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Catalytic Activities of Bimetallic Catalysts for Low Temperature Water Gas Shift Reaction

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A comparative study on the activity of bimetallic Pt/M/$CeZrO_4$(M=Na,Mo,Sn,Cu,Zn) catalysts is presented. The catalysts were prepared by wet impregnation method, by loading separately the two metals, with a Pt/M molar ration of 1. All the catalysts were fully characterized by several physical-chemical analytical techniques (ED-XRF, XRD, B.E.T., H_2-TPR) and the performance compared with the corresponding monometallic Pt/$CeZrO_4$derivate. The 1Pt/1Sn/$CeZrO_4$and 1Pt/1Na/$CeZrO_4$catalysts showed a similar CO conversion to that of the monometallic Pt-based catalyst in the temperature range of 473- 675 K, however a reduced occurrence ofmethanation, allows a higher production of hydrogen with the bimetallic systems.

1. Introduction

The water gas shift is one of the most studied reaction in the field of industrial chemistry, the thermodynamic profile and the necessity to reach the maximum CO conversion make it necessary to operate with a wasteful two-stage process. The HT Shift is generally performed on Fe/Cr-based catalysts in the temperature range 873 - 623 K; at this stage the most of CO is converted, although the thermodynamic limitations prevent to reach the complete conversion, and a favourable kinetic can be exploit. The LT Shift is performed on Cu/Zn-based catalysts in the temperature range 453 - 653 K, at this stage the conversion of CO is thermodynamically favoured and it’s possible to reach few ppm in concentration. These two catalytic systems are inexpensive and ensure the effectiveness of the process, however, they present several drawbacks; in addition to the burden of working with a two-stage system, the Cu/Zn catalysts are not suitable for fuel cell applications. Several alternative have been proposed to replace the conventional catalytic systems, actually used for industrial application; good results were obtained with noble metals such as gold (Yang et al., 2013), platinum (Miao et al., 2016), rhodium (Lombardo et al., 2016), palladium (Shan et al., 2015) and rhenium (Azzam et al., 2013). These catalytic systems are highly active in a large temperature range even at low concentration and are compatible with fuel processor systems, thus they seem to be the best choice for a process intensification (Palma et al., 2016). Comparative studies, on the activity of ceria/zirconia supported noble metals catalysts, showed the highest activity of platinum in the temperature range 473-593 K (Radhakrishnan et al., 2006), moreover in our previous studies the role of the support was investigated (Palma et al., 2014, 2015), highlighting the excellent performance of the ceria/zirconia system, however, these systems suffer of serious deactivation, by sintering and coking (Zalc et al., 2002), in real process conditions and a high methane selectivity (Torrente-Murciano et al., 2015). A strategy to overcome these problems consists in the adding of metallic low cost stabilizers; for example the Pt sintering was inhibited by the sodium promotion on Pt-Na/TiO_2 catalyst (Zhu et al., 2011) obtained by co-impregation of TiO_2 by the two relative salts, otherwise the coke formation was inhibited also by the $Ce_{0.78}Sn_{0.2}Pt_{0.02}O_{2-\delta}$ catalyst, obtained by solution combustion method (Gupta et al., 2010). A molybdenum promotion effect was recently reported, for Pt-carbon supported catalysts, increasing the turnover frequency up to a factor of 4000 (Sener et al., 2016); while a comparative study of platinum catalysts supported on M-doped cerium oxide (M = Ca, La, Mg, Zn, Zr, Yb, Y, Gd) have shown a promotion effect on the activity, depending on the nature of the dopant, varying in the order of Yb>Gd>Zr>Mg>La>CeO_2(undoped) >Ca>Y>Zn (Panagiotopoulou et al., 2007). Recently Kugai et al., (2015) have demonstrated the stabilizing effect of copper in Pt-Cu/CeO_2 catalysts in oxygen-enhanced water gas

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shift reaction (OWGS), the bimetallic system showed a higher activity than the monometallic Pt-based catalyst and a higher stability for about 70 h in OWGS conditions. In this paper we report a comparative study on the activity of bimetallic 1 % Pt/ 1 % M/ $CeZrO_4$ (M= Na, Mo, Sn, Cu, Zn) catalysts for water gas shift reaction.

