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Extraction of SiO_2 from Rice Husk and activity studies of Ni-RHSiO_2catalysts for conversion of Levulinic acid to γ-Valerolactone

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Abstract:*A series of Ni catalysts supported on Silica extracted from rice husk are prepared by wet impregnation method with variable Ni content ranging from 5 to 40wt% have been tested for the hydro-cyclization of levulinic acid to γ-valerolactone in vapour phase at atmospheric pressure. These catalysts have been characterised by different techniques such as XRD, BET Surface area, Pore size distribution, TPR etc. XRD pattern suggests that the structure of SiO_2 is intact even after incorporation of Ni. Pyridine adsorbed IR patterns suggest that the incorporation of Ni creates Lewis acidity which is responsible for the dehydration of 4-hydroxy valeric acid (intermediate) to result γ-valerolactone. Among all the catalysts, 30wt.%Ni-RHSiO_2 gave good resultwith 85% yield and almost 91% conversion at 250°C in vapour phase at ambient conditions. This high activity can be attributed to higher number of surface active Ni species and also due to the Lewis acidity created by Ni.*

Keywords*-Rice Husk, Silica, Nickel, Levulinic acid, Velerolactone*

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I. Introduction

Biomass is a practically inexhaustible renewable source that can potentially facilitate the transition from the exhaustible fossil fuels [1]. Hence, there is a need to search for alternatives such as other than coal, natural gas and petroleum reserves. Since last three decades R&D focus is projected on biomass. The fourth most abundant renewable source is the biomass, which is providing 14% of energy to the society globally.In this aspect, utilisation of biomass and/or biomass derived derivatives is promising not only due to the dwindling of fossil fuels but also the stringent regulations on the composition and quality of the transportation fuels. Among the biomass derived chemicals, levulinic acid (LA) is an important chemical that has been classified as the top 12 promising attractive chemicals [2, 3]. It can be produced by acid hydrolysis of cellulose[4], furfuryl alcohol [5] and as byproductin paper industry[6]. Moreover, LA is considered as an important intermediate for the production of commodity products by different methods such as oxidation [7], reduction [8], condensation [9], reductive amination [10,11] and esterification [12]. Among all these processes, reduction gave plenty of useful chemicals, fuels and fuel additives.

Accordingly, reduction is accomplished by two different methods such as formic acid as a sole hydrogen source [13-17] and H2 as an external hydrogen source [18-23]. To date, most of the reports were observed by both homogeneous [24-25] and heterogeneous catalysts [26] at high pressures in presence of solvents in batch and vapour phase conditions. Despite the use of solvents, high pressures and recovery of catalyst is still a challenging task. However, very few reports were cited in the literature for the vapour phase hydrogenation levulinic acid using noble metals and non-noble metal as catalysts by using 1, 4-dioxane as solvent.To avoid the separation of solvent from the product and unreacted reactant, new and innovative approaches are needed for the green production of fuels. In this connection, we have carried out the LA hydrogenation in vapour phase under solvent free conditions at atmospheric pressure to produce γ-valerolactone, which has lot of applications as fuel andfuel additive[27-32]. These fuels have an advantage of low net emissions of global warming gas, CO_2 due to the utilisation of CO_2 by plant kingdom via photosynthesis to produce biomass again.

SiO_2 based supports are reported for the hydrogenation reactions. Among the SiO_2 based supports will have ordered mesoporous silica materials owing to their remarkable properties such as high surface area, thermal stability, and uniform pore size (46-300 Å). This high surface area and uniform pore size of silica facilitates the high metal dispersion even at high loadings without destroying the structure of the silica matrix [33-39]. Rice husk, an agro waste material, contains about 20% ash which can be retrieved as amorphous, chemically reactive silica. This silica finds wide applications as filler, catalyst support, adsorbent and a source for synthesizing high performance silicon and its compounds. Various metal ions and unburnt carbon influence the purity and color of the ash. Controlled burning of the husk after removing these ions can produce white silica of high purity. India produces around 25 million tons of rice husk as widely available waste. From silica ash composites it is understood that characteristics such as a fine particle size (<50 micron) and high reactivity due to its irregular shape, porosity and presence of surface hydroxyl groups,it can be used as support. With open air burning, a variety of silica ash can be produced with acceptable level of carbon impurities [40]. Amorphous white (low-carbon) silica ash is obtained at temperatures above 500°C and depends on the time and the temperature of combustion [41].Amorphous silica of high purity, small particle size and high surface area has tremendous potential as an adsorbent and catalyst/support in fine chemical synthesis. In order to prepare amorphous silica of high purity, treatment of the husk with chemicals before and after combustion was attempted by various researchers.The present study is focused on extraction of SiO_2 from Rice Husk, activity studies of Ni-RHSiO_2 catalysts for conversion of Levulinic acid to γ-valerolactone and correlation of catalytic performance of these catalysts with their characteristic results.

