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Characterization of Sn doped Ni/Al_2O_3 steam reforming catalysts by XPS

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XPS measurements have shown that tin oxides are more readily reduced to metallic tin by hydrogen in Ni/Al_2O_3 systems than on pure Al_2O_3. During the reductive activation of Sn doped Ni/Al_2O_3 catalysts, surface segregation of the dopant was observed. This finding may explain that tin enhances the selectivity of the steam reforming catalysts only when added in very low concentrations and that it acts as a poison at higher loadings.

Keywords: Steam reforming catalysts; Sn doped Ni/Al_2O_3; surface segregation of tin; XPS of Sn/Ni mixtures

1. Introduction

Carbon formation on steam reforming catalysts is a well known deactivation process, which causes major problems in reforming plants. Carbonaceous overlayers inhibit the access of the reactants to the catalyst and carbon deposits increase backpressure in the reactors and lead to breakdown of the reaction plant [1,2].

On supported nickel steam reforming catalysts, coke is often found in the form of whiskers with Ni-particles sitting on top, explained as formed in a dissolution–precipitation process [2]. Carbon formed by thermal decomposition of methane or disproportionation of carbon monoxide dissolves into the nickel and diffuses through the metal particles. At the nickel–support interface the carbon is precipitated and polymerizes, leading to bigger conglomerates and to coke [2].

Selective poisoning of steam reforming catalysts with sulphur to prevent carbon formation has been described by Rostrup-Nielsen [3,4]. Small quantities of sulphur in the feedgas stream slightly reduce the steam reforming activity, but also reduce the rate of carbon formation significantly. The effect was explained by ensemble size control of the reactions. It was shown, that the polymerization of carbon needs larger ensembles of active nickel sites than the steam reforming reaction. The added sulphur is believed to form arrays of atoms relatively strongly bonded to the nickel surface which limit the size of free nickel ensembles to a size unsuitable for carbon polymerization.

The disadvantage of selective poisoning with sulphur is the relatively quick removal of sulphur from the catalyst by reacting gases during the steam reforming process. A source of sulphur has to be added to the reactant stream continuously.

The possibilities of metals, rather than sulphur, acting as more stable selective poisons have been examined experimentally [5]. It was found that elements of group IV (i.e. Sn and Pb) and group V (Sb and Bi) of the periodic table showed a similar behaviour to sulphur, when added in low quantities (typically $< 1\%$ of the total metal loading) [6]. Possible interpretations of this behaviour include ensemble size control similar to sulphur, dopant-blocking of the sites where carbon particles could grow and/or the reduction of the rate of diffusion of carbon through the nickel particles because electronic interaction of the dopants with nickel lowers the solubility of carbon in the nickel particles.

The aim of this study was to obtain a better insight into the effects of tin doping of nickel catalysts using surface analysis techniques.

2. Experimental

2.1. SAMPLE PREPARATION

Supported catalysts were prepared using impregnation and co-impregnation techniques followed by drying and calcination in air at 500°C for 3 h [5]. An α-alumina support was used which had been prepared from γ-alumina by calcination at 1125°C for 2 h in order to reduce the surface area to about 5 m^2/g. The total metal loading was always 20% by weight. Dopant concentrations are given in wt% of the metal loading.

To prepare the unsupported Sn/Ni oxide used as the reference system, a mixed carbonate was precipitated from mixed 1 M solutions of nickel nitrate in water and tin chloride in 10% HCl by adding small portions of solid ammonium carbonate until the precipitation was complete. After washing with water and ethanol the carbonate was dried at 120°C over night and then decomposed to the mixed oxide by heating at 500°C for 2 h.

2.2. XPS

The XPS spectra were recorded on a Kratos XSAM AXIS 800pci spectrometer equipped with a concentric hemispherical analyzer with three channeltron detectors. A Mg Kα X-ray source was used at 180 W. The base pressure in the analyzer chamber was less than 10^{-9} Torr. The analyzer was run in the fixed transmission mode at pass energy 80 and 40 eV for wide scan and high resolution spectra, respectively. The binding energy scale of the spectrometer was calibrated against the Cu $2p_{3/2}$ line ($E_B = 932.7$ eV) and the Ag $3d_{5/2}$ line ($E_B = 386.2$ eV). Instrument control as well as data collection and processing were performed using Kratos DS800 software on a PDP 11 computer.

The samples were ground to fine powders and suspended in acetone. The resulting slurry was deposited on the sample holder. After evaporation of the solvent, the powder was sufficiently strongly bound to the holder to be introduced in the vacuum system. A reaction cell was attached to the spectrometer, in which samples could be treated in flowing hydrogen at atmospheric pressure at temperatures up to 500°C. After cooling, the reaction cell was evacuated and the samples were transferred to the spectrometer without contact with air. Most samples were insulators and subject to electrical charging during the measurements. The binding energy scale of these spectra was calibrated against the Al 2p line of α-alumina at $E_B = 73.8$ eV [7].

