



Systematic Investigation of Products Formed During Synthesis of Ni, W, Cu/Kieselguhr Catalyst by X-ray Diffraction

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Catalytic hydrogenolysis of sucrose is industrially important for the production of glycerol, ethylene glycol and propylene glycol. Nickel(II) catalyst promoted by W and Cu and supported on kieselguhr was synthesized in the aqueous medium by co-precipitating compounds of nickel, copper and tungsten on kieselguhr from solution of their salts using sodium carbonate. The composition of the constituents present along with desired catalyst formed during synthesis has profound impact on its catalytic activity. Therefore, the present study deals with the synthesis and characterization of all the constituents' major and minor products formed during synthesis of catalyst both unreduced and reduced by X-ray diffraction studies. The results indicated the formation of appreciable amount of nickel hydro silicates and small amount of ionic nickel carbonate and nickel carbonate hydrate in the unreduced catalyst. Besides the formation of major product, heteropoly acid and nickel tungsten silicide were also present in the unreduced catalyst. The catalyst was reduced at 600 °C before carrying the hydrogenolysis reactions and the reduced products were also analyzed for the composition, when the catalyst activity was the maximum. The various chemical reactions involved in the synthesis procedure have been discussed.

Key Words: Hydrogenolysis, Catalyst, Kieselguhr, Glycerol.

INTRODUCTION

Catalytic hydrogenolysis of sucrose yields industrially important glycerol, ethylene glycol and propylene glycol. There is a need of a catalyst providing high product yields under milder reaction conditions. Keeping this in view the catalyst promoted by W and Cu and supported on kieselguhr was synthesized for the catalytic hydrogenolysis of sucrose¹. In order to improve and optimized the procedure, the understandings of the chemistry of catalyst synthesis is imperative. Kieselguhr supported catalyst has been synthesized by various workers by employing different raw material but their synthetic chemistry has not been discussed. Kusama *et al.*² found that catalyst prepared from nickel chloride was less studied than various Ni catalysts deposited on classical support (SiO₂, AlO₃, MgO) and on less conventional material. Preparation conditions were so chosen that avoid strong metal interaction of Pt/TiO₂ type. Aguinagr *et al.*³ investigated the factors reactive than that prepared from nickel nitrate because presence of unreduced chlorides. Waterman and Tusenbroch⁴ used nickel sulphate to precipitate nickel on kieselguhr and investigated the effect of heat treatment on the activity of the resulting catalyst. Norman⁵ investigated the effect of calcinations temperature on the

activity of nickel-kieselguhr catalyst in relation to the thermal conditions of precipitation, drying and reduction. Tuslier *et al.*⁶ influencing the activity and selectivity of supported Ni catalysts. Nishiyama⁷ studied activation of supported Ni catalyst through modification of surface or catalyst support.

The presence of different ions in the solution at the same time makes the chemistry of Ni, W, Cu/Kieselguhr a very complex one. The paper focuses on the synthesis of catalyst Ni, W, Cu/Kieselguhr. As the activity of the catalyst is minor affected by the presence of constituents during their preparation therefore a detailed study of the various constituents formed besides the desired catalyst has been carried out by X-ray diffraction method. The chemistry involved for various side products formed during synthesis is proposed.

EXPERIMENTAL

Kieselguhr was obtained from M/s. S.D. Fine Chemicals, Mumbai (India). Chemicals used in all the reactions are of analytical grade. High purity hydrogen gas was used for hydrogenolysis reaction.

The set up used in various experimental steps is described as below. Nickel, tungsten and copper salts were co-precipitated on kieselguhr using Heidolph Rotary Vacuum evaporator

(Germany) with electronic temperature and speed control. The reactions were carried out in a microprocessor controlled 450 mL high pressure Parr reactor assembly (USA). The technique of thin-layer chromatography coupled with flame ionization detector was used to analyze the products of sucrose hydrolysis. Iatron TH-IO MK IV TLC/FID analyzer was used for this purpose.

