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Sulphur poisoning of Ni catalysts used in the SNG production from biomass: Computational studies

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ABSTRACT

The purpose of this study was to investigate the sulphur deactivation mechanism during an industrial methanation process, but also after catalyst regeneration. In the present work we extended our computational investigations to study the adsorption of sulphur poisoning compounds on the Ni/Al_2O_3 catalyst. The focus was to study possible catalyst changes and thus the modified catalytical behaviour of the nickel particles, as well as to see differences in the poisoning behaviour, when sulphur adsorbs either on the Ni particle or on the support. This was done using Density Functional Theory calculations (StoBe) with cluster model and non-local functional (RPBE) approach. For modelling the catalyst, an $Al_{15}O_{40}H_{35}$ cluster has been selected representing the γ-Al_2O_3(1 0 0) surface, and Ni metal particles of different sizes were cut from a Ni(1 0 0) surface and deposited on the $Al_{15}O_{40}H_{35}$ cluster. Several poisoning agents have been found to be stable on both Ni clusters and alumina support such as COS, H_2S, or hydrogen thiocarbonates.

1. Introduction

Recently, surface modifications on a commercial Ni/Al_2O_3 catalyst during the production of methane from synthesis gas were investigated by *quasi in situ* X-ray photoelectron spectroscopy (XPS) [1,2]. Further, we studied the sulphur poisoning processes on the Ni/Al_2O_3 catalyst used for the methanation process [3]. The purpose of this study was firstly to investigate deactivation mechanisms caused by sulphur adsorption during an industrial methanation process and secondly possible regeneration routes. The reactivation attempt was done with water at methanation relevant temperature with idea to remove carbon and hydrocarbons from blocking nickel surface sites. It was reported by us [3] that after a reactivation the catalyst was active for a much shorter time when compared with a newly loaded Ni/Al_2O_3 catalyst. The samples had been collected from a methanation reactor fed with producer gas from the industrial biomass gasifier in Güssing (Austria). S 2p X-ray photoelectron spectroscopy (XPS) pointed at the presence of sulphide and sulphate, but the data were too noisy to reach more specific conclusions as well as the samples had been transported in air conditions. XANES analysis of S K-edge showed unequivocally that the catalyst could not have been deactivated by inorganic H_2S only, but more by organic-type sulphur compounds.

Also from other fields of research [4], it was observed that sulphur compounds, such as SO_2, significantly degraded the Pt electrocatalysts in fuel cells. Sulphur compounds deactivate heterogeneous catalysts by adsorbing to metal active sites, forming a strong chemical bond between sulphur atoms and the active metal catalysts. Another common air contaminant, carbonyl sulphide (COS), has not been studied in conjunction with SO_2 or H_2S. In industrial catalysts, considerable attention has been focused on the role of sulphur transition-metal complexes in catalysis poisoning [5], where also CS_2 and COS were found to be important sulphur-transfer reagents. Both compounds have been considered as possible sulphur sources for preparing thin layers of semiconductor materials.

Several studies have been initiated to understand the mechanism of the sulphur poisoning process, to improve the sulphur tolerance, and to find ways to regenerate the catalyst. It has been proposed that the mechanism of sulphur poisoning is very similar to that of the NO_x storage process [6,7]. Under lean conditions, SO_2 is oxidized on the precious metal site and then reacts with the support and the NO_x storage component. Under rich conditions, sulphur containing species interact with the noble metal and sulphides, such as PtS, are formed.

The effect of the carrier material and additives on the sulphur adsorption–desorption behavior was noticed for the first time by the researchers from Toyota [8]. By increasing the acidity of the support, they obtained a decrease of the sulphur deposit. The amount of the formed sulphated species was lower for the TiO_2 and SiO_2 in