3. Results and discussion

3.1. OXIDATION STATE AND LOCATION OF Sn IN Sn/Ni-SYSTEMS

Our considerations on the mechanism of the reduction in carbon formation were based on the assumption that the dopant would be present in the metallic state. In fact, it cannot be excluded that tin would remain in an oxidised state in the reductive activation process. For a Pt–Sn/γ-Al_2O_3 catalyst it is reported, that no reduction of Sn occurred in hydrogen up to 500°C [8]. Our own measurements on 1% Sn on Al_2O_3 confirmed these findings. The Sn 3d spectra showed no difference and no sign of metallic Sn before and after reduction in hydrogen at atmospheric pressure at 500°C for 30 min.

On Sn/Ni/Al_2O_3 catalysts XPS measurements were carried out on samples with dopant concentrations of 1 and 5% of the total metallic content, which is at the upper limit of the positive effect in the steam reforming process [5], and at the lower limit of quantifiable XPS signals. In the reference system used, the Sn/Ni ratio was even higher (1 : 6).

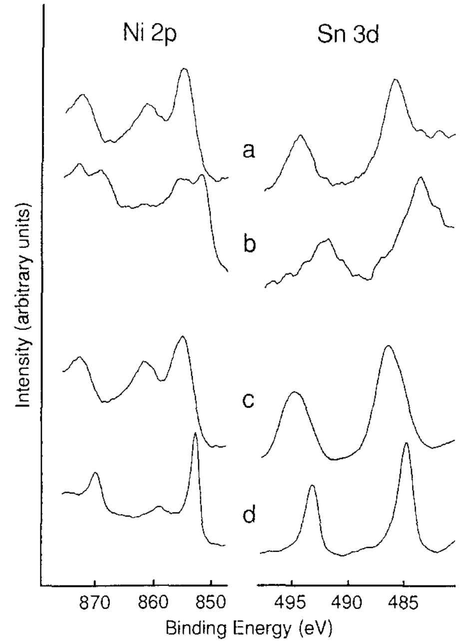

Fig. 1. Ni 2p and Sn 3d spectra of a 5% Sn/Ni/Al_2O_3 catalyst (a = calcined, b = reduced) and a 15% Sn/Ni oxide reference system (c = calcined, d = reduced). Reduction conditions: flowing hydrogen, 1 atm, 500°C, 30 min.

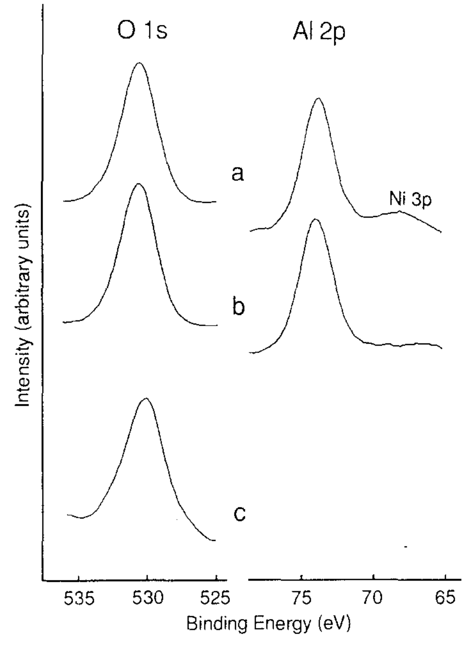

Fig. 2. Al 2p and O 1s spectra of a 5% Sn/Ni/Al_2O_3 catalyst (a = calcined, b = reduced) and of a calcined 15% Sn/Ni oxide reference system (c).

Figs. 1 and 2 show the XPS spectra of the 5% Sn/Ni/Al_2O_3 catalyst and of the unsupported Sn/Ni system in the calcined state and after 30 min reduction in flowing hydrogen at 500°C. The peaks from the catalyst samples and from the unsupported calcined Sn/Ni-oxide appeared much broader than the peaks from the reduced Sn/Ni-oxide. This effect is most probably due to differential charging in the non-conducting materials [9].

For the calcined unsupported sample, the Ni 2p peak position and shape (pronounced shake up satellites) indicate the presence of Ni^{2+}. The position of the Sn 3d lines indicates Sn^{+II} and/or Sn^{+IV}. It is reported to be impossible to distinguish between Sn^{+II} and Sn^{+IV} from XPS spectra [10,11]. In the spectra of the reduced unsupported sample an almost complete reduction of nickel and tin during the treatment in hydrogen is evident from the chemical shifts of the Ni 2p and Sn 3d lines and the disappearance of the Ni 2p shake up satellites.