2. Experimental

2.1 Catalysts preparation

The CeO_2/ZrO_2 (Actalys® 922, 57.4 %wt of ceria) support was provided by Rhodia, the Platinum(IV) chloride (99.9 %-Pt) was provided by Strem Chemicals, the Tin(II) chloride dehydrate (≥99.99 % trace metals basis), Sodium nitrate (≥99.0 %), Ammonium molybdate tetrahydrate (99.98 % trace metals basis), Copper(II) nitrate trihydrate (puriss. p.a., 99-104 %) and Zinc nitrate hexahydrate (98 %) were provided by Sigma-Aldrich. The 1%Pt/$CeZrO_4$ catalyst was prepared by wet impregnation of the support with a water solution of $PtCl_4$ (the amount of the salt corresponded to a loading of 1 % of metallic platinum with respect to the ceria-zirconia support), the suspension was vigorously stirred and heated until complete evaporation of the solvent occurred, the resulting suspension was dried at 393 K for three hours and calcined at 873 K for three hours. The bimetallic catalysts were prepared by loading firstly the "etero-metal (M)" and subsequently the platinum, both metals were loaded with the same method of the monometallic catalyst, with an intermediate step of calcination, in all cases the amounts of the salts used were calculated with the intent of obtain a ratio Pt/M = 1 and a total loading of 2 % (Pt+M). All the samples were compacted, crushed and sieved to achieve a granulometric distribution 180-355 µm, prior to the H_2-TPR experiments and catalytic activity tests.

2.2 Catalysts characterization

The real metal loading of the catalysts was evaluated by means of Energy Dispersive X-ray Fluorescence spectroscopy with an ARL^{TM} QUANT'X EDRF Spectrometer; the samples was compressed to form a tablet and analysed by the Fundamental Parameters method for determining the elemental composition. The B.E.T. surface area measurements were performed with a Sorptometer 1,040 K (Constech International); the samples were weighted and inserted in the apparatus tubes, degassed in vacuum for 30 min at 423 K and the specific surface area evaluated with adsorption-desorption isotherms of nitrogen at 77 K. The crystal phases and the crystallite size were evaluated by X-ray Powder Diffraction with a D8 Advance (Brucker); the samples were submitted to a Cu Kα radiation (35kV, 40 mA) in the 2θrange20-80° (Stp = 737; Stp size = 0.0814; t/Stp = 0.5 s). The crystallite sizes were calculated by using the Scherrer equation. The H_2-TPRexperiments were performed in the same reactor used for the catalytic tests, and immediately before the tests, with a reducing stream of 1,000 Ncc/min of 5 % H_2 in N_2, with a heating rate of 10 °C/min, in the temperature range of 300-723 K. The hydrogen uptake was calculated by integration of the curve, expressing the concentration change of hydrogen vs. temperature.

2.3 Catalytic activity tests

All the catalysts were reduced prior the activity tests, as indicated in the previous paragraph. The WGS tests were performed at atmospheric pressure, with a reacting mixture of 8 % CO, 30 % H_2O, nitrogen balance and a flow rate of 1,000 Ncm^3/min, at a gas hourly space velocity (GHSV) of 10,000 h^{-1}, in the temperature range 423-673 K, starting form the highest temperature and by applying a descending ramp of 2 K/min. The tests were performed in a fixed bed tubular stainless steel reactor with an internal diameter of 22 mm, 6 cm^3 of each catalysts (180-355 µm) were diluted with quartz (500 - 700 µm) to reach 12 cm^3 of total volume, to minimize the pressure drop and the thermal effects. Products streams were continuously monitored by an ABB system, the nondispersive infrared photometer Uras 14 for CO, CO_2 and CH_4 and the thermal conductivity analyser Caldos 17 for hydrogen. The GHSV was calculated as the ratio between the volumetric flow rate and the volume of the catalyst. The CO conversion was calculated as the ratio between the difference of the moles, between input and output, and the input moles. The hydrogen selectivity was calculated as the ratio between the hydrogen moles and the converted carbon monoxide moles.

