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Sintering of alumina-supported nickel particles under amination conditions: Support effects

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Abstract

The sintering of alumina-supported nickel particles has been studied after heat-treatment in ammonia + hydrogen at 523 K and 250 bar. The investigated samples were nickel supported on γ-alumina, transalumina and α-alumina, and co-precipitated nickel oxide-alumina. The sintering process was mainly followed by hydrogen chemisorption. The samples were also characterised by specific surface area measurements, X-ray diffraction, temperature programmed desorption of ammonia, *in situ* FTIR spectroscopy and temperature programmed reduction. For nickel supported on γ-alumina, up to 40% of the initial metal surface area remained after the heat-treatment in ammonia + hydrogen compared with α-alumina or transalumina where only 10–20% of the initial metal surface area remained after the heat-treatment. The sintering can be correlated to the bond strength between the metal particle and the support. The larger the number of low-coordinated surface aluminium sites is, as for γ-alumina, the stronger the metal–support interaction is and this in turn suppresses diffusion of nickel particles and/or atoms.

Keywords: Sintering; Nickel; Alumina; Lewis acids sites; Coordination number; Amination catalysis

1. Introduction

Heterogeneous catalysed amination of alcohols is established as the most important industrial process for manufacture of different aliphatic and aromatic amines [1–3]. A typical catalyst used for this application is nickel dispersed on a support material like silica or alumina [3]. Although supported nickel catalysts usually have high initial activity and selectivity for amination reactions the activity will decrease with time-on-stream, i.e. the catalyst is deactivated.

Deactivation is a problem of great and continuing concern in industrial catalysis and has thus been a subject of many reviews [4–7]. One of the most serious aspects of deactivation of supported catalysts is thermal degradation with concomitant loss of active metal surface area [5,8–16]. This phenomenon has proven to be the major deactivation mechanism of supported nickel catalysts in ammonia/hydrogen atmosphere, i.e. under amination conditions [17]. This type of degradation is normally referred to as sintering since small metal particles are converted into larger ones with lower surface-to-volume ratio. The driving force for sintering is to minimise the surface energy by increasing the co-ordination number of the surface atoms. Larger particles are more stable than smaller ones due to the fact that the metal–metal bond energies usually are considerably higher than the metal–support interactions. The detachment of a nickel atom from a nickel cluster requires typically 431 kJ/mol [18] whereas the binding energy between metal particles and the support is in the range of 5–15 kJ/mol [4,19].

Factors affecting the stability of the metal particle towards sintering include temperature, surrounding atmosphere (gas composition), support material, metal–support interaction, particle shape, particle size, support roughness, pore size and impurities of the support or in the metal. The most pronounced factor of these is the temperature, the process is strongly temperature dependent and sintering is generally observed for temperatures above 700 K [4,20,21]. The so-called Hüttig and Tamman temperatures indicate the temperature at which sintering starts [6]. When $T_{\text{Hüttig}}$ is reached atoms at defects

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will become mobile and at T_{Tamman} atoms in the bulk will start to diffuse. The following semi-empirical relations for $T_{\mathrm{Hüttig}}$ and T_{Tamman} are commonly used $T_{\mathrm{Hüttig}} = 0.3 \times T_{\mathrm{melting}}$ and $T_{\mathrm{Tamman}} = 0.5 \times T_{\mathrm{melting}}$. However, the temperature when the particle becomes mobile depends on texture, size and morphology, e.g. small particles may diffuse at temperatures below $T_{\mathrm{Hüttig}}$ [6]. Previously we have shown that fairly large nickel particles, nm sized, on γ-alumina sinter rapidly at the relatively low temperatures between 483 and 523 K in ammonia + hydrogen atmosphere [17], this is equal or below the $T_{\mathrm{Hüttig}}$ for nickel ($T_{\mathrm{Hüttig,Ni}} = 518$ K).