RESULTS AND DISCUSSION

The catalyst was synthesized in the aqueous medium by the reaction and coprecipitation of compounds of nickel, copper and tungsten on kieselguhr using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and a slurry of $\text{WO}_3 \cdot x\text{H}_2\text{O}$ ($2 < x > 1$) in liquor $\text{NH}_3 \cdot \text{H}_2\text{O}$ in the presence of Na_2CO_3 - analyses of the precipitated compounds dried at 120°C (unreduced catalyst) [Ni-34.8 %, W-9.9 % and Cu-1.1 %]. It also contains a large proportion of SiO_2 not analyzed but estimated by EDAX spectra. Trace amounts of aluminum, calcium and iron were also detected in the spectra as in Fig. 1. The unreduced catalyst was reduced at 600°C by H_2 gas.

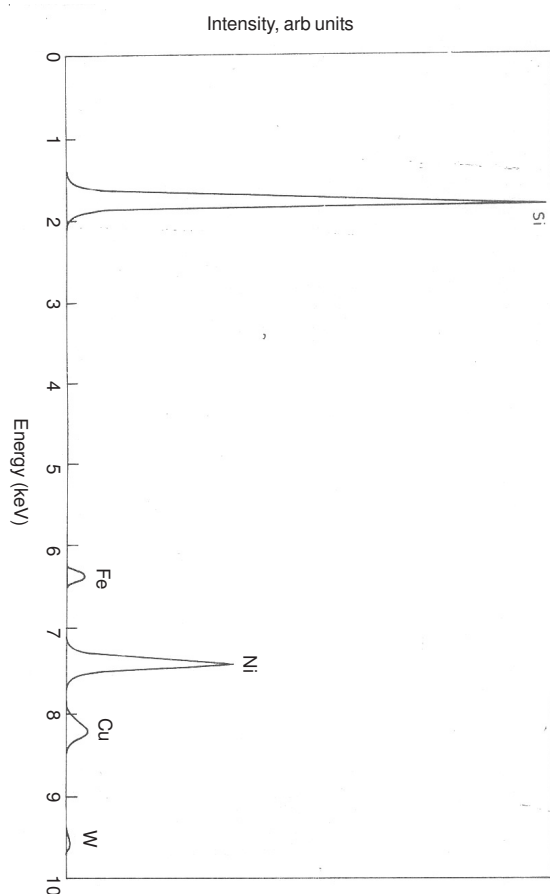
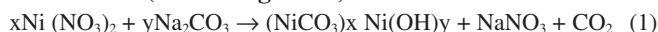


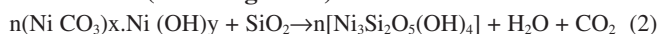
Fig. 1. X-ray spectrum of unreduced (Ni, W, Cu)/Kieselguhr catalyst

Reaction during coprecipitation: X-ray diffraction studies of the unreduced catalyst indicated an appreciable amount of a compound having the formula $[\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4]$ (known as nickel silicate hydroxide in ASTM No. 22.754). The formation of the nickel silicate hydroxide as the major compound formed during the reaction can be explained on the basis of the following reactions:

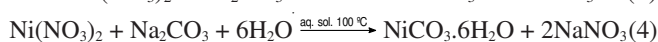
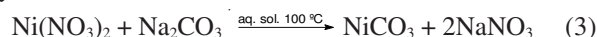
Reaction -1 (Before digestion)



Reaction -2 (After digestion)



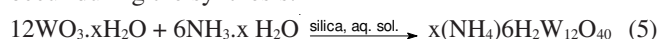
The excess SiO_2 in the catalyst is due to the presence of kieselguhr. Assuming entire silica reacts with nickel nitrate to form $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ the percentage of nickel in the catalyst is calculated to be 46 % (by wt). The lower percentage of nickel analyzed (34.8 %) vs. calculated (46 %) in the unreduced catalyst may be because of the presence of some unreacted silica and other compounds containing Ni, W, Cu besides $[\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4]$. X-ray powder data also indicated the presence of a small amount of ionic nickel carbonate $[\text{NiCO}_3]$ (ASTM series No. 12.771) and nickel carbonate hydrate $[\text{NiCO}_3 \cdot \text{H}_2\text{O}]$ (ASTM series No. 12.276). The latter compounds may be formed because of the following side reactions occurred during the formation of the unreduced catalyst.



