Study of Characterization and Cracking of Sucrose over supported Ni, Mo, Cu/Kieselguhr Catalyst

Tanuja Srivastava[1], D. C. Saxena[2]

[1]Director, Bhai Gurdas Institute of Engineering and Technology, Sangrur, India

[2]Professor, Department of Food Technology, Sant Longowal Institute of Engineering and Technology, Longowal, India

Abstract: *Sucrose hydrogenolysis is industrially important for the production of glycerol, ethylene glycol and propylene glycol. There is a need of a catalyst providing high product yields under milder reaction conditions. Ni catalyst promoted by Mo and Cu and supported on kieselguhr was synthesized with this purpose. Ni, Mo, Cu/Kieselguhr nano catalyst prepared by simultaneous Co precipitation and digestion method on dilution showed three times higher activity than the reported earlier readings. The catalyst was characterized using the techniques of electron microscopy, X-ray diffraction and magnetic measurements. The maximum yield of glycerol and simultaneously highest conversion of sucrose with water to nickel nitrate ration of 12 was obtained. Present water and nitrates solution ratio reveals that under this condition sucrose may be hydrogenolysis to yields glycerol, ethylene glycol and propylene glycol directly instead of first producing glucose and fructose. Thus the overall picture of the hydrogenolysis of sucrose is quite complex. A large number of consecutive and parallel reactions are involved. Various routes of product formation are shown in fig. The use of suitable catalyst under appropriate conditions may produce desired mixture. Magnetic moments studies have revealed a decrease in the magnetic moment of nickel when dropped with copper. This indicates some electron transfer from copper and molybdenum to 3d band of nickel. Electron microscopy studies indicated a marked change in morphology of the kieselguhr grains. Coprecipitation of the catalyst seems to change the morphology of support particles from sharp edged particles into fibrous state. Transmission electron micrograph of unreduced catalyst shows this fibrous stage. The surface area measurement of the optimum (Ni,Mo,Cu)/kieselguhr catalyst is recorded as 789m^2/g.*

Keywords: catalyst, nickel, copper, Response Surface Methodology, Glycerol, Hydrogenolysis

1. Introduction

Heterogeneous catalyst, including nickel, molybdenum, copper, keiselguhr catalysts in the form of metallic powders, metal oxides and activated metals were impregnated on an activated carbon support. Copper or copper based catalysts exhibited higher selectivity towards ethylene glycol and degradation by-products. Hydrogenolysis is a reaction where splitting of a chemical bond is accompanied by hydrogen addition. In general the following chemical reaction can represent hydrogenolysis.

$$XY + H_2 \rightarrow XH + YH \ (1.1)$$

Where X is usually a carbon atom and Y may be a carbon, nitrogen, oxygen or halogen atom.

When Y is oxygen, the reaction of hydrogen with oxygen should be regarded as hydrogenolysis of oxygen, but is arbitrarily considered as the oxidation of hydrogen. Sirkar et. al. [3] described that the catalytic hydrogenolysis of carbon-oxygen bonds occurs only with much difficulty over metallic catalysts and is uncommon. Studies have been made on the hydrogenolysis of carbon-nitrogen bond over evaporated films of a number of metals including nickel as reported by Etinbury. A [12]. Typically ethylamine has been hydrogenolysed to yield ethane and ammonia as explained Mozingo. R [13].

Vasyumina et. al. [25] studied catalyst synthesis parameters systematically to select conditions yielding maximum glycerol amount. Catalyst has been synthesized using the method of co-precipitation [23, 24, 25]. A catalyst similarly synthesized was used for hydrogenolysing glucose.

Synthesis procedure was optimized by varying parameters of each step one at a time starting from the first step.

The effect of each variation on the product distribution and on nickel peak width at its half height in X-ray diffraction patterns of the catalyst was observed as mentioned by Vanling G [29]. It is known that peak width at half height is directly proportional to the surface area of the catalyst particles. While optimizing a particular parameter of the synthesis procedure, the values used in the previous literature were selected for the parameters falling later in the sequence and were still to be optimized as explained by Sulman et.al. [33].

Klesment studied that salts of nickel, copper and molybdenum are impregnated in kieselguhr before they are co-precipitated using sodium carbonate [35]. Silica is major constituent of kieselguhr nickel nitrate is known to [36] reacts with silica forming hydrosilicates. These silicates may be formed as a layer on kieselguhr pores and may affect impregnation of salts of molybdenum added later in the sequence. This sequence of contacting of nitrates and molybdenum salt with kieselguhr may affect eventual properties of the catalyst. There may be two possible sequence of the catalyst synthesis in steps a and b.