Metal–support interactions affect the spreading, wetting and re-dispersion of metal particles on the support [22], however, the fundamental understanding of these metal–support interactions is still limited. Metal–alumina interactions have experimentally been studied for surfaces of ordered aluminium oxide films [23,24]. Theoretical calculations have also been performed for α-alumina and, recently, also for γ-alumina surfaces [25–27]. These calculations have shown that transition metals like Co, Rh, Ir and Pd bind in bridge or hollow sites both to oxygen and aluminium on the alumina surfaces. The physicochemical properties of alumina can be controlled by the calcination temperature, where the number of Lewis acid sites decreases in the following order γ-alumina > δ-alumina > θ-alumina > α-alumina. The influence of the type of support material on the sintering of different active metals has previously been studied. For Pt, the stability against sintering decreases in the following order Pt/alumina > Pt/silica > Pt/carbon in vacuum [4]. The stability of supported metals decreases in the following order Pt > Pd > Ni > Cu in reducing atmosphere [4].

The presence of specific additives or reactions between the support and the active metal are also known to reduce the sintering of the active metal particles [28–32]. We have previously shown that the stability may be enhanced by co-impregnation of nickel and different promoters (i.e. oxides of Li, Na, K, Mg, Ca, La and Ce) and by creation of interlaying nickel aluminate between the active nickel species and the alumina support [33]. The support can also affect the sintering by physical hindrance, e.g. the pore structure and surface roughness which may affect the final size of the nickel particles [34]. Reactions between the nickel particles and the feed, for instance carbon monoxide, can also accelerate the sintering [32,35].

The aim of the present study is to investigate the stability (against sintering) of nickel supported on five different alumina support materials in ammonia + hydrogen atmospheres, in view of the industrial application as an amination catalyst. The tested samples were nickel impregnated on γ-alumina tablets, transalumina tablets, α-alumina tablets, γ-alumina extrudate and co-precipitated nickel alumina extrudate. Hydrogen chemisorption, nitrogen physisorption, X-ray diffraction, temperature programmed desorption of ammonia, *in situ* FTIR spectroscopy and temperature programmed reduction were used to follow the sintering process.

2. Experimental methods

2.1. Catalyst preparation

The 10 wt.% nickel on γ-alumina tablets were prepared by incipient wetness impregnation. The support material, γ-alumina tablets Al-4504 T1/8″, from Engelhard, used as received, with a specific surface area of 90 m^2/g, was impregnated with an aqueous solution of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) from Merck, p.a. quality. The impregnation was performed using a nickel nitrate concentration of 5 mmol/g at a pH of 2.3. The impregnated sample was then dried at 393 K for 2 h and finally calcined in flowing air at 673 K for 4 h.

The 3.6 wt.% nickel on transalumina tablets, 1 wt.% nickel on α-alumina tablets and the 10 wt.% nickel on γ-alumina extrudates were prepared accordingly to the method described above with different nickel nitrate concentrations to achieve a comparable nickel dispersion on the alumina. The γ-alumina extrudates Al-3992 E1/8″, transalumina tablets and α-alumina tablets Al-3980 T1/8″, from Engelhard, with a specific surface area of 165, 39 and 10 m^2/g, respectively, were used as received.

The co-precipitated 16 wt.% nickel with alumina as extrudate, from Engelhard, was used as received.

To establish homogeneous sampling and to avoid mass- and heat transfer limitations in the experiments, the calcined samples were crushed and sieved and the particle size fraction between 150 and 300 μm was used in the heat-treatment experiments.

2.2. Heat-treatment

One sample from each catalyst batch was subjected to heat-treatment in ammonia + hydrogen atmosphere. The heat-treatment was performed in a 95 ml stainless steel cylinder. The cylinder was loaded with fresh sample together with 10.5 g ammonia and pressurised with hydrogen to 42 bar at room temperature. The cylinder was then placed in a furnace at 523 K for 96 h. The cylinder was finally cooled to room temperature and the pressure was released. The weight of the loaded cylinder was measured before and after the heat-treatment to assure no leakage.

2.3. Sample characterisation

The fresh samples and heat-treated samples were divided into several portions where different portions were used for different analyses. This was done to avoid correlations between the treatments in different analysis methods.

2.3.1. Chemisorption measurements

The nickel dispersion of the samples was determined by hydrogen chemisorption using an ASAP 2010C instrument from Micromeritics. The samples were reduced at 723 K for 2 h before each analysis. The measurements were carried out volumetrically at 308 K. A detailed description of the experimental procedure and the treatment of the results from