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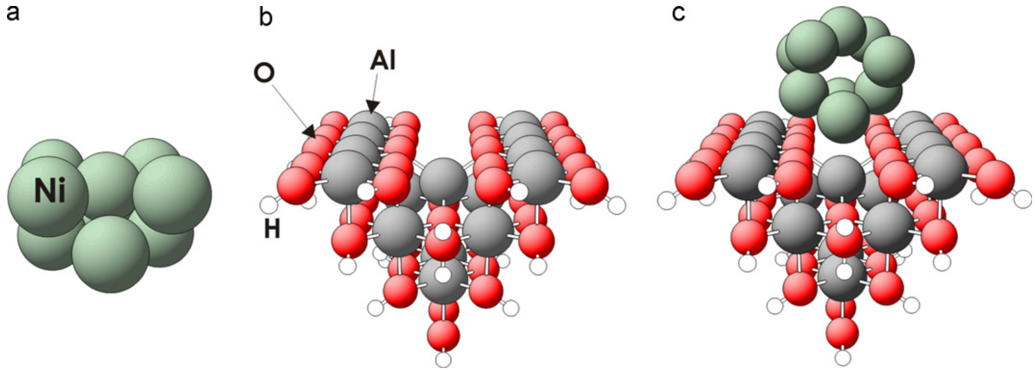

Fig. 1. Geometric structure of clusters: (a) $Ni_9(1\,0\,0)$, (b) $Al_{15}O_{40}H_{41}(1\,0\,0)$, (c) $Ni_9/Al_{15}O_{40}H_{35}$.

comparison to the γ-Al_2O_3 support. This suggests that the lower S deposit is more related to the improvement of the SO_2 poisoning resistance. The influence of different promoters on the sulphate decomposition temperature has also been studied [8,9]. It was observed that a beneficial effect is produced by doping Al_2O_3 with Li and afterwards mixing with TiO_2. A further thermal stability improvement was recently obtained by using a Ti doped nanocomposite of Al_2O_3 and ZrO_2–TiO_2 as support [10].

In the present work we extended our computational investigations to study the adsorption of sulphur containing compounds on the Ni/Al_2O_3 catalyst for a better understanding of chemical processes appearing on regenerated catalysts. The focus was to study possible catalyst changes and the thus modified catalytical behaviour of the nickel particles, as well as to see differences in the poisoning behaviour when sulphur either adsorbs on Ni particles or on the support.

2. Computational details

In our DFT studies the Ni and γ-Al_2O_3 support surfaces are modelled by Ni_9 (Fig. 1a) and $Al_{15}O_{40}H_{35}$ clusters (Fig. 1b). Both clusters represents (1 0 0) surface of catalysts. For the γ-Al_2O_3, cluster neutrality with respect to the surface is achieved by saturating the peripheral oxygen centres with hydrogen atoms placed at the standard OH distance, $R_{OH} = 0.97$ Å. Fig. 1c shows cluster $Ni_9/Al_{15}O_{40}H_{35}$, which represents nickel particle at the support.

The electronic structure of clusters was calculated by *ab initio* density functional theory (DFT) methods (program code StoBe [11]) using the non-local generalized gradient corrected functionals according to Perdew, Burke, and Ernzerhof (RPBE) [12,13], in order to account for electron exchange and correlation. All Kohn-Sham orbitals are represented by linear combinations of atomic orbitals (LCAO's) using extended basis sets of contracted Gaussians from atom optimizations [14,15]. During relaxation, the nickel atoms in the supported clusters had allowed to move in 3D space.

3. Results and discussion

Several poisoning agents have been found to be stable on both Ni clusters and pure alumina support (see Fig. 2), such as carbonyl sulphide (COS), hydrogen sulphide (H_2S), or hydrogen thio-carbonates in different orientations on the surface (OHOCS or SHOCO). The adsorption energy for particular adsorbates is shown in Table 1.

Our results clearly demonstrate that sulphur particles are not only stabilized on the nickel, but also on the support surface. The latter two species can be expected present at the catalyst surface during SNG production from biomass-based producer gas [16].

