Surface Science 603 (2009) 2210–2217

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Nickel deposition on γ-Al_2O_3 model catalysts: An experimental and theoretical investigation

Francois Loviat, Izabela Czekaj *, Jörg Wambach, Alexander Wokaun

General Energy Department, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

ARTICLE INFO

Article history:
Received 19 January 2009
Accepted for publication 27 April 2009
Available online 6 May 2009

Keywords:
Nickel catalyst
Alumina support
XPS
γ-Al_2O_3
DFT
Methanation
Metal deposition
Metal–support interactions

ABSTRACT

Recently, surface modifications on a commercial Ni/γ-Al_2O_3 catalyst during the production of methane from synthesis gas were investigated by *quasi in situ* X-ray photoelectron spectroscopy (XPS) [I. Czekaj, F. Loviat, F. Raimondi, J. Wambach, S. Biollaz, A. Wokaun, Appl. Catal. A: Gen. 329 (2007) 68]. The conclusion was that the reactivity and the observed reaction mechanisms on the different Ni particles are influenced directly by both the size and the composition of the particles on the γ-Al_2O_3 support.

In this investigation, Ni deposition and cluster growth on model catalyst samples (10 nm thick, polycrystalline γ-Al_2O_3 on Si(100)) were investigated by XPS. Several steps in the binding energy during Ni deposition indicate changes in the cluster growth. The molecular structure of the catalyst was investigated using Density Functional Theory calculations (StoBe) with a cluster model and non-local functional (RPBE) approach. An $Al_{15}O_{40}H_{35}$ cluster was selected to represent the γ-Al_2O_3(100) surface. Ni clusters of different size were cut from a Ni(100) surface and deposited on the $Al_{15}O_{40}H_{35}$ cluster in order to validate the deposition model determined by XPS.

1. Introduction

The activity and selectivity of supported metal catalysts are strongly influenced by the amount of metal employed, the size of the dispersed metal particles, the composition of the support, and metal–support interactions. In the case of supported metal catalysts, attention has focused on the effect of dispersion, which involves both a surface size effect and a relation between reactivity and the electronic properties of various systems. Nickel-based catalysts supported on γ-Al_2O_3, TiO_2, Pt, zeolites or SiO_2 [2–9] are interesting examples due to their usage in numerous industrial processes [2–5]. Previously, it was shown that nickel particles change their morphology during catalytic reactions by cluster growth processes, and that part of the active clusters are lifted from the support due to carbon deposition and carbon whisker formation [1]. The industrial application of these types of catalysts [2,10] makes the investigation of the role of metal–support interactions for the Ni particle growth and detachment during methanation an important issue. However the complex structure of these catalysts demands further exploration on model catalysts.

The structure, the electronic properties and the reactivity of supported model catalysts have been studied applying a large number of surface science techniques [1]. It was found that the electronic properties of small metal particles depend not only on their size but also on their shape. Thus, the surface structure of the particles is closely related to the chemisorption properties. The presence of the support was recognised to play an important role in the control of the particle morphology. The intrinsic heterogeneity of the supported model catalysts has to be taken into account to understand in detail the catalytic reactions.

Three different theoretical growth modes during metal deposition have been suggested [6–9]: “Volmer–Weber” mode, where the deposited metal forms clusters immediately on the support; “Frank van der Merwe” mode describes a layer-by-layer growth; and “Stranski–Krastanov” mode, which includes transition from an initial layer-by-layer to a consecutive three-dimensional cluster growth at a critical layer thickness. An additional model for the growth mechanism was suggested by Jacobs et al. [4], who describe a complex growth mechanism of Ni on Al_2O_3 when atomic layer epitaxy is applied. Determining the surface composition with LEIS and XPS, the authors conclude that in the initial stage nickel adsorbs as well dispersed atoms and interacts with the strongest binding sites on the alumina support. These Ni centres are the base for the subsequent growth of nickel particles. Some literature data [3,11–13] suggest the possibility that Ni ions migrate from the surface into the bulk forming nickel aluminate, $NiAl_2O_4$, where nickel appears in NiO form. The latter is extremely stable and difficult to reduce to metallic Ni, which is the catalytically active form. Ni^0 particles grow on top of the NiO interface later [1]. Furthermore, charge transfer processes accompanying the metal–support interactions are important additionally as they strongly influence the

---

* Corresponding author. Tel.: +41 056 310 4464; fax: +41 056 310 2199.
E-mail address: izabela.czekaj@psi.ch (I. Czekaj).

0039-6028/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2009.04.032

electronic structure of the Ni surface and therefore the chemical activity of Ni-based catalysts. Applying XPS, Sarapatka [5] studied the interactions between nickel particles and the Al_2O_3/Al support as well as the charge transfer from Al_2O_3 to the deposited Ni. The observed chemical shift of the nickel core levels are attributed to a transfer of electrons from anions of the oxide surface to the dispersed Ni particles. However, there are still many open questions concerning the modification of the electronic structure of Ni-particles and the support (e.g. Al_2O_3).