(a) Digestion of slurry of kieselguhr and aqueous solution of nitrates and addition of milky suspension of ammonium molybdate to it.
(b) Digestion of slurry of kieselguhr, ammonium molybdate and addition of the aqueous solution of nitrates to it.
(c) The sequence which gave better glycerol and glycol yields was finally selected.

The paper focuses on the synthesis of catalyst Ni, Mo, Cu/ kieselguhr and effect of dilution on it. As the activity of the catalyst is major affected by the dilution during coprecipitation. Therefore a detailed study of catalyst i.e. characterization has been carried out by X-ray diffraction, electron microscopy and magnetic measurement method.

2. Experimental

2.1 Materials

Kieselguhr was obtained from M/s. S.D. fine Chemicals, Mumbai (India). Analytical grade salt of nickel, Molybdenum, and copper as well as sodium carbonate and ammonium hydroxide were used for catalyst preparation. Laboratory grade sucrose (Qualigens, Mumbai, India) were used for hydrogenolysis reaction.

2.2 Methods

2.2.1 Catalyst preparation
Nickel, Molybdenum, and copper were co-precipitated on kieselguhr using a Heidolph rotary vacuum evaporator with electronic temperature agitation and control and incorporating various attachments and fittings [38]. Nickel concentration in the catalyst was varied by changing nickel nitrate and kieselguhr ration, Molybdenum concentration by changing molybdic acid (in the presence of ammonium hydroxide) and kieselguhr ration, and the copper concentration by changing cupric nitrate and kieselguhr ration for catalyst synthesis.

The percentage of nickel, copper, and Molybdenum was estimated by standard gravimetric analysis. After digestion of above slurry of nickel, Molybdenum, and copper, sodium carbonate of 10% concentration was added to the slurry at 80^oC. The slurry was finally digested for 90 minutes at 90^oC. It was thereafter filtered, washed with 2 liters of hot distilled water, and dried under vacuum at 150^oC. The dried green catalyst is ground to pass through a 200 mesh sieve.

The catalyst was activated by reduction in pure hydrogen current 600^oC for two hours. The reaction was carried out in a microprocessor controlled 450 ml high pressure Parr reactor assembly (USA) under the following conditions: Catalyst amount: 12.5% of sucrose weight; Sucrose concentration: 17% by weight. Temperature: 150^oC; Pressure: 50atm; Reaction time: 45 min. The technique of thin layer chromatography coupled with flame ionization detector was used to analyze the products of hydrogenolysis of sucrose. Iatron TH-10 MK IV TLC/FID analyzer was used for this purpose.

2.2.2 Characterization of the optimized catalyst
Physicochemical properties of the catalyst were studied using techniques of electron microscopy, X-ray diffraction, and magnetic measurements under following conditions:

Electron Microscopy: The activated catalyst was powdered and suspended in double distilled water [40,41]. The suspension was allowed to settle for about an hour. A drop from the suspension was carefully placed on 200 mesh carbon coated copper grids. After drying, the grid was examined under a JEOL GEM 2000 FX transmission electron microscope having a resolution 1.5 Ao and operating at 120 KV. Gold diffraction pattern was use as a standard for interpreting the diffraction patterns.

X-ray diffraction technique: The finely powdered samples of catalyst were mounted individually on SEIFERT (JSO DEBYE FLEX 2002) X-ray generator [41]. The X-ray data were recorded at a scanning speed of 1.2^o per minute (2 psi) between psi=10o and 62o. The monochromatic beam of Cuk(alpha) radiation was used. The diffractometer was operated at a count rate of 5J CPM and a time constant of 10 sec. the scanning slit was fixed at 2mm and the receiving slit at 0.3 mm. The X-ray tube was driven at 30 KV and 20 mA. Diffracted scintillating column at a chart speed of 30 mm/min. the correction for instrumental breadth of diffraction peak under identical conditions was evaluated using standard aluminum samples annealed for 4 hours at 300^oC.