The presence of nickel hydroxide was not indicated by the X-ray diffraction studies. It implies that either it is not formed during the reaction or was present in very small amounts, which could not be detected by X-ray diffraction studies. The excess of SiO_2 in catalyst is due to presence of kieselguhr. The small amount of copper as indicated by the elemental analysis could be due to the formation of $(\text{CuCO}_3)_x \cdot [\text{Cu}(\text{OH})_2]_y$ by the reactions similar to those described for nickel nitrate.

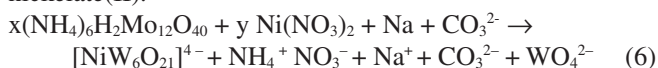
Minor products formed during co-precipitation:

Chemical analyses indicated the presence of very small amount of molybdenum in the filtrate collected after filtering and co-stirring the co-precipitated unreduced catalyst. The pH of the filtrate was found to be in between 4 and 5. Since in this pH range one expects the presence of tungsten in the form of ammonium metatungstate as the major species in aqueous solution⁸, it is expected that most of the tungsten in the filtrate is present in this form. The possibility of the presence of a small amount of ammonium paratungstate as well, can however not be completely ruled out. Although under normal experimental conditions it is difficult to prepare ammonium metatungstate by the reaction of tungstic acid and $\text{NH}_3 \cdot x\text{H}_2\text{O}$, but this formation is also supported by the Ritsco^{9,10} who synthesized ammonium metatungstate by digesting H_2WO_4 in $\text{NH}_3 \cdot x\text{H}_2\text{O}$ in the presence of 3.6 % silica. Since kieselguhr contains mainly silica, the formation of some ammonium metatungstate is therefore expected during the synthesis when slurry of tungstic acid (prepared by heating tungstic acid in presence of liquor $\text{NH}_3 \cdot x$ over a steam bath) is digested in presence of kieselguhr. The following reaction may therefore occur during the synthesis:



The ammonium metatungstate thus formed may further react with nickel nitrate in the presence of sodium carbonate to give hexatungstonnickelate(II)¹⁰⁻¹² (not characterized), which might be adsorbed on kieselguhr. Reducing the latter heteropolyacid at 600°C by H_2 gas may yield tungsten blues precipitated on kieselguhr. The following reaction sequence

is tentatively proposed for the formation of hexatungstonickelate(II).



However, its presence is confirmed after reduction, as the latter heteropolyacid acid reduced at 60 °C. One can also not rule out the absorption of some metatungstate present in solution on kieselguhr.

Formation of (Ni, W, Si) H: X-ray diffraction studies of the unreduced catalyst indicated the presence of small amount nickel tungsten silicide [(Ni, W, Si) H] (ASTM series No. 15.602). The co-precipitated catalyst was heated at 120 °C under vacuum in the absence of H₂ before the X-ray diffraction was taken. This compound may be formed because of the following side reaction along with the reactions described above.



It has been found that the maximum activity of the catalyst is obtained when the sample dried at (*ca.*120) is reduced at 600 °C by H₂ gas¹. X-ray powder data that shows the presence nickel in the reduced catalyst in the metallic nickel state as shown by the appearance of nickel peaks in the diffraction pattern. The heights of these peaks increased with the increase of temperature 400-600 °C prior to become practically constant [*cf.* Ni (2θ peak in Fig. 2)]. This conclusion was further confirmed by the fact that peak intensity due to [NiSi₂O₅(OH)₄] gets reduced simultaneously and finally becomes a flat (Fig. 2). It is also know that the nickel in Ni(OH)₂ and NiCO₃ gets completely reduced to metallic state at 450 °C⁸.