Table 1: Metal loading, specific surface area and crystallite size

Sample	Pt %wt	M %wt	S.S.A. [m^2/g]	Cryst. Size [nm] $CeZrO_4$ (111)
1Pt/CeZr	0.90	-	49.1	9.0
1Pt/1Na/CeZrO4	0.85	0.98	34.5	9.4
1Pt/1Mo/$CeZrO_4$	0.84	0.79	47.3	9.4
1Pt/1Sn/$CeZrO_4$	0.85	0.90	48.7	9.3
1Pt/1Cu/$CeZrO_4$	0.83	0.93	48.5	9.5
1Pt/1Zn/$CeZrO_4$	0.83	0.89	48.5	9.3

3. Results and discussion

3.1 Characterization

In table 1 the effective metal loading, the specific surface area and the crystallite sizes, for all the catalysts, are reported. The metal loading, measured on the calcined catalysts, was in a good agreement with the theoretical, while the deviation was attributed to the experimental error. The B.E.T. specific surface area measurements showed that the addition of the two metal involved a significant reduction of the s.s.a., only in the 1Pt / 1Na / $CeZrO_4$ catalyst; a similar effect was recently reported for Ni/Na/CeO_2 catalyst (Ang et al.,), and it was attributed to the penetration of sodium into the pores of the support, resulting in the occluding and consequent decrease of the surface area; for the other catalysts this phenomenon was not present, so no significant change in the surface of the support was assumed.

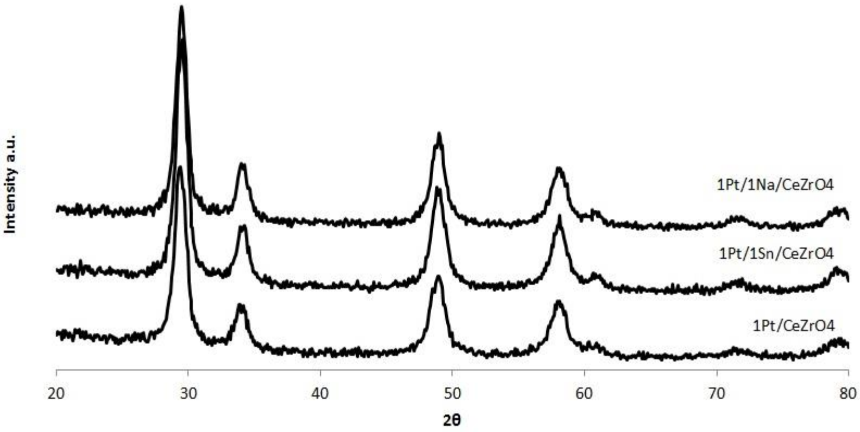

Figure 1: Comparison of the X-ray diffractograms of 1Pt/$CeZrO_4$, 1Pt/1Sn/$CeZrO_4$ and 1Pt/1Na/$CeZrO_4$ catalysts

The XRD diffractograms of all the catalysts showed the co-existence of two phases for the ceria/zirconia solid solution, the typical cubic fluorite type phase and tetragonal t' phase, attributed to the broadening of reflections at high-angle profiles (Liotta et al., 2003), in no case reflection of the metals loaded were detected, probably because of the high dispersion (Figure 1). The average crystallite sizes of $CeZrO_4$ were calculated from the broadening of the (111) reflection, centred at 2θ 29.36, using the Scherrer equation; the results showed a slight increase in dimensions probably due to the incorporation of the metal into the lattice of the support, resulting in the increasing of the grain dimensions.

Table 2: Experimental H_2 uptake and temperature of the main reduction peak

Sample	Exp. H_2 uptake [mmol/g]	T. of the main reduction peak [K]
1Pt/CeZr	0.81	523
1Pt/1Na/CeZrO4	0.90	536
1Pt/1Mo/$CeZrO_4$	0.83	545
1Pt/1Sn/$CeZrO_4$	0.97	495
1Pt/1Cu/$CeZrO_4$	0.67	445
1Pt/1Zn/$CeZrO_4$	1.03	510