Magnetic measurement: finally powdered catalyst samples were pressed in cylindrical pellets (3 mm diameter and 3mm height) in inert atmosphere to avoid oxidation [38,40]. A polymer coating was applied to the surface in order to impart mechanical strength to the pellets and to prevent further oxidation of the reduced catalyst[42]. The measurements were carried out at room temperature using a Varian V-7200 series 9 inch electromagnet and a parallel field vibrating samples magnetometer (Model 150 A PARC, USA).

3. Results and Discussions

Dilution of slurry of kieselguhr and aqueous solution of nitrates was varied by changing water to nickel nitrate ratio [41]. Several catalyst samples were thus made. X-ray diffraction patterns of the samples were obtained and sucrose hydrogenolysis was carried out with them. **Table 1** lists the observations. The product distribution after a reaction time of 240 min. is shown in **Fig. 1.**

Table 1: Effect of dilution of nickel nitrate and cupric nitrate solution on nickel percentage in the catalyst

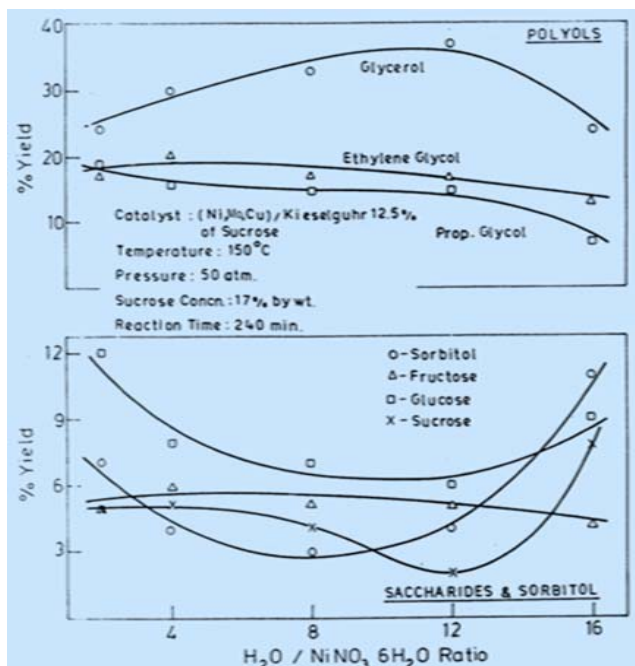| S. No.	$H_2O/Ni(NO_3)_2\ 6H_2O$ ratio	% Ni in the catalyst
1	200	31.40
2	400	31.57
3	600	31.84
4	800	31.97
5	1200	32.17
6	1600	31.87

Figure 1: Effect of dilution of Nickel Nitrate and Cupric Nitrate solution on product distribution

Fig. 2 shows the effect of dilution on nickel percentage in the catalyst. Water to nickel nitrate ratio of 12 is seen in **Fig.2** to yield maximum glycerol and is recommended for the catalyst synthesis. Conversion of sucrose was also maximum at this ratio [40].
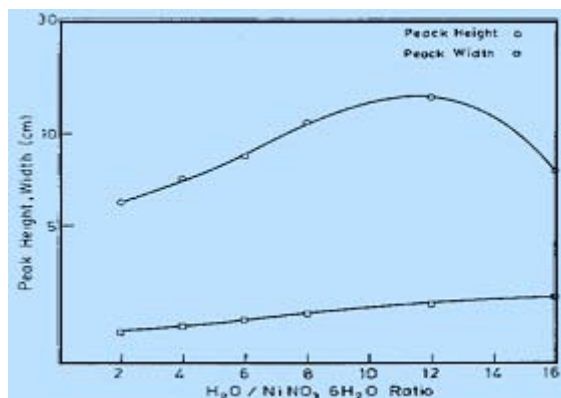

Figure 2: Effect of dilution of Nickel Nitrate and Cupric Nitrate solution height and width of Nickel (200) peak

Propylene glycol yield registered a mild decrease of 4% with increase in dilution from a ratio of 2 to 12, and then suddenly decreased by 8% as the ratio increased further upto 16. Ethylene glycol yield changed from 18% to 14% with maxima of 19% at a ratio of 5.

3.2 Characterization of the catalyst

Physicochemical properties of the catalyst were studied using techniques of electron microscopy, X-ray diffraction and magnetic measurements. Electron microscopy is a direct method for examining the location of metal on the support, information relevant to the problem of diffusion control of reaction rates. X-ray diffraction is a convenient method to find interplaner spacings of the components present and thus helps in identifying them. It also helps to assess metal dispersion and relative amounts of various components using X-ray line broadening and ratios of peak areas, respectively.