Several theoretical investigations (mostly DFT calculations) of the pure Ni system [14–16] focussed on the stability and diffusivity of surface species, possible mechanisms for the methane activation and also try to explain graphite/graphene formation on the surface of nickel particles, which could lead to the formation of carbon whiskers. Numerous theoretical studies about pure and modified γ-Al_2O_3 systems were performed previously [17–19]. However to our knowledge, theoretical studies about the combined Ni/γ-Al_2O_3 system are still missing in the literature. A promising study of combined systems – Mo-based catalysts, mainly Mo-methylidene over γ-Al_2O_3 – was already achieved by Handzlik et al. [17] using a cluster model. Following the strategy outlined in this combined model, the effect of metal–support interactions, the role of edges as well as their effect on catalytic reactivity can be studied for the combined Ni/γ-Al_2O_3 system. It is well known from the literature [2] that hydrogenation processes take place on metallic Ni^0 sites, only. Therefore, any other Ni particles, like oxides, hydroxides or carbides are not active for the methanation reaction. However, the co-existence of these inactive Ni compounds either as separate clusters or even inside an otherwise catalytically active metallic cluster are observed over γ-Al_2O_3 support, as well [1]. The latter is likely due to better structural compatibility of these kind of not-reactive nickel compounds (Ni_3C, NiO or $Ni(OH)_2$) with the γ-Al_2O_3 support (see Table 1) thus forming the interface of the otherwise metallic nickel particles.

In contrast to the Ni case, theoretical investigations of the metal–support interactions for the adsorption of Pd on γ-Al_2O_3 have been published already [21,22]. The conclusions are that metal atoms prefer tetrahedral Al sites and create localised atom–surface bonding. Metal–support interface formation is determined by the acid properties of the cationic sites available at support. However, these studies include only single metal adsorption on the support, which correspond only to a very low metal coverage.

When atoms or small metal particles are deposited on a surface, they may create geometrical and electronic structures different from their bulk. This is due to differences in the lattice constants between metal and support. By starting from a small cluster-level, orbitals still have discrete levels. By increasing the number of atoms in the particles so that the particles reach several nm diameters, a band structure appears [23]. In this sense, a model system must consider several surface scenarios, namely the presence of small clusters and large agglomerates, as well as different surface compounds. Furthermore, small particles require studies including support interactions, while in the case of large particles (with sizes of several nm) on the support just a (pure) metal model will be valid for the description.

The goal of the theoretical part of this work is to define the geometry and favourable localisation of metal particles on the support (disregarding steps or kink sites), metal–support interactions and the role of the support in the modification of the geometrical/electronic structure of metal particles and active sites. For the experiments, model catalysts have been chosen due to the fact that they (a) possess flat surfaces, which allow the application of AFM, SE, etc., and (b) allow a sufficient electron tunnelling through the (10 nm thin) γ-Al_2O_3 layer, making XPS and AES investigations possible. This "ideal" definition of the surface allows the comparison of experimental data with theoretical modelling, leading to additional insights into the topology of metal particles on the support. The interactions of different nickel clusters are presented in details as a prerequisite to understanding the role of metal–support interactions in catalytic activity and stability of metal particles.

This paper consists of the following parts: information about the crystal structure of the material used in our theoretical calculations is presented in Section 2. Experimental and computational details are described in Section 3. The results are presented in Section 4. In Section 4.1, THE results obtained from XPS experiments are presented and the role of the deposition time with regard to changes of the chemical state of surface is shown. The DFT modelling of Ni/Al_2O_3 interface is described in Section 4.2. Finally, the conclusions are summarised in Section 5.

2. Crystal structure of Al_2O_3 and nickel clusters

The cubic phase [24,25] of defective alumina spinel, Al_2O_3, is described by the space group Fd-3m (No. 227) with lattice constants $a = b = c = 7.911$ Å. The crystal unit cell of defective alumina spinel contains 56 atoms, where Al occupies two different types of positions – 8a, 16d, and oxygen 32e sites.

Inside the bulk both AlO_6 octahedra and AlO_4 tetrahedra are present with Al–O distances equal 1.94 Å and 1.78 Å, respectively. The bulk is built by sixfold and fourfold coordinated aluminium and threefold and fourfold coordinated oxygen. Fig. 1 shows the structure of the γ-Al_2O_3(100) surface. Two different aluminium sites with fourfold and fivefold coordinated aluminium, AlO_4 and AlO_5, as well as two different threefold coordinated oxygen sites, O(3) and O′(3), have been distinguished. It is important to note that Al(4) is always located below the Al(5) centres and that the rows of AlO_5 pyramids are separated from each others by rows of AlO_4 tetrahedra.

Two surface planes are predominantly detected in the diffraction patterns of γ-Al_2O_3, namely the (1 1 0) and (1 0 0) surfaces. Following some previous studies of alumina by Handzlik et al.

Table 1
Comparison of structure parameters.

Compound	M and Y definition	M–M distance (Å)	Differences in respect to Ni/γ-Al_2O_3 (%)	M-Y distance ((Å)	Crystal structure
(a) NiY_x compounds and support [24–26].					
Ni	Ni_{metal}	2.49	–/−10.4	–	Cubic
NiO	Ni, O	2.95	+18.5/+6.1	2.08	Cubic
$Ni(OH)_2$	Ni, OH	2.71	+8.8/−2.5	2.01, 2.39	Trigonal
$NiAl_2O_4$	Ni or Al, O	2.85	+14.5/+2.5	1.83, 1.96	Cubic
γ-Al_2O_3	Al, O	2.78	+11.6/–	1.78, 1.93	Cubic
Compound	M–M lateral distance (Å)	M–M distance (Å)	Differences in respect to γ-Al_2O_3 (%)	M–O/O–O distance (Å)	
(b) Si, SiO_2 and γ-Al_2O_3 compounds with cubic structure [32,33]					
Si	3.80/5.38	2.33/3.80	−28.9/−39.2	–	
SiO_2	7.15/5.05	3.09/5.92	−5.8/−5.3	1.55/2.53	
γ-Al_2O_3	7.91/2.78	3.28/6.25	–	1.78, 1.94/2.78	