



An FTIR study of the dispersed Ni species on Ni-YSZ catalysts

Carlo Resini^{a,b}, Tzvetomir Venkov^c, Konstantin Hadjiivanov^c, Sabrina Presto^{b,d}, Paola Riani^{b,d}, Rinaldo Marazza^{b,d}, Gianguido Ramis^{a,b}, Guido Busca^{a,b,*}

^a Dipartimento di Ingegneria Chimica e Processo, Università di Genova, P.le J.F. Kennedy, 1, 16129 Genova, Italy

^b Consorzio INSTM, Via Benedetto Varchi n. 59, 50132 Firenze, Italy

^c Institute of General and Inorganic Chemistry, The Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

^d Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, 16146 Genova, Italy

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ABSTRACT

IR spectroscopy of low temperature adsorbed CO and CO + NO has been used to characterize the surface species on a 5% Ni-YSZ catalyst. Dispersed surface Ni species are present on the fresh catalyst, essentially formed by Ni²⁺, although it is evident that these species are very easily reduced in very mild conditions to zerovalent atomic nickel. Reduction in stronger conditions gives rise to small Ni metal particles, which are however easily reoxidized to bivalent nickel. This work has demonstrated how elastic is the redox state of this catalyst. This is supposed to be a key properties explaining the behaviour of this catalyst in converting ethanol in the presence of water.

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1. Introduction

Supported Nickel catalysts find application in several industrial processes. Among others, methane steam reforming catalysts for the production of hydrogen and syngases are based on Ni supported on alumina-based carriers. In general, they also contain components or additives characterized by medium strong basicity. Typical methane steam reforming catalysts contain 10–25% wt Ni, 70–85% Al₂O₃ or MgAl₂O₄ support and up to 5% K, Ba, Ca [1–3]. In autothermal steam reforming reactors Ni on Ca aluminates is typically applied. The addition of basic components is mostly associated to the limitation of coking, with the formation of carbon whiskers. However, also the stabilization of alumina by large alkali and alkali earth cations is useful for these catalysts that typically work in the presence of much steam at 700–900 °C, 30–50 bar. Similar Ni-based catalysts have more recently been proposed for

the steam reforming of bio-ethanol [4–6] to produce renewable hydrogen.

Catalysts based on supported nickel, usually on alumina, may be applied for methanation and for the synthesis of substituted natural gas [1,2,7]. This reaction is actually just the reverse of steam reforming of methane, being however performed at definitely lower temperature (300–400 °C).

Several studies have been reported concerning the mechanisms of these reactions. The most popular ones, today, for methane steam reforming and methanation suppose the reaction to occur essentially on Ni crystal faces via nickel alkyls, nickel carbide, and carbon species. As reviewed by Røstrup Nielsen et al. [2], these mechanisms have been proposed for methane steam reforming over Ni-based catalysts mostly on the base of studies on Ni single crystals performed far from practical conditions, and on DFT calculations also performed on Ni monocrystals [8,9]. Until some decade ago, instead, mechanisms occurring via adsorbed oxygenated species were considered at least for methanation [10]. Some of us recently showed that a way through oxygenates may also be observed for methanation on Ni alumina. As we have already remarked, studies of metal monocrystals give likely an incomplete

* Corresponding author. Fax: +39 010 3536028.

E-mail address: Guido.Busca@unige.it (G. Busca).

picture of what happens on real supported metal catalysts [11] where the role of the support and of the support-nickel interface is probably very relevant. On the other hand, more recent DFT calculations suggest the possibility of formation of oxygenated species on Ni crystals during steam reforming [12].

In a previous paper some of us reported on the activity of Ni-yttria stabilized zirconia (YSZ) composites, used as precursor for the preparation of SOFC anodes, as catalyst of the ethanol SR reaction [13]. The catalyst containing 50% nickel, where well defined Ni crystals are present, was found to be quite efficient, with the production of hydrogen in the temperature range 700–950 K being only limited by the water gas shift and the methane steam reforming equilibria. However, the data suggested that the very complex ESR activity could not be only attributed to large Ni metal particles but also to dispersed Ni on the YSZ support surface. As a confirmation of this, also a 5% Ni-YSZ (which do not reveal the presence of definite Ni crystals to TEM) showed some ESR activity, together with dehydration and dehydrogenation activity.

The aim of the present work is to investigate the nature of such dispersed Ni species over this catalyst, in order to have information on their possible role in steam reforming of ethanol. Vibrational spectroscopic studies of adsorbed carbon monoxide represent, since decades, very informative investigations on the surface state of bulk and supported metal catalysts [14,15]. Infrared studies of CO adsorption at low temperature are largely applied to the characterization of the oxidation and coordination state of cationic metal centers on oxide surfaces [16,17]. This technique can be applied to real powdered supported metal catalysts, in contrast to other more sophisticated techniques. Thus IR spectroscopy of adsorbed CO seems to be the best to reveal the redox properties of Ni-based catalysts.