Electron Microscopy
Support (unactivated, activated and spent) catalyst and kieselguhr were powdered and suspended separately in double distilled water. The suspensions were allowed to settle for about an hour. A drop from each of these suspensions was carefully placed on a 200 mesh carbon coated copper grids. After drying, the grids were examined under a JEOL GEM 2000 FX transmission electron microscope having a resolution of $1.5A^o$ and operating at 120KV. Gold diffraction pattern was used at a standard for interpreting the diffraction patterns.

Fig. 3 shows the scanning electron micrograph of kieselguhr particles. The round sharp edged particles have broad size distribution with larger fraction of smaller particles above or below 5μm.

Figure 3: Scanning Electron micrograph of kieselguhr particles

The transmission electron micrograph shown in Fig. 4a reveals the presence of sharp edged, round intermingled kieselguhr particles. The electron diffraction obtained from the same region is shown in Fig. 4b. Interplaner spacing corresponding to this pattern match with those obtained from X-ray diffraction peaks of the same materials. Coprecipitation of the catalyst seems to change the morphology of support particles from sharp edged particles into fibrous state.
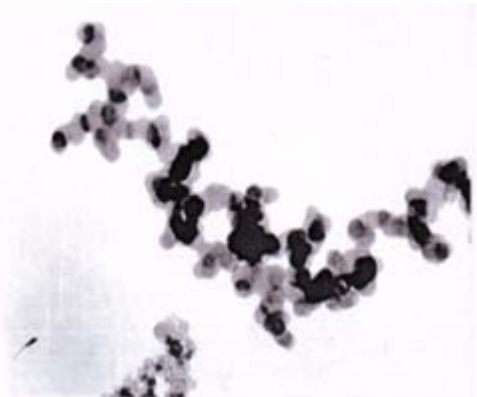

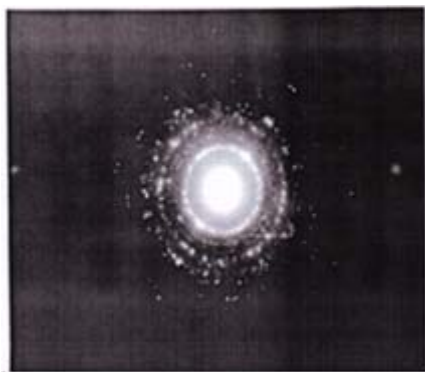**Figure 4 (a):** Transmission Electron micrograph of kieselguhr particles

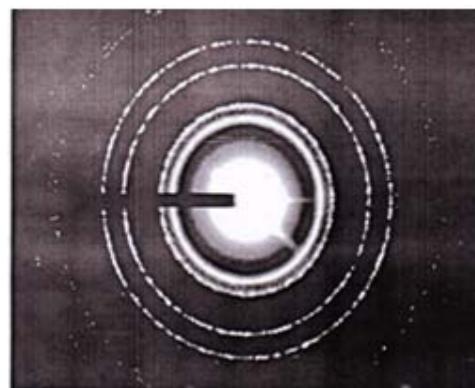**Figure 4 (b):** Electron diffraction pattern of kieselguhr particle from the area

Transmission electron micrograph (Fig. 5a) of unreduced catalyst shows this fibrous stage. Electron diffraction of this region is shown in Fig. 5b. Figures of reduced catalyst show these fibres covered with catalyst particles. Fig. 6 shows an electron diffraction pattern of gold used as a standard for the electron diffraction studies.
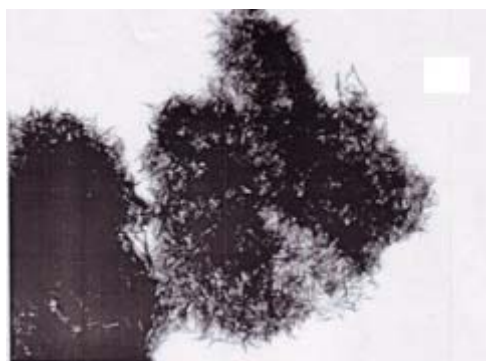

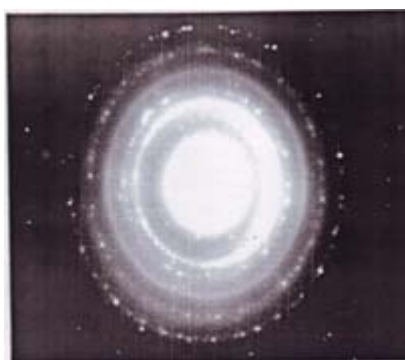**Figure 5 (a):** Transmission electron micrograph of unreduced catalyst