In Table 2 the experimental H_2 uptake and the temperature of the main reduction peak in TPR experiments, for all catalysts, are reported. The hydrogen uptake was, for all catalysts, higher than the theoretical, due to the occurrence of the "spillover effect" (Norman et al., 2001), moreover, except for the 1Pt / 1Cu/ $CeZrO_4$, all the other bimetallic catalysts presented a hydrogen uptake higher than the monometallic 1Pt / $CeZrO_4$.Concerning the H_2-TPR profiles, all catalysts showed a broad peak in the 445 - 550 K temperature range, attributed to the overlapping of the active metal reduction and the metal-induced reduction of the surface of the support, moreover a second broad peak in the 600 - 700 K temperature range was attributed to the bulk reduction of the support. The presence of a single peak at low temperatures, corroborated the hypothesis of the formation of a strong interaction between the two metals species, for all catalysts, inducing a shift on the platinum reduction peak. The presence of copper caused the higher shift towards lower temperatures, but a similar trend was also found with tin and zinc, on the other hand the presence of sodium, and molybdenum shifted the Pt-reduction peak towards higher temperatures.

4. Activity tests

The catalytic activity tests, performed in the conditions above mentioned, showed a strong dependence of the CO conversion from the type of the "etero-metal" used (Figure 2). The 1Pt / 1Cu/ CeZrO4 catalyst provided the lowest conversion in all the temperature range. Much better performance were obtained with all other bimetallic catalysts, for which, above 560 K, the CO conversions were higher than 85 %. However, if we consider the lowest temperatures, only 1Pt / 1Na/ $CeZrO_4$ and 1Pt / 1Sn / $CeZrO_4$ showed an activity similar to that of the monometallic 1Pt/$CeZrO_4$, approaching the equilibrium above 500 K. For temperature below 500 K the CO conversion obtained with the monometallic Pt-based catalyst was higher than those obtained with the bimetallic systems, in any case.

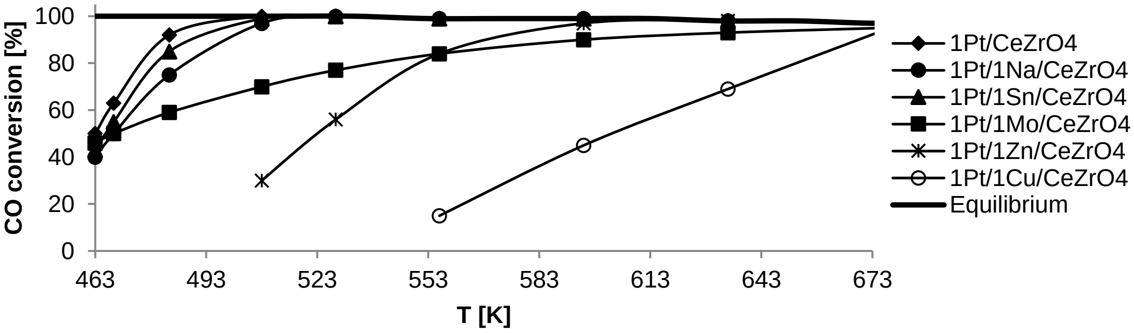

Figure 2: Comparison of the CO conversion of all the catalysts

More interesting was the trend of the hydrogen selectivity (Figure 3); the monometallic 1Pt /$CeZrO_4$ catalyst showed a lower H_2-selectivity with respect to all the bimetallic systems, in all the temperature range studied, and reached the same H_2-selectivity of the bimetallic Pt/Na and Pt/Sn systems, only at 463 K. Between the bimetallic catalysts, the best performance, in terms of hydrogen selectivity were obtained with the 1Pt /1Sn / $CeZrO_4$in all the temperature range studied. The reduced hydrogen selectivity of the monometallic Pt-based catalysts was justified by the occurrence of the methanation reaction therefore, despite it showed the same CO conversion of the bimetallic Pt/Sn and Pt/Na catalytic systems, part of the carbon monoxide and hydrogen product, was consumed to produce methane. A large difference of H_2-selectivity was obtained from above 468 K, with a maximum in the loss of hydrogen at 673 K, in the order of 15 %. The stoichiometry on the methanation reaction provides three moles of hydrogen per CO consumed, so a small amount of methane correspond to a large loss of hydrogen. The activity data were cross-checked with the characterization results, however no simple correlation was found, probably due to the different character of the "etero-metal" used.