II. Experimental

2.1 Extraction of Silica from rice husk

First, 10 g of pyrolytic rice husk char were pretreated with 200 ml of HCl (1 M) to remove most of the impurities and to improve the purity of the silica. The char was introduced in a flask and the suspension was boiled for 3 h under reflux condenser and vigorous stirring. Then, the suspension was filtered and the solid was washed with distilled water until neutral pH. Finally the char recovered was dried for 15 h at 120 °C. The next step was to remove the silica with a 15 wt. % Na_2CO_3 solution. The char and 200 ml of this solution were introduced in a flask and boiled for 4 h under reflux condenser. The suspension was filtered and the precipitate was washed with distilled water until the pH becomes neutral followed by drying at 120°C for 24 h. The precipitate is the resulting carbon material from which activated carbon materials can be prepared chemical activation process. The filtrate is a solution of sodium silicate, which was subjected to a carbonation process in order to recover the silica. Thus, the solution was heated to around 80°C under continuous flow of carbon dioxide. After 1 h, the carbon dioxide flow was stopped and the solution was cooled down. Finally, the silica precipitate was filtered and dried at 120°C for 24 h and labelled as RHSiO_2.

2.2 Catalyst preparation

Silica extracted from rice husk from above procedure is used as support for preparation of Ni catalysts. Ni/RHSiO_2 catalysts with various loadings of the Ni were prepared by wet impregnation method. An aqueous solution containing requisite amount of $Ni(NO_3)_2$ $6H_2O$ salt was added to the silica support particles taken in a beaker and heated on a hot plate at 80°C to remove the excess water. The prepared solid mass was dried for 12 h at 100 °C and then calcined at 400 °C for 4 h in air. The catalysts so prepared were designated as xNi-RHSiO_2 where x represents the loading of Ni in wt. %.

2.3 Catalyst characterisation

All the above catalysts are characterized by XRD, BET method, FTIR, Py-FTIR, TPR.

2.4 Activity studies

About 1g of the catalyst particles were sandwiched between the two quartz wool plugs placed at the middle of a fixed bed tubular reactor made up of glass. Prior to the reaction, the catalyst was reduced in a H_2 flow for 4h at 500°C. The reaction was carried out in the temperature range of 250-295 °C with a liquid feed flow rate of 1 ml h^{-1} using H_2 as carrier. The reaction products were collected at regular intervals of temperature in an ice cooled trap and analyzed by a Flame Ionization Detector (FID) equipped gas chromatograph, with OV-1 capillary column (30 m length, 0.53 mm id).

III. Results and discussion

3.1 Surface Area and Pore size

The surface area and average pore size of the samples are illustrated in Table-1. The surface area of RH$SiO_2$is 595.2 m^2/g and pore size is 3.12 nm. However, there is a notablechange is observed in surface area from 595.2 to 345.6 m^2/g and there is no much variation in pore size after loading of Ni on silica.Variation of surface area and pore volume is observed as the Ni loading increases from 5 to 40 wt% which is due to agglomeration of Ni particles leading to the pore blockage. The pore sizes of Ni incorporated RH$SiO_2$are in the range of 2.87-3.11 nm which in agreement with the reported results. As can be seenfrom the XRD, there is no ample change in structural properties of RHSiO_2 which clearly indicates that the basic structure of SiO_2 frame work is intact even after Ni loading.

3.2 XRD studies

The XRD patterns of reduced catalysts are displayed in Fig.1. Sharp diffraction peaks of metallic Ni at 2θ values of 44.2, 53.0 and 78.0 can be seen in XRD patterns of reduced catalysts.
As percentage of Ni increases the intensity of nickel peak increases.

3.3 FT-IR Studies

The FT-IR patterns of the all the catalysts are shown in Fig.2. For $RHSiO_2$ and various loadings of Nion $RHSiO_2$ catalysts, the bands at 3734, 3600-3200 and1624cm^{-1} respectively are attributed to isolated, hydrogen-bonded surface silanol groups and adsorbed water molecules respectively which are in agreement with literature [42, 43]. In these materials, the typical Si–O-Si bands around 1078, 812 and 457 cm^{-1} associated with the formation of a condensed silica network are present. The siloxane – $(SiO)^{n-}$ peak appears as a broad and strong peak in the range 1000-1200 cm^{-1}. The strong bands at 1076,1050 cm^{-1} are attributed to the Si-O-Ni which are in agreement with the earlier reports[44].

