h. Pd impregnation on these oxides was done by wet impregnation method using $PdCl_2$ solution (Pd=2% by mass of sample). After impregnation, the sample was heated in hydrogen flow at 473 K for 2 h for reducing $PdCl_2$ to Pd metal followed by heating in air at 773 K for 2 h. These samples were characterized by powder XRD technique using Philips 1820 diffractometer with CuK_α radiation. TPR experiments were carried out from room temperature to 1223 K using an indigenously fabricated instrument. 25 mg sample was placed in a quartz tube and heated at 15°C min^{-1} in H_2+Ar stream (8% H_2 by volume). All samples were given an *in situ* pretreatment of heating in Ar flow at 573 K for 2 h followed by cooling to room temperature before a TPR run. Change in H_2 concentration in the effluent gas due to the reduction of samples, was monitored by a thermal conductivity detector. ^{119}Sn Mössbauer spectra of pure and metal impregnated samples were recorded at room temperature after heating the samples under different conditions. The source used was $Ba^{119}SnO_3$ and all values of isomeric shift are reported with respect to this source. The spectra were least square fitted using Lorenzian line shape to estimate the relative fractions of Sn^{2+} and Sn^{4+} species in the catalyst samples.

Results and discussion

Powder X-ray diffraction patterns of SnO_2, $\{(1–x)SnO_2+xCeO_2\}$ with and without Pd metal impregnation and heated at 773 K in air for 2 h are shown in Fig. 1. SnO_2 showed broad Bragg reflections with average '*d*' values corresponding to the tetragonal (rutile) phase. CeO_2 showed better crystallinity and the unit cell parameter '*a*' was found to be 0.5402 nm. Mixed oxides existed in two phases as that of SnO_2 and CeO_2. The crystallinity of mixed oxides improved with CeO_2 concentration as can be seen from

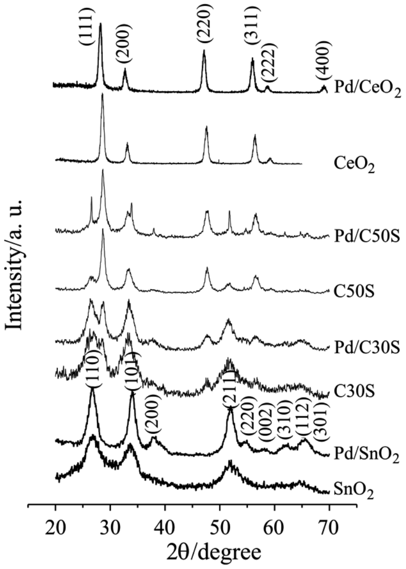

Fig. 1 XRD patterns of SnO_2, Ce–Sn mixed oxides and CeO_2 with and without Pd heated in air at 773 K for 2 h

their XRD patterns. These patterns were not affected much after Pd metal impregnation and heat treatment. The peaks due to Pd metal were not seen in any of these patterns, as its concentration was very small. All these patterns were indexed and the values of lattice parameters were calculated for those samples, which showed reasonable crystallinity and were found to be close to the values reported for individual SnO_2 and CeO_2 phases (ASTM card no. 41-1445 for SnO_2 and 34-394 for CeO_2). For C50S and Pd/C50S the values for SnO_2 phase were '*a*'=0.4770 and 0.4737 and '*c*'=0.3168 and 0.3185 nm, respectively. The CeO_2 phase present in C50S and Pd/C50S had the values of unit cell parameter ('*a*') 0.5378 and 0.5399 nm, respectively.

TPR profiles of pure SnO_2 and Pd impregnated SnO_2 heated in air at 773 K for 2 h are shown in Fig. 2. For pure SnO_2 an intense peak centered at 973 K is present besides some small peaks at ~548 and 673 K. The low intense peaks are assigned to the reduction of surface oxide species and the intense peak present at 973 K to the bulk reduction of SnO_2 to Sn metal.