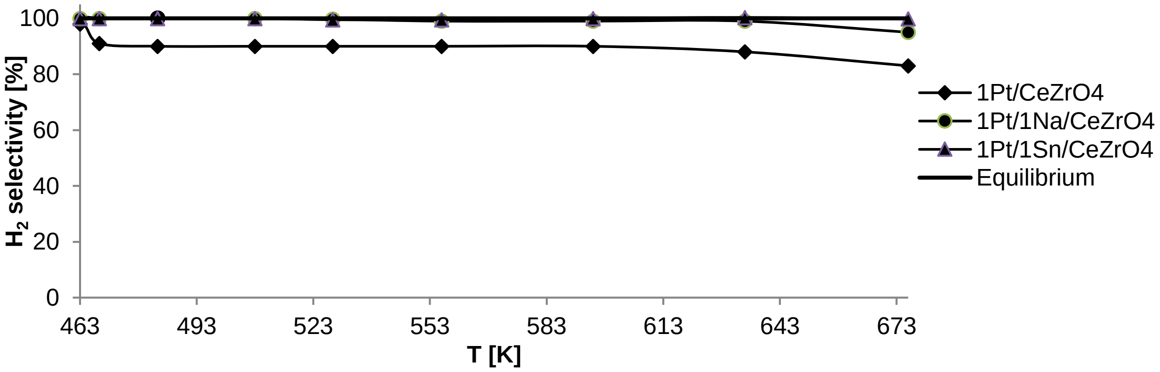

Figure 3: Comparison of the hydrogen selectivity between the monometallic 1Pt/$CeZrO_4$ and the bimetallic 1Pt/1Sn/$CeZrO_4$ and 1Pt/1Na/$CeZrO_4$ catalysts

Concerning a possible correlation between the activity of the catalysts and the H_2-TPRresults, the differences in the activities of 1Pt / 1Sn / $CeZrO_4$ and 1Pt / 1Na / $CeZrO_4$ catalysts, at low temperatures, is probably due both to the lower reducibility and to the lower specific surface area of the latter. Further study seems to be necessary to clarify the role of each “etero-metal” used.

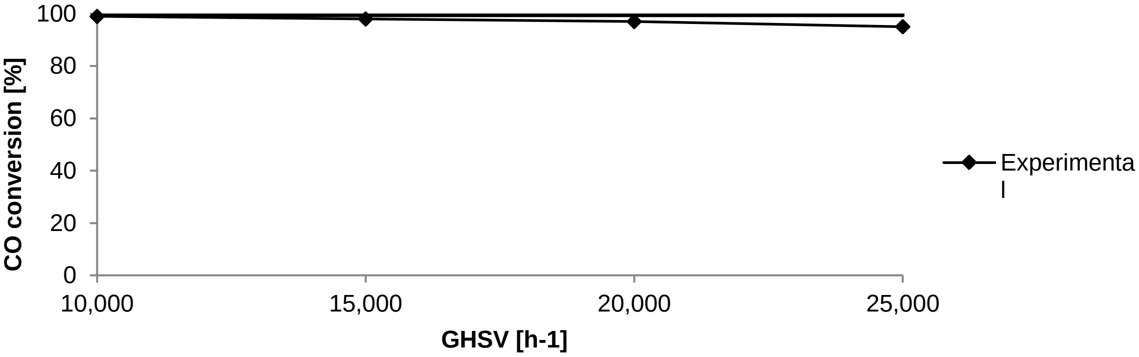

Figure 4: CO conversion trend of 1P t/1Sn / $CeZrO_4$ catalyst at 513 K

The effect of the GHSV on the activity of the 1Pt/1Sn/$CeZrO_4$ catalyst, at 513 K, was also investigated (Figure 4); the obtained results showed a slight reduction of the activity at 25,000 h^{-1}, however the hydrogen selectivity was not affected by the higher space velocity, highlighting the good performance of this catalyst.

5. Conclusion

In this paper we have presented a comparative study on the activity of bimetallic 1%Pt/1%M/$CeZrO_4$catalysts (M=Na,Mo,Sn,Cu,Zn), for CO water gas shift reaction. The best performance, in terms of conversion and H_2-selectivity were obtained with the 1Pt /1Sn / $CeZrO_4$ catalyst, in the temperature range 480-673 K, while at lower temperatures the monometallic 1Pt / $CeZrO_4$ catalyst showed the best performance. These results highlighted the possibility to enhance the performance of the Pt-based catalysts by using a second metal for alloy formation. Further study are in progress to evaluate the coke formation and sintering resistance of the bimetallic systems.

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