Figure 5 (b): Electron diffraction pattern of unreduced catalyst from the area

Figure 6: Electron Diffraction of Gold film

X-ray spectra of kieselguhr, unreduced and reduced catalysts were obtained using EDAX attachment in Jeol JSM 840M scanning electron microscope. The kieselguhr is seen to consist of mainly silicon with traces of aluminum, calcium and iron. The percentage compositions of these elements obtained using the spectrum is given in Table 2.

Table 2: Composition of Kieselguhr based on its Edax Spectra

Element	Wt. % composition
Si	89.35
Ca	5.4
Fe	3.97
A1	1.27

X-ray diffraction analysis discussed later, also indicated presence of various silica components and iron oxide in the kieselguhr.

3.3 X-ray diffraction

The finely powdered samples of pure kieselguhr, (Ni,Mo,Cu) on kieselguhr (unactivated, activated and spent catalysts) were mounted individually on SEIFERT MZ III goniometer and were examined using a SEIFERT (JSO DEBYE FLEX 2002) X-ray generator. The x-ray data were recorded at a scanning speed of 1.2^o per minute (2ϕ) between $\phi=10^o$ and 62°. The monochromatic beam of cukα radiation was used. The diffractometer was operated at a count rate of 5K CPM and a time constant of 10 sec. The scanning slit was fixed at 2mm and the receiving slit at 0.3mm. The X-ray tube was driven at 30KV and 20mA. Diffracted intensities were measured by means of a scintillating column at a chart speed of 30mm/min. The correction for instrumental breadth of diffraction peak under identical conditions was evaluated using standard aluminum samples annealed for 4 hours at 300^oC.

Although, kieselguhr has been extensively used as a support for catalysts, its X-ray data are rarely available in literature. It mostly contains various forms of silica and some other materials in traces. The exact composition of kieselguhr is not definite and depends on the source.

Table 3 gives data for different peaks of Ni, Mo and Cu in the reduced catalyst. After reduction the catalyst exhibited (111), (200), (220), (311), (222) and (400) diffraction lines of Ni but those from Mo and Cu were not detected. This

could happen either due to the microcrystalline nature of Mo and Cu or due to their presence in the Ni lattice as substitutional solute atoms. From the respective binary phase diagram Cu is known to be completely soluble with Ni and Mo upto 30% (wt.) i.e. Cu will mostly remain in solid solution (substitutional). For Cu the second possibility can, therefore be given a larger weightage. This is also supported by the absence of Cu peak in the X-ray spectrum of the reduced catalyst obtained using EDAX attachment in scanning electron microscope.

The presence of particles of dissimilar elements such as Mo during co-precipitation should prevent coalescence of like type of Ni particles and thus result in their finer size. But not all of % Mo present in the catalyst appears to have caused coalescence prevention as Mo diffraction peaks were not detected.

Table 3: List of d values Ni,Mo and Cu peaks in X-ray Diffraction Charts of (Ni, Mo, Cu)/Kieselguhr Activated catalyst

Catalyst (Ni, Mo, Cu)/Kieselguhr	
hkl	activated d values
Nickel	
111	2.025
200	1.755
220	1.245
311	1.062
222	1.016
400	0.881
Molybdenum	
111	--
200	--
211	--
220	--
310	--
222	--
Copper	
111	--
200	--
220	--
311	--
222	--
400	--

Except (101) peak of $\propto$-cristobalite silica, all kieselguhr peaks also disappeared. This indicate chemico-structural degradation of the support to some amorphous state and conversion of metallic nickel into some non metallic amorphous material probably nickel hydroxide.

3.4 Magnetic Measurements

The magnetic measurements involved study of magnetization as a function of magnetic field at constant temperature (298°K). Finally powdered catalyst samples were pressed in cylindrical pellets (3mm dia and 3mm ht) in inert atmosphere to avoid oxidation. A polymer coating was applied to the surface in order to impart mechanical strength to the pellets and to prevent further oxidation of the reduced catalyst. The measurements were carried out at room temperature using a varian V-7200 series 9 inch electromagnet and a parallel field vibrating samples magnetometer (MODEL 150 A PARC, USA). Magnetization

data for a pure nickel sample of identical shape was also obtained under similar conditions for interpretation of the magnetic data.

