



Regeneration of a 15% Ni/SiO₂ phosphorus poisoned catalyst and subsequent effects of the support on recovery of the catalytic activity

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ABSTRACT

The deactivation of a 15 wt.% Ni supported on SiO₂ (15 NiSi) catalyst by triphenylphosphine during the hydrogenation of octanal to octanol, and subsequent regeneration, was studied. Characterization of the catalyst by hydrogen chemisorption, TPR, powder XRD, ICP-OES, BET surface area analysis, and TEM showed the presence of large nickel clusters with a poor metal dispersion for the fresh catalyst prior to deactivation. This, however, had a positive effect, since the catalyst was very active and highly tolerant of the triphenylphosphine poison, taking significantly longer on stream to deactivate compared to a 15% Ni supported on alumina catalyst (15 NiA). The 15 NiSi catalyst was also effectively regenerated using a tandem octanol wash-hydrogen treatment regeneration protocol, which restored the conversion to 76%, after deactivation to 20%, and restored the octanol selectivity to that observed for the non-poisoned 15 NiSi catalyst, which was 86%. The present catalyst was also shown to be more effectively regenerated when compared to the 15 NiA catalyst. Regeneration of the poisoned catalyst did not remove phosphorus, but restored large nickel particles and resulted in the formation of Ni₂P, which is active for octanal hydrogenation.

1. Introduction

The hydrogenation of oxo-aldehydes to primary alcohols makes use of supported nickel catalysts, and these alcohols find use in a number of industrial applications, such as solvents for chemical processes, as surfactants for detergents, or as polymer plasticizers [1–3]. These catalysts are easily exposed to phosphorus via process upsets from the hydroformylation section [4]. Previous studies have shown that nickel catalysts undergo deactivation by phosphorus poisoning, brought about by the irreversible chemisorption of phosphorus onto nickel active sites, thereby passivating the nickel surface, rendering it inactive [5]. Additionally, it has been shown that the exposure of nickel catalysts to phosphorus also leads to sintering of the active phase, induced by the reaction of nickel and phosphorus, forming an amorphous nickel phosphide phase that makes recovery of the catalytic activity difficult under process conditions [6–10].

Studies have reported that the support may influence the sensitivity of the catalyst to deactivation by poisoning, with acidic supports reportedly providing a measure of robustness against poisoning [11]. This was attributed to the formation of small, electron deficient metal particles on the acidic supports [12,13].

Furthermore, the interaction between the support and some poisons was reported to improve the catalysts robustness against poisoning.

Studies that have investigated the deactivation of alumina supported catalysts by sulfur poisoning have reported that alumina acts as a sulfur trap, which reportedly improves the catalysts' sulfur tolerance [12,14,15]. Furthermore, Czekaj et al. [12] mention that an increase in the acidity of the support improves poison resistance by lowering the sulfur deposition on the catalyst surface.

The support also affects the dispersion of the metal, and this is influenced by the strength of the interaction between the metal and the support. A strong metal support interaction results in the formation of small, well-dispersed catalyst particles, while a weak metal support interaction results in the formation of large, poorly dispersed metal particles. The strength of the metal support interaction (MSI) varies for different oxides, and metals tend to interact more strongly with alumina compared to silica [16–18].

It has been reported that smaller supported metal particles are electron deficient, which is attributed to the strong withdrawal of electron density from the metal particles by the support, when the support used interacts strongly with the metal [19]. Hence, due to their electron deficient character, it has been mentioned that smaller metal particles are more robust against deactivation by poisoning [20]. The robustness of electron deficient metal centres against poisoning was also mentioned by Garreto et al. [21], whose study found that alloying Pt with Ge resulted in a catalyst that was resistant to sulfur poisoning

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due to Ge reducing the electron density of Pt centres [21]. Sheu *et al.* [22] also found that smaller Pd particles were more robust against poisoning by hydrogen sulfide.

In a previous study, we showed that the regeneration of an alumina supported nickel catalyst after phosphorus poisoning could be successfully demonstrated [4]. The catalytic activity was recovered using different regeneration methods, which included a hydrogen treatment, octanol wash and a tandem octanol wash-hydrogen treatment regeneration protocol. The tandem regeneration experiment was found to be most effective. The present study is focused on the regeneration of a silica supported nickel catalyst, and a comparison is made to the alumina-supported catalyst to establish whether the support has any effect on the regeneration of the deactivated nickel catalysts.

2. Experimental

2.1. Catalyst synthesis

Silica supported nickel with a 15 wt.% loading (15 NiSi) was prepared using the wet impregnation technique. Silica (Alpha Aesar, $140 \text{ cm}^2 \text{ g}^{-1}$) was impregnated with a solution of a nickel precursor ($\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$, Sigma Aldrich) at room temperature, with continuous stirring. The support and nickel nitrate solution were stirred for three hours at room temperature, ultrasonicated at room temperature for half an hour, and then heated slowly to evaporate the excess solvent. The resulting paste was then dried in an oven overnight at 110°C . The resultant solid was calcined at 550°C for five hours under flowing air, pelletized to between 300–600 micron, and reduced *in situ* at 350°C prior to the hydrogenation reactions.