In the calcined supported system Sn and Ni peak positions and shapes are similar to the unsupported sample (Ni^{2+} and $Sn^{+II/+IV}$). The Sn spectra of the reduced catalyst indicate a complete reduction of the Sn during the reduction process. The Ni spectra of this sample show a superposition of Ni^{2+} and Ni^0 contributions, indicating an incomplete reduction of nickel. As expected, the Al 2s and O 1s spectra are not greatly affected by the reduction process.

Spectra of the 1% Sn/Ni/Al_2O_3 catalyst showed the same features as 5% Sn/Ni/Al_2O_3, but with a relatively poor signal to noise ratio in the Sn 3d region.

The fact that Sn is so easily reduced in the Sn/Ni/Al_2O_3 catalyst suggests that most Sn is present in or on the nickel particles, rather than directly on the support, where it would be stabilized in higher oxidation states.

3.2. SURFACE CONCENTRATIONS

Surface concentrations were calculated from peak areas using linear background subtraction and tabulated response factors [12]. For Sn, the $3d_{3/2}$ line was used instead of more intense $3d_{5/2}$ line which is partially obscured by a Mg Kα induced Ni(LMM) Auger transition. The results of the quantifications have neither been corrected for different escape depths of the electrons nor for the transmission function of the instrument used, and can only be used as semiquantitative indications of trends.

Table 1 summarizes results from the area quantification of six different samples. The data from 5% Sn/Ni/Al_2O_3 are in line with the findings of the 1% Sn/Ni/Al_2O_3 sample in which the Sn content is too close to the detection limit even for semiquantitative results on its own.

On the two supported systems, the reduction process resulted in a lowering of the relative amount of nickel at the surface. This effect is often found during reduction of various supported metal catalysts and is interpreted as reduction of the coverage of the support because small metal particles conglomerate to

Table 1
Surface concentrations of Sn, Ni, Al and O in supported and unsupported Sn/Ni samples before and after reduction in hydrogen at 500°C calculated from Ni $2p_{3/2}$, Sn $3d_{3/2}$, Al 2p and O 1s peak areas and tabulated response factors [12]. Samples: 1% Sn/Ni/Al_2O_3 calcined (a) and reduced (b), 5% Sn/Ni/Al_2O_3 calcined (c) and reduced (d), and 15% Sn/NiO calcined (e) and reduced (f).

Sample	Ni (wt%)	Sn (wt%)	Al (wt%)	O (wt%)	Sn/(Sn+Ni)	
					experimental	nominal
a	20.3	0.2	31.8	47.7	0.01	0.01
b	7.0	0.7	40.4	51.9	0.09	0.01
c	19.5	1.0	32.1	47.4	0.05	0.05
d	10.2	1.4	39.1	49.3	0.12	0.05
e	64.7	15.5	–	19.8	0.19	0.17
f	71.8	24.1	–	4.1	0.25	0.17

bigger particles during reduction, thus lowering their effective surface area for analysis [13].

In all three samples the amount of Sn present at the surface increases during the reduction process. In all cases a level significantly higher than the nominal composition is found after reduction. Surface segregation of Sn in the metal particles could be responsible for this observation.

Several models for the prediction of surface segregation of components in metal solid solutions and the calculation of equilibrium surface compositions have been reported in the literature [14,15]. The complex nature of real catalysts, however, makes application of such models difficult. Since the minimisation of the overall surface free energy is the main driving force for surface segregation phenomena, comparison of the surface free energies of the components of a system can be a useful indication if surface segregation is likely to occur in such complex systems [16].

In the case of Sn and Ni, there exists a considerable difference in the surface free energies of the two metals (2450 mJ/m^2 and 710 mJ/m^2 for Ni and Sn respectively [17]). This gives a strong indication that Sn should segregate to the surface, as has been found experimentally. At lower dopant concentrations, catalytic activity may be affected only to a small extent, but a total coverage of the nickel particles by tin at higher dopants concentrations should cause total loss of catalytic activity.

4. Conclusions

XPS measurements have been used to clarify the surface composition in Sn doped Ni/Al_2O_3 steam reforming catalysts. In the co-impregnated calcined catalyst, tin oxide is dispersed in the NiO particles. During the activation process in hydrogen, tin oxide is readily reduced in Sn^0 and starts to segregate to the surface of the Ni particles. When present in small quantities, it acts as a selective poison for carbon formation reactions, possibly by limiting the nickel ensembles to a size unsuitable for carbon formation. When added in high amounts, surface segregation leads to a total coverage of the nickel particles by tin and to loss of catalytic activity. Due to the complexity of the system and the low concentration of the dopant, no evidence was found by XPS for electronic interaction of Sn and Ni. It can nevertheless not be excluded that tin could also reduce the amount of carbon whisker growth by lowering the solubility of carbon in nickel.

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