Ni/Kieselguhr catalyst was synthesized for magnetic measurements by excluding cupric nitrate and the addition of ammonium molybdenate from the synthesis procedure of (Ni, Mo, Cu)/Kieselguhr catalyst. It was found to contain 47.1% nickel by chemical analysis. The magnetization curves for standard Ni, Ni/Kieselguhr catalyst, (Ni, Mo, Cu)/Kieselguhr catalyst and spent (Ni, Mo, Cu/Kieselguhr) catalyst are shown in Fig. 7. Electron microscopy studies revealed an average Ni particle size of less than $500A^{o}$ in (Ni, Mo, Cu) kieselguhr catalyst. However, isolated particles smaller than this size should normally not exhibit saturation at room temperature. The saturation in the present case, therefore, appears to be due to nickel particles lying very close as a result of high nickel loading.
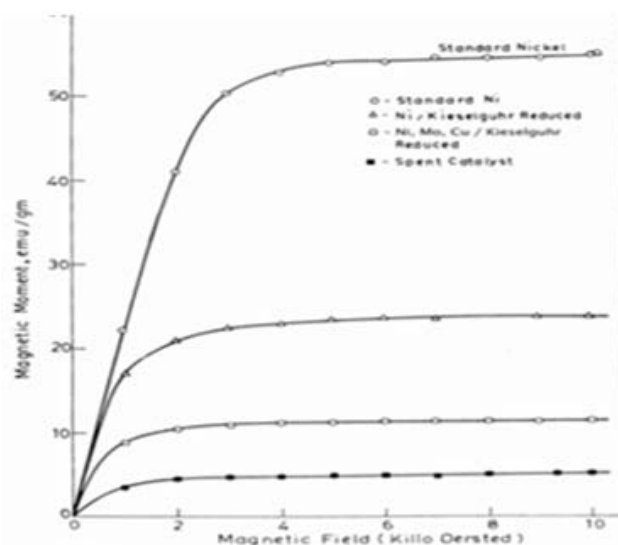

Figure 7: Effect of Applied Magnetic Field on Magnetic Moments

The saturation values of standard Ni samples, activated Ni/Kieselguhr catalyst, activated (Ni,Mo,Cu)/kieselguhr catalyst and spend (Ni,Mo,Cu) / kieselguhr catalyst are listed in Table comparing saturation values of the catalyst with standard Ni sample, the percentage of Ni in Ni/kieselguhr catalyst was estimated to be 47.83% which is very close to actual composition of the catalyst (47.1%). Similarly in case of (Ni,Mo,Cu) / kieselguhr catalyst, the Ni content was found to be 20.26%. This is about 8% less than the actual composition (34.86%). This apparent decrease in Ni content of 8% may be attributed partially to 3d band filling of nickel by electron transfer from Mo and Cu and partly to large decrease in size of the nickel particles due to prevention of their coalescence by the presence of molybdenum. Kuznetsov et al.[54] have also found an improved dispersion and consequently a change in activity of Ni/SiO$_2$ catalyst when it is doped with Mo.

A considerable decrease of about 55% in the saturation value of (Ni,Mo,Cu)/kieselguhr catalyst after its use is indicative of a faster rate of deactivation of (Ni,Mo,Cu)/kieselguhr catalyst. This also suggests that particles are becoming highly dispersed in nature. Maschkilleisolm have noted that

nickel has an optimum degree of dispersion if to be used as a catalyst, any finer dispersion is accompanied by a reduction and finally by a cessation of its activity. Thus becoming highly dispersed may be one of the means of deactivation of the catalyst. This also bears out by X-ray diffraction where nickel peak almost vanishes in case of spent catalyst.

3.5 Surface Area

The surface area measurement of the optimum (Ni,Mo,Cu)/kieselguhr catalyst were carried out by single point BET method with the help of Quanta chrome, Model 0S.7 (Quanta chrome corporation, Green vale, N.Y. 111548), using N_2 as adsorbent. The specific area for catalyst is recorded as $789m^2/g$.