The low temperature peaks are assigned to surface reduction, as these peaks are not seen for sintered SnO_2 sample, which has been heated in air at 1073 K for 18 h [11]. The total volume of hydrogen consumed during TPR corresponds to the complete reduction of SnO_2 to Sn metal. The presence of Sn metal in the reduced samples was also established from the XRD patterns of the samples recorded after TPR. The TPR profile of Pd/SnO_2 showed an intense peak at 923 K corresponding to the bulk reduction besides small peaks due to surface reduction. It can be noted that the bulk reduction peak of SnO_2 has shifted to lower temperature in Pd/SnO_2 indicating that Pd is playing a role

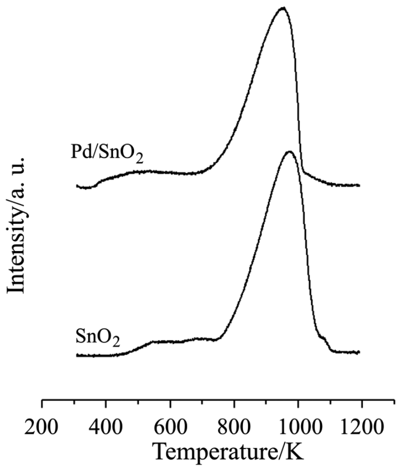

Fig. 2 TPR profiles of SnO_2 and Pd/SnO_2

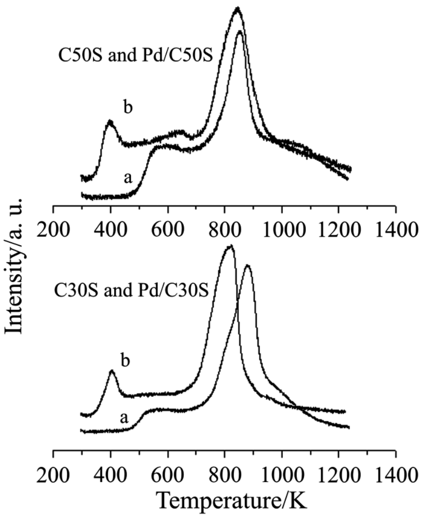

Fig. 3 a – TPR profiles C30S and C50S, b – Pd/C30S and Pd/C50S

in the reduction process. The TPR profiles of Ce–Sn mixed oxides heated in air at 773 K for 2 h and Pd impregnated mixed oxides are shown in Fig. 3.

C30S showed two main peaks centered around 543 and 881 K corresponding to the surface and bulk reduction of SnO_2. Contribution to the reduction peaks from CeO_2 is very little as the reducibility of CeO_2 is very poor as compared to SnO_2, which has been demonstrated in our earlier work [11]. The enhanced reduction seen in mixed oxides as compared to pure SnO_2 at the low temperature region (around 543 K) is attributed to a synergistic effect existing in these mixed oxides [11]. The shoulder peak seen around 973 K corresponds to the reduction of CeO_2 whose reduction is incomplete in the temperature region studied [8, 12]. Similarly, two main peaks are seen for C50S also around 563 and 855 K. The peak seen around 993 K has become more pronounced due to the increased concentration of CeO_2 in this composition. The TPR profiles of Pd impregnated samples clearly show the shifting of reduction peaks to lower temperatures, as is clear form Fig. 3. The low temperature peaks seen up to 673 K for Pd/C30S and Pd/C50S can be attributed to the reduction of surface oxygen species. The bulk reduction peak of both these mixed oxides also shift to lower temperature, though the effect is less for Pd/C50S. It can also be seen that for Pd/C50S, the width of the bulk reduction peak is more compared to C50S, indicating that the bulk reduction of CeO_2 is taking place at lower temperature due to the presence of Pd metal in these samples.

The decreased shift seen in the high temperature reduction peak of Pd/C50S as compared to C50S can be due to a metal support interaction occurring in this sample. It has been reported that [13] during high temperature reduction of Pd/CeO_2, CeO_2 reduces to form CeO_x and these suboxides can encapsulate Pd metal which retards further reduction process of CeO_2. As the concentration of ceria is more in Pd/C50S, the effect becomes more pronounced in it and hence a decreased shift is observed in this sample as compared to that observed for Pd/C30S and C30S.

The XRD patterns of Pd/SnO_2 and Pd/CeO_2 after TPR are shown in Fig. 4. It can be seen that SnO_2 has been completely reduced to Sn metal. The pattern has been indexed and the lattice parameters have been calculated ('*a*'=0.5582 and '*c*'=0.3182 nm) which are very close to the value reported for Sn metal (ASTM card no. 4-673). In case of Pd/CeO_2, the reduction is partial and the reduced sample retains its CeO_2 structure. It

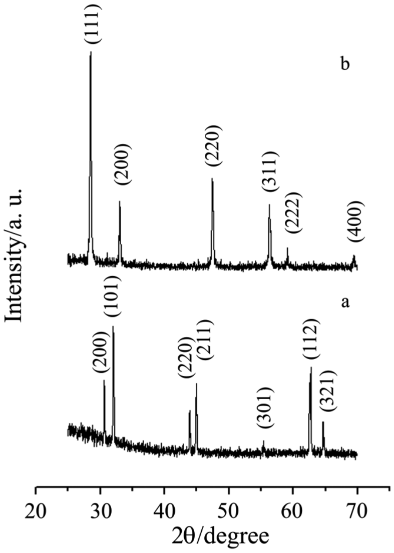

Fig. 4 a – XRD patterns of Pd/SnO_2 and b – PdCeO_2 after TPR

is well known that ceria can retain its fluorite structure with a non-stoichiometric composition, $CeO_{2-x,}$ where $0\leq x\leq 0.5$ [14].