Carbonyl sulphide and hydrogen sulphide species have been found to be most stable adsorbates in the systems investigated

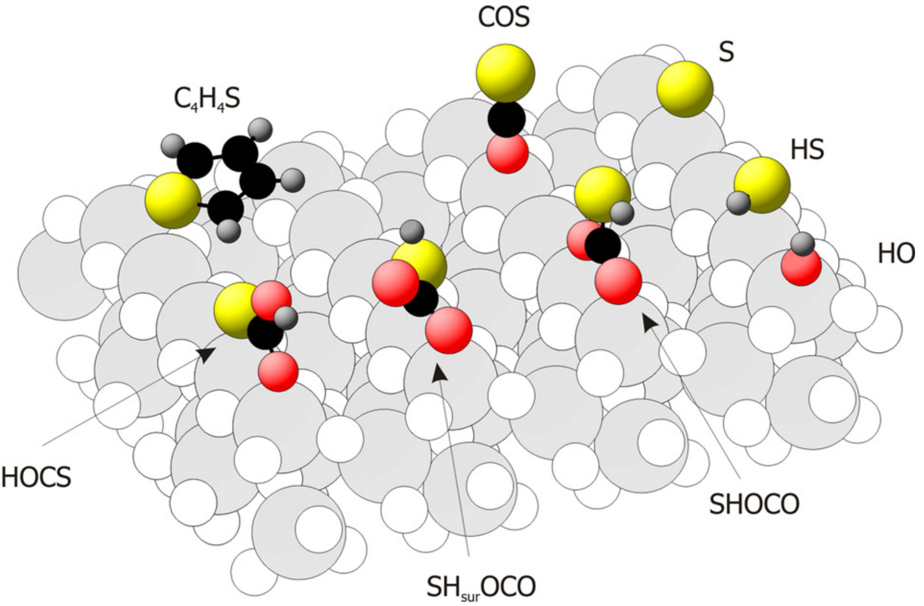

Fig. 2. Sulphur compounds at γ-Al_2O_3.

Table 1
The adsorption energies [eV] for different sulphur compounds at Ni/Al_2O_3.

Species	Ni_9	Al_2O_3	Ni_9/Al_2O_3
COS	−4.64	−4.58	−4.44
OHOCS	−2.42	0.02	−0.84
SHOCO	−3.86	−2.77	−2.93
HS	−5.11	−3.35	−4.93
C_4H_4S	−1.74	−0.31	−1.46

here, i.e., pure nickel, γ-alumina as well as the combined Ni/Al_2O_3 system. We found that the COS species is more strongly bound (adsorption energy −4.58 eV) to the support surface than to the supported nickel particles (adsorption energy −4.44 eV). Whereas HS^- is much more strongly bound into nickel pure (−5.11 eV) and supported particles (−4.93 eV) compare to support (−3.35 eV). The hydrogen thio-carbonates in different orientations on the surface, OHOCS and SHOCO, are also found to be stable, however with lower adsorption energies compare to COS or HS^- (see Table 1).

Additionally, we found out from our theoretical calculations that thiophene is relatively weakly bound to the catalyst compared to the other adsorbates investigated here. But, in our opinion, thiophene could still play a crucial role in forming COS species and poisoning the Ni nanoparticles with its carbonaceous segment. Moreover, our results suggest that, during the catalyst re-activation process, a part of the COS species residing at the support are responsible for re-poisoning of the nickel particles under methanation reaction conditions. After catalyst regeneration in the hydrogen/water-rich conditions, the COS species hydrolysed via OHOCS/SHOCO intermediates into H_2S (or alike species), which can easy re-poison the yet not deactivated Ni particle sites.

Summarizing the information presented above, a possible mechanism of surface processes occurring during the methanation, including carbon and sulphur poisoning over the Ni/Al_2O_3 catalyst surfaces, is shown in Fig. 3 (see also [1]). The "as delivered" catalyst surface consists of NiO and $Ni(OH)_2$ particles both in oxidized and hydratized form (Fig. 3a). The oxidized/hydratized Ni particles are not active in the methanation reaction. Activation under H_2 leads to a partial reduction of the surface Ni^{2+} species forming Ni^0 (reduced catalyst; Fig. 3b). The reactive surface contains, beside the Ni^0, also mixed Ni^0 + hydratized/oxidized NiO_xH_z particles, e.g. NiO and $Ni(OH)_2$. The mixed nickel compounds (e.g. nickel oxides and hydroxides) can be present in the core of large particles (differences between (a) and (b) in Fig. 3). During the methanation process and in the presence of hydrocarbons, the surface becomes decorated with carbon as well as slowly by different sulphur species (working catalyst, phase 1; Fig. 3c). This picture is typical for the results after a few hours of methanation. Longer methanation results in a severe carbon deposition and C-whiskers formation, followed by a detachment of the Ni particles from the support, and the impact from sulphur poisoning (working catalyst, phase 2; Fig. 3d and [1]). This picture is typical for long methanation runs: up to 200 h. Due to methanation conditions (rich in carbon, oxygen, hydrogen, and water), the catalyst surface is poisoned by different sulphur compounds (as discussed above). It is important to remove the deposited carbon, which results in partial loss of the Ni particles (regenerated catalyst; Fig. 3e). However, part of stable sulphur–carbon compounds stay at the support and lead to a re-poisoning of the recovered Ni^0 surface with the regenerated catalyst. In our opinion, possible ways to deal with this problem is to change the regeneration conditions, or, the support, or to develop a more-sulphur resistant support material, such as metal alloys. Whatever the case, more studies are required on supported catalyst materials and different sulphur poisoning agents. Studies in this direction are actually being performed at the PSI, both at experimental and theoretical level.