4. Conclusion

It is concluded that the yield of glycerol from catalytic hydrogenolysis of sucrose can effectively be optimized by changing dilution during co-precipitation of catalyst. Nickel, molybdenum and copper supported on kieselguhr. Dilution of slurry of kieselguhr and aqueous solution of nitrates ratio varied in between 200 to 1600. Water to nickel nitrate ratio of 12 is seen to yield maximum glycerol and is recommended for synthesis because conversion of sucrose was also maximum at this ratio with highest percentage of glycerol 32.17%. This is the most expensive polyols produced by the reaction. The work presented here paves the way to synthesize a commercial catalyst to produce various polyols, particularly glycerol by hydrogenolysis of sucrose.

The catalyst was characterized using the techniques of X-ray diffraction, electron microscopy and magnetic measurements. The interplaner spacings of various components obtained from X-ray diffraction agreed from those obtained from electron microscopy. Further, electron microscopy studies indicated a marked change in morphology of the kieselguhr grains. Round kieselguhr grains were found to change into the fibrous catalyst synthesis, thus giving very high nickel surface area. X-Ray spectra of reduced catalyst obtained using EDAX attachment in scanning electron microscope has confirmed the presence of Ni, W and Cu in the catalyst.

An interesting phenomena was noticed when nickel was co-precipitated on kieselguhr. It was found that some of the kieselguhr, instead of remaining inert, formed a compound with nickel. This was indicated by decreasing kieselguhr peak heights in its X-Ray diffraction chart. The peak height became constant when percentage of nickel was increased beyond 31.7%. Nickel is deposited on the surface of the pores of kieselguhr and reacts with silica then kieselguhr peak becoming constant implies that all exposed kieselguhr surface has been covered by nickel and no more silica would react if nickel amount is increased further. Magnetic moment studies have revealed a decrease in the magnetic moment of nickel

References

[1] Catalysis by Metals G.C. Bond Academic Press, 1962 pp 395.
[2] Vidyarthi, S.R., Nigam, P.C., Rai, K.N; and Gehlawat, J.K., Applied Catalyst (Netherland) (Communicated).
[3] Sirkar, Amalesh (Hydrocarbon, Research, Inc.) Brit, U.K. Pat. Appl. 28 Jul. 1982, US Appl. 1981, Chem. Abstr. 182800 u.
[4] Sauran, G.N., Diemel, S., Tempere, J.F., Guilemese (1980) 8133 g.
[5] Nadirov, N.K., Erzhanova, M.S.; Ashirov, A.M.; & Zibrova, N.A. (USSR) Vs. B. XI mendeleevesk 1975 (3) 167-8 (Russ) Chem. Abstr. 85 (1976) 48968 z.
[6] P.Sabatier and J.B. Senderens; Am. Chim Phys. (8), 4, 319 (1905).
[7] C. Kelber, Ber. 54-B, 1701 (1921).
[8] E. Mashkilleisalm, J. Am. Chem. Soc. 47, 2501 (1925).
[9] Aubrey. J.; Bull Soc. Chim, France, 5, 1333 (1938); 41974 (1937).
[10] Watermann. J; and Tussenbrdi. P; J.A. Chem. Soc. 60, 1501 (1938).
[11] Dupond, G; and Piganiol. P; Bull Soc, Chim, France. 6, 322 (1939).
[12] Etinbury. A; J. Am. Chem. Soc. 61, 3564 (1939).
[13] Mozingo. R; Wolf. DE; Harrs. Am. Chem. Soc. 65 (10103) (1936).
[14] Lenth. C.W. & Dupuis R.N; Ind. Engng. Chem. 37 (1943) 152-57.
[15] Dupuis R.N.; US pat. 2, 282, 603. 12 May 1942, Chem. Abstr. 36 (1942) 6039 p.
[16] Lenth C.W. & Dupuis R.N.; US Pat. 2, 290, 439, Chem. Abstr. 37 (1943) 387 p.
[17] Sakae Jyodai, J. Chem. Soc. Japan Ind. Chem. Sect, 52 (1949) 196.
[18] Murphy Nelson. F; Bull Va Polytech. Inst. Eng. Exptsta Ser. No. 129 (1958) 52 Chem. Abstr. 53 (1959) 14946 i.
[19] Norman W; J.A. Chem. Soc. 56, 1804 (1942).
[20] Folkers, K; J. Am. Chem. Soc. 65, 10103 (1946).
[21] Paul, R, Bull. Soc. Chim. France (1946), 208.
[22] Conradin E; Bertossa, G. and Giesen. J, US Pat. 3, 030, 429, Apr 17, 1962 Chem. Abstr. 57 (1962) 10086 d.
[23] Vasyumina; N.A; Balandin A.A.; and Mamatov, Yu, kinetika i katali 4 (3), 443-9 (1963). Chem. Abstr. 59 (1963) 11637 b.
[24] Kashegan, L, Belg Pat. 635, 207, 20 January 1964; Chem. Abstr. 61 (1964) p 9660 b.
[25] Vasyumina; N.A; Balandin A.A.; and Mamatov, Yu, kinetika i kataliz 4 (3), 443-9 (1963). Chem. Abstr. 55 (1961) 7307 g.
[26] Vasyumina; N.A; Balandin A.A, Slutskin R.L, Dokl. Akad. Nauk, SSSR 169 (5), 1077-9 (1966), Chem. Abstr. 66 (1967) 11143 x.
[27] Kasehagan L; US Pat. 3, 396, 199, 6 August 1968, Chem. Abstr, 69 (1968) p. 78609 z.
[28] Vasyumina, N.A.; Slutskin, R.L. & Batandin A.A.; Katal, Reakts, Zhidk, Faze, Tr, Uses, Konf 2nd Alma-Ata, Kaz, SSR 1966 Pub. 1967 511-14 (Russ). Chem. Abstr. 69 (1968) 10638 c.
[29] Vanling G; Vlugter J.C; J. appl. Chem. Lond. 19 (11) (1969) 43-5.