2.2. Catalyst characterization

The surface area of the calcined 15 NiSi and deactivated/regenerated catalyst were measured using the BET method with a Micromeritics Tristar II 3020 surface area and porosity analyser, using physisorbed nitrogen at 77.5 K. Prior to analysis, the samples were degassed under nitrogen flow at 150°C for two hours, then overnight at 200°C under a flow of nitrogen. The samples were then cooled under a flow of nitrogen, weighed, and analysed.

The accurate nickel and phosphorus loadings were quantified using inductively coupled plasma-optical emission spectroscopy on a Perkin Elmer Precisely Optima DV 5300 optical emission spectrometer. The samples were digested in 65% nitric acid prior to analysis, and the calibrations were performed using phosphorus and nickel standard solutions.

Hydrogen chemisorption measurements were carried out to determine the dispersion and crystallite size of nickel on silica. The measurements were performed on a Micromeritics ASAP 2020 Chemisorption analyser. A 50 mg sample of the catalyst was placed between two layers of quartz wool in a quartz U-tube and degassed at 200°C overnight under vacuum on the instrument. The catalyst was then heated at a rate of $10^\circ\text{C min}^{-1}$ to 400°C , then reduced at this temperature for 240 min. The catalyst was then cooled to 50°C , the temperature at which the chemisorption analysis was carried out.

Powder X-ray diffraction (PXRD) patterns were obtained with a Bruker Advance D8 diffractometer equipped with an Anton Paar XRK 900 reaction chamber and TCU 750 temperature control unit. The instrument employed a Cu K α radiation source with a wavelength of 0.15406 nm. Where X-ray analysis of the reduced catalyst was required, after reduction at 350°C for 12 h, the catalyst was removed from the reactor and taken to the XRD instrument as quickly as possible.

A temperature programmed reduction experiment was carried out to study the reducibility of the catalyst, and the analysis were performed on a Micromeritics Autochem 2920 coupled with a MKS Instruments Cirrus Mass Spectrometer. The sample (approximately 50 mg) was placed between two layers of quartz wool in a quartz U-

tube. The tube was fitted with a thermocouple for continuous temperature measurements. Prior to analysis, the sample was dried under helium at a flow of 50 ml min^{-1} by heating the sample from room temperature, at a rate of 5°C min^{-1} , to 120°C and held there for ten minutes to remove any adsorbed moisture. The sample was thereafter cooled to room temperature. The analysis was performed by heating the sample from room temperature to 950°C , at a rate of $10^\circ\text{C min}^{-1}$ under a flow of pure hydrogen at 50 ml min^{-1} . The sample was subsequently held at 950°C for ten minutes, while mass spectrometry was used to detect the evolved gases. The amount of hydrogen consumed by the sample during reduction was measured using a thermal conductivity detector (TCD).

Transmission electron microscopy images were obtained with a Jeol JEM-1010 electron microscope, and the images were processed with iTEM software. High resolution transmission electron microscopy imaging and selected area electron diffraction patterns were obtained on a Jeol JEM-2100 microscope using iTEM software for imaging and an accelerating voltage of 200 kV. The catalyst samples were suspended in ethanol and sonicated for ten minutes, then loaded on copper grids prior to analysis.

2.3. Catalyst testing

Catalytic tests were conducted in a stainless steel, down flow fixed bed reactor. For each test, 2 mL (1.1 g) of the catalyst was diluted with 2 mL of 24 grit carborundum, then packed in the reactor tube between two layers of glass wool to make the catalyst bed. The rest of the tube was packed with 24 grit carborundum. The catalyst was reduced at 350°C for twelve hours prior to each reaction, then cooled to 140°C , the temperature at which the hydrogenation reactions were carried out. Afterwards, the reactor was pressurized to 50 bars.

Catalytic tests were conducted for the hydrogenation of 10% octanol in octanol (labelled clean feed), accelerated deactivation experiments were conducted by doping the feed with 500 ppm of triphenylphosphine (TPP-feed). During each experiment, the clean feed was first hydrogenated until steady state activity was reached, then the feed was switched to the one containing triphenylphosphine, and the decline in conversion was monitored by a Perkin Elmer Clarus 500 gas chromatograph equipped with a flame ionization detector. After the conversion stabilized with the poisoned feed, it was stopped, and the clean feed was reintroduced until once again steady state activity was achieved. For the regeneration experiments, the feed was stopped, and the pressure was slowly released to atmospheric pressure. The temperature was increased to 200°C , followed by the applicable regeneration experiment. Three different regeneration experiments were attempted, as reported previously [4]. Briefly, the catalyst after deactivation was regenerated by either flowing hydrogen over it, washing with octanol, or conducting a tandem octanol wash-hydrogen treatment (combined regeneration). All three regeneration experiments were carried out at atmospheric pressure. All experiments were conducted in duplicate, with carbon balances of 99–101%.

3. Results and discussion

3.1. Characterization results

3.1.1. Powder X-ray diffraction of the calcined 15 NiSi catalyst

Fig. 1 shows the X-Ray diffractogram of the calcined 15 NiSi catalyst, which displays sharp peaks of a relatively high intensity that correspond to NiO (JCPDS card number 78-0643) [23], and a broad peak at the 2θ angle of 20° was attributed to silica [24]. The sharpness of the peaks indicates highly crystalline and large nickel oxide particles, due to a weak interaction between the metal oxide and silica [18]. This leads to a poor dispersion of the metal oxide on silica and, hence, results in the formation of large nickel oxide clusters [18].

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