2. Experimental

2.1. Materials

The catalyst powders (5% and 50% Ni) were prepared by wet impregnation/precipitation technique starting from yttrium-stabilized ZrO₂ (8% yttria, Aldrich powder, 110 m²/g) with Ni nitrate Ni(NO₃)₂·6H₂O (Analytical Carlo Erba, 99%); stoichiometric amount of nitrate precursors was dissolved in distilled water and the amount of YSZ was calculated and added to provide a final loading. As obtained solutions were dried for 4 days at 393 K producing powders, that were calcined at 673 K in Argon for 1 h. Finally the oxide powders were reduced in H₂ at 673 K.

2.2. Characterization techniques

TEM measurements were performed with a transmission electron microscope (JEOL 2010). The powders were suspended in iso-propanol and a drop of the resultant mixture was deposited on a gold grid previously covered with a thin carbon layer.

EDX analysis of elements has been carried out by using a Pentafet Si(Li) detector with a probe diameter of 5 nm.

X-ray powder diffraction patterns have been carried out with a XPert Philips diffractometer using a Cu K α radiation with 0.03 steps in a range from 15 to 100 2 θ with counting time equal to 4 s per step.

FTIR spectra were recorded with a Nicolet Avatar 360 spectrometer accumulating 128 scans at a spectral resolution of 2 cm⁻¹. Self-supporting pellets (ca. 10 mg cm⁻²) were prepared from the sample powders and treated directly in a purpose-made IR cell allowing measurements at ambient and low temperatures. The cell was connected to a vacuum adsorption apparatus allowing a residual pressure below 10–3 Pa. Prior to adsorption, the samples

were activated by treatment at first in oxygen (13.3 kPa) for 1 h at 673 K and then in dynamic vacuum for 1 h at the same temperature.

Carbon monoxide (>99.997 purity) was supplied by Linde AG. Nitrogen monoxide was provided by Messer Griesheim GmbH, and had a purity of >99.0%. Before adsorption CO was passed through a liquid nitrogen trap while NO was additionally purified by fraction distillation.

3. Results

3.1. XRD and TEM data

The XRD patterns of the sample 5% Ni-YSZ as such and after reduction in hydrogen are reported in Fig. 1. The patterns correspond to that of the fluorite-type cubic structure of YSZ, with an extremely small trace of NiO in the pattern of the unreduced sample and of Ni metal in the pattern of the reduced one. The TEM micrograph of the reduced sample, reported in Fig. 2, shows quite homogeneous globular particles of YSZ with 5–10 nm diameter. EDS analysis shows Ni dispersed on such YSZ particles. These data indicate that the sample 5% Ni-YSZ is mostly constituted by Ni species highly dispersed on the YSZ support.

3.2. Low-temperature adsorption of CO on 5% Ni/YSZ

The background spectrum of the activated sample contains, in the OH stretching region, two bands with maxima at 3772 and 3678 cm⁻¹. Lowering the temperature of the sample provokes a small blue shift of both bands and they are settled at 3782 and 3685 cm⁻¹ (Fig. 3, spectrum a). These bands are in positions typical for ZrOH groups of zirconia polymorphs [18] although components due to NiOH groups (found at 3680 cm⁻¹ on NiO [19]) or of YO₂H cannot be excluded.

Adsorption of CO was initially performed at low temperature in order to prevent eventual reactive adsorption. Introduction of CO (2 mBar) at 100 K to the sample results in the appearance of an intense band at 2171 cm⁻¹ and a weak feature at 2083 cm⁻¹ (Fig. 4, spectrum a). Simultaneously, the intensity of the OH bands decreases without production of any OH band at lower frequencies (Fig. 3, spectrum b).

Evacuation at 100 K (Fig. 4, spectra b–n) leads to a decrease in intensity of the principal band at 2171 cm⁻¹ with a simultaneous red shift. At lower coverages two components of the bands become well discernible: (i) one gradually shifting to higher frequencies

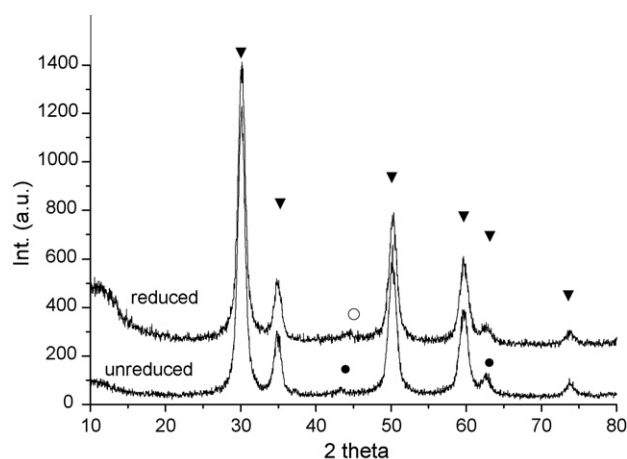


Fig. 1. XRD pattern of 5% Ni/YSZ sample, unreduced and reduced. (▼) Cubic YSZ; (○) Ni; (●) NiO.

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