[30] Vanling G; Driessen, A.J; Piet Ac & Vlugter J.C. Ind. Eng. Chem. Prod. Res. Develop; 9 (2) (1970) 212-12.

[31] Driessen, Alfons J, Chem. Weekbl. 1969, 65 (15) 13-18 (Meth). Chem. Abstr. 71 (1969) 4717 c.

[32] Rozdestvenskaya, I.D; Fadeeva, T.N. & Titova, N.B; kinetics and catalyst. 11 (1970) 568-73.

[33] Sulman, E.M. & Popov, O.S; Zh, Fiz, Khim, 1971, 45 (11) 2948-9 (Russ) Chem. Abstr. 76 (1972) 59919 d.

[34] Fadeeva, T.N.; Klabunovskii, E.I. & Rodestvenskaya, I.D; Izv, Akad. Nauk SSR, Ser. Khim. 1972 (8) 1742-6 (Russ) Chem. Abstr. 77 (1972) 152473 j.

[35] Klesment, I. J; Chromatogr. 1972, 69 (1), 160872 (Eng) Chem. Abstr. 77 (1972) 83228.

[36] Wright Leon W; Vs pat, 3, 691, 100, 12 September 1972, Chem. Abstr, 78 (1973) p 3676 w.

[37] Balaraju B;Rekha V; Sai Prasad P.S; Prasad R.B.N; Lingaiah N(2008) 126:119-124

[38] Srivastava Tanuja; Saxena D.C. Ind. Engg. Chem. Res. 2009, 44,1466-1473.

[39] Mane Rasika B.; Hengne Amol M.; Ghalwadkar Ajay A.; Vijayananad Subramanian, Mohite Pravin H.(2010) 135:141-147.

[40] Srivastava Tanuja; IJEST, Volume 3, No.10, Oct. 2011, 0975-5462.

[41] Srivastava Tanuja; Saxena D.C. IJSTM, Volume 3 Issue I (2012) 2229-6646.

[42] Srivastava Tanuja; Saxena D.C. IJCT (2012), 2277-3061, Volume 2, No.3, June 2012.

[43] Tronconi E; Ferlazo, N; Farzatti, P; Pasgum I; Casoli, B; (Dip. Chim. Ind. Khim.) "G. Natta" Politec Milan; (Milan Italy) Chem. Eng. Sci. (1992), 47 (9-11) 2451-6; 92608 q.

[44] A comprehensive Treatise on Inorganic and theoretical chemistry by J.W. Mellor.

[45] Smith, J.M.; Chemical Engineering kinetics 2nd edition, McGraw Hill Book Company 1970, pp.77.

[46] Paresh, L.D; Atsushi Fukuolea. Catal Surv Asia (2007). 11: 186-191

[47] M.Balaraju; V. Reisha;P.S. Sai Prasad, R.B.N. Prasad;N. Lingaiah. Catal Lett (2008). 126: 119-124.

[48] Jing Zhao;Weijuiang Yu;Chen Chui; Hang Miao; Hong Ma; Jie Xu. Catal Lett (2010). 134: 184-189.