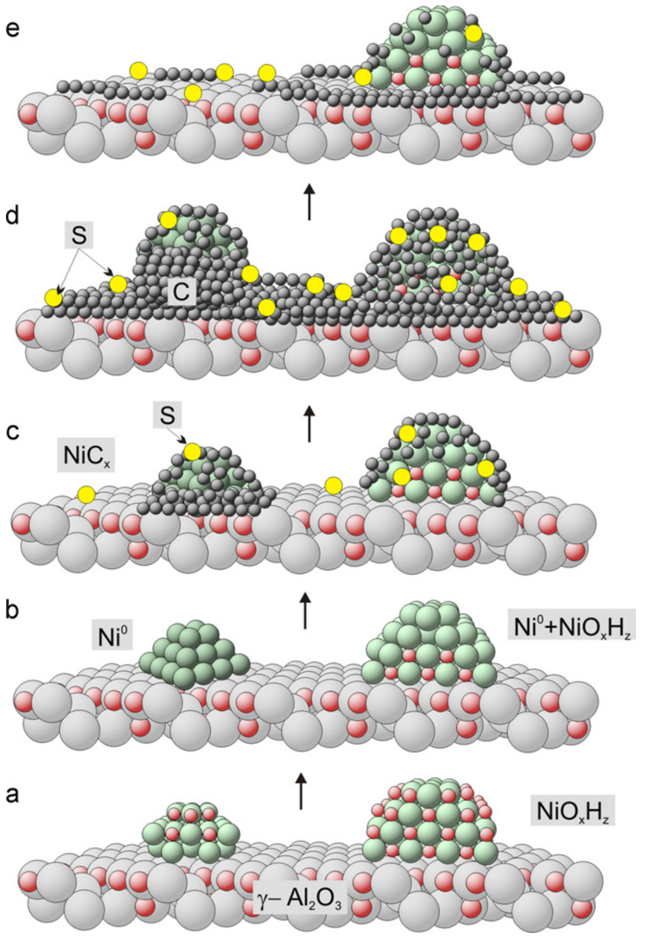

Fig. 3. The suggested mechanism of processes during the methanation at the Ni/Al_2O_3 catalyst surface: (a) fresh catalyst; (b) reduced catalyst; (c) initial state of working catalyst; (d) working catalyst with carbon and C-whiskers as well as sulphur deactivation (S) and (e) catalyst after regeneration (with some reminding C- and S-poisons).

4. Conclusions

Different sulphur poisoning agents have been found to be stable on both Ni over alumina support system, such as carbonyl sulphide (COS), hydrogen sulphide (H_2S), or hydrogen thio-carbonates in different orientations on the surface (OHOCS or SHOCO).

Our results clearly demonstrate that sulphur particles are not only stabilized on the nickel, but also on the support surface with different strength. The most stable species are carbonyl sulphides and hydrogen sulphide. The latter two species are suspected to be present at the catalyst surface under SNG production conditions [16].

Carbonyl sulphide and hydrogen sulphide species have been found to be more stably bound to the support compared with S species bound to the supported nickel particles. In conclusion, during the catalyst re-activation process, a part of the COS species remained at the alumina surface and can principally re-poison the nickel particles under methanation (or other) conditions and hereby shorten the activity of the Ni/Al_2O_3 catalyst considerably.

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