The shifting of the bulk reduction peak to low temperature cannot be due to surface effects arising from the difference in the crystallite size of oxides and Pd impregnated oxides as is evident from the width of the XRD peaks of these samples shown in Fig. 1. It can be seen from this figure that the line widths are more for oxide samples, which do not contain Pd metal indicating smaller crystallite size for them. Even then, low temperature reduction is seen for metal impregnated samples, ruling out the role of crystallite size effect during reduction.

The role of spilt over hydrogen from metal centers to oxide support has been emphasized during hydrogenation reaction by a number of investigators [15] and methods for detecting spilled hydrogen has been reviewed by Sermon *et al*. [16]. The spilled hydrogen may reside on the surface of the support or diffuse into the bulk of the support and a variety of interactions with the support can take place like remaining adsorbed on the support, the partial reduction of the support or reaction with the support forming a new compound like hydrogen bronze. When the spilt over hydrogen reacts with the support leading to its reduction, the reduction of the support should take place at lower temperatures or at a faster rate in the vicinity of metal centers due to the migration of activated hydrogen after dissociation at the metal centers. The shifting of reduction peaks to lower temperatures is observed in the TPR profiles of Pd metal impregnated samples indicating a spillover effect of hydrogen during reduction. Hence, temperature programmed reduction technique can be used to study the spillover phenomenon in metal impregnated oxides.

Figure 5 shows ^{119}Sn Mössbauer spectra of SnO_2 and Pd/SnO_2 after heating in hydrogen at 473 K for 2 h. Spectrum of untreated SnO_2 is also included for comparison. The spectrum of SnO_2 shows an unresolved quadrupole doublet characterized by isomeric shift $\delta\approx 0.0$ mm s^{-1} and quadrupole splitting $\Delta Eq\approx 0.75$ mm s^{-1}. The spectra of the reduced samples show peaks corresponding to Sn^{2+} whose isomeric shift is

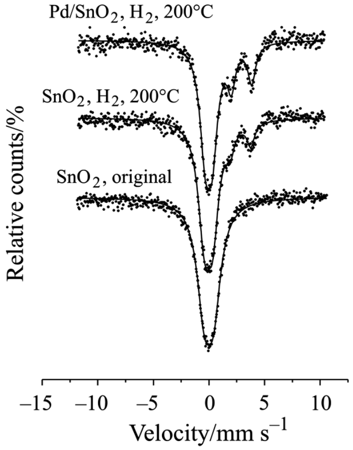

Fig. 5 ^{119}Sn Mössbauer spectra of SnO_2 and Pd/SnO_2 after heat by hydrogen for 2 h

$\delta \approx 3.0$ mm s^{-1} and $\Delta Eq \approx 1.9$ mm s^{-1}. The fraction of $Sn^{2+}/(Sn^{4+}+Sn^{2+})$ calculated for SnO_2 and Pd/SnO_2 are 0.13 and 0.23 respectively. From this result it is clear that under identical conditions of hydrogen treatment the fraction of Sn^{2+} species formed for metal impregnated sample is more than that of pure SnO_2. This provides a direct evidence for the spillover of activated hydrogen from metal sites to SnO_2. This observation is consistent with the TPR results of these samples shown in Fig. 2. The low temperature portion of the TPR patterns of SnO_2 and Pd/SnO_2 clearly shows that the onset of reduction takes place at lower temperature in the case of Pd/SnO_2 as compared to SnO_2. However, a comparison of the quantity of SnO_2, which has undergone reduction by both these techniques, cannot be made due to the fact that TPR is done in a dynamic mode whereas the Mössbauer spectra were recorded after the reduction of these samples for 2 h at 473 K.

Conclusions

TPR studies of tin oxide and mixed oxides of Ce and Sn with and without Pd metal give a clear evidence for the existence of spillover of hydrogen in Pd impregnated samples during reduction as the reduction peaks shift to lower temperatures in these samples as compared to oxides not having Pd metal. ^{119}Sn Mössbauer results further confirm this effect from the increased concentration of Sn^{2+} present in Pd/SnO_2 as compared to pure SnO_2.

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