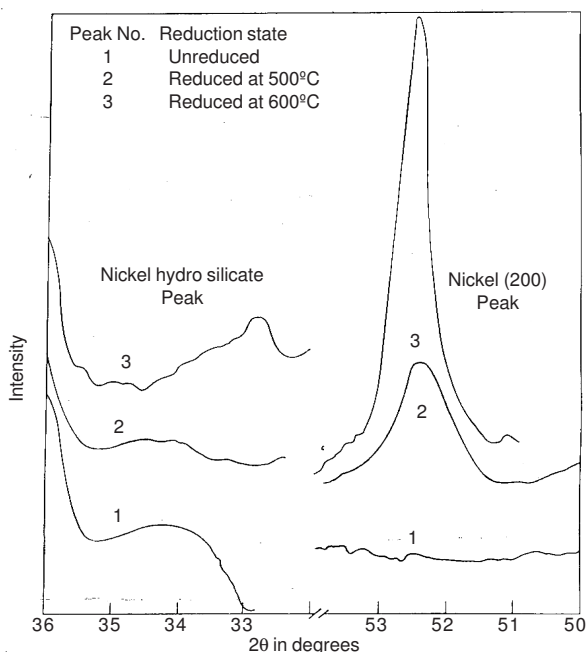
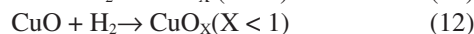
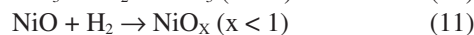
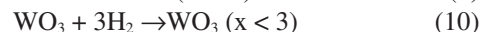
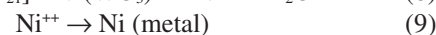
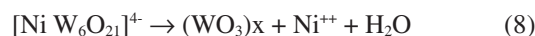


Fig. 2. Effect of temperature of nickel silicate hydroxide and Ni (2θ) peaks in X-ray diffraction pattern of (Ni, W, Cu)/kieselguhr-catalyst

The peaks due to metallic copper were not exhibited by the X-ray powder spectra, probably because of its lower percentage in: the catalyst; copper might have gone in the solid solution with nickel during catalyst reduction¹⁰. Although one should expect the presence of metal tungsten peaks in the X-ray

diffraction spectra but its absence implies that it is not present in the metallic state. However, there is a possibility of reduction of tungsten in the form of tungsten blues. Since X-ray powder data is not available in the literature, the exact formulation of tungsten could not be estimated, but the spectra show some extra peaks in the region of WO₃. The presence of copper and tungsten in the unreduced catalyst however was confirmed by the scanning electron microscope using EDAX attachment (Fig. 1).

The unreduced catalyst containing ions of nickel heteropoly acid acid [NiW₆O₂₁]⁴⁻ metatungstate and possibly of copper heteropolyacid acid will be decomposed and reduced at 600 °C in the hydrogen atmosphere from [Ni W₆O₂₁] molybdenum blues¹¹, nickel and copper compounds to NiO_x and CuO_x (x < 1). In tungsten blues the oxidation state of tungsten can be any between 0 and 6. While NiO_x and CuO_x are non-stoichiometric compound of Ni and Cu having oxidation state of the metals lower +2. The following reaction may represent the above transformation occurring during the reduction of the catalyst.



Conclusion

X-ray diffraction studies indicated the formation of nickel hydrosulfates, heteropoly acid of nickel and tungsten and nickel tungsten silicide in the unreduced state of the catalyst during its synthesis. Nickel is partially reduced below 600 °C. This was evident by the increase of nickel and decrease Ni₃Si₂O₅(OH)₄ peak heights, respectively as the temperature is increased from 400-600 °C. However, the maximum reduction of nickel compound to metallic nickel was possible only at 600 °C.

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