3.3.1 Pyridine adsorbed FTIR studies

FTIR analysis of adsorbed pyridine is an excellent technique to discriminate nature of acid sites present in the catalysts (i.e., Bronsted and Lewis acid sites) [45]. It can be seen from the Fig.3 that all samples exhibited a prominent peak at around 1638 cm^{-1}, which can be attributed to the pyridine adsorbed on Bronsted acidic sites [46]. It can be seen from the Fig.3 that all samples exhibited IR bands at 1490 and 1455cm^{-1} which can be due to the pyridine adsorbed on combination of Bronsted& Lewis acidic sites and Lewis acidic sites, respectively. It is obvious from the figure that all the prepared catalysts exhibit more number of Lewis acid sites accompanied by very low number of Bronsted acid sites. The presence of Lewis acidic sites is helpful to promote the dehydration.

3.4 TPR studies

Temperature Programmed Reduction (TPR) experiments were carried out in order to explore the extent of reducibility of nickel species and the metal–support interactions [47]. Fig.4 shows the reduction profiles of calcined supported nickel catalysts. It is well known that nickel catalysts supported on rice husk extracted silica ($RHSiO_2$) showed different reduction patterns depending on the nature of interaction between nickel oxide and silica support. Bulk nickel oxide gets reduced at around 400°C [48]. The peak at a Tmax of 450°C can be ascribed to the typical reduction peak of Ni^{2+} to NiO that interacts strongly with silica. The shoulder peak at higher temperature can be assigned to the reduction of nickel oxide that can be very strongly interacted with the silica.

3.5 Catalytic activity

The effect of Ni loading on the activity is shown in Fig.5.At 250°C and 1 atm pressure, 5Ni-$RHSiO_2$ shows 75% conversion of levulinic acid in to gamma velerolactone. As metal loading increases the conversion also increases and reaches to 91% over 30Ni-$RHSiO_2$catalyst thereafter a slight decrease in conversion was observed on 40Ni- $RHSiO_2$ which is due to increase in the intensity of Lewis acidity shown in Fig.3.Increase in lewis acidic nature on catalysts helps in cyclisation as well as dehydration reactions. The selectivity to GVL is independent of Ni particle size, but depends on the number of surface Ni species and also Lewis acidity. The uniform porosity of $RHSiO_2$ through which the reactant/product molecules can easily be passed through the pores is the main reason to show good yields towards products. The stability of catalyst 30Ni-$RHSiO_2$ which has shown 91% conversion is also studied for 30 hrs. It is observed that the catalyst is showing almost constant performance up to 24 hr. and later marginal decline is observed in conversion of levulinic acid which may be due to coke formation.

IV. Figures & Tables

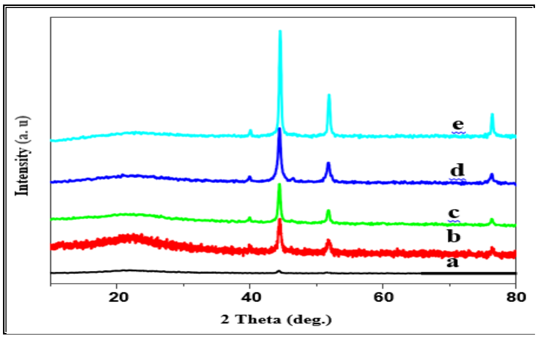


Fig.1 XRD patterns of reduced catalysts (a) 5Ni-$RHSiO_2$ (b) 10Ni-$RHSiO_2$ (c) 20Ni-$RHSiO_2$ (d) 30Ni-$RHSiO_2$ (e) 40Ni-$RHSiO_2$

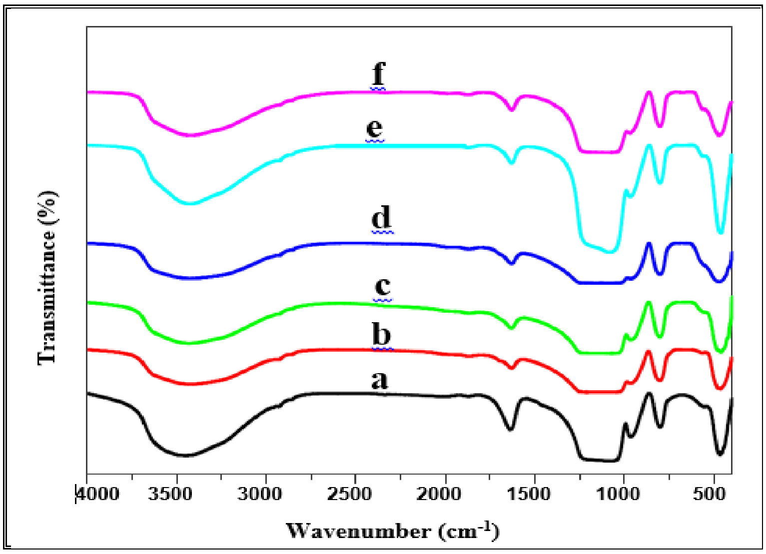


Fig.2 FT-IR patterns of (a) $RHSiO_2$ (b) 5Ni-$RHSiO_2$ (c) 10Ni-$RHSiO_2$ (d) 20Ni-$RHSiO_2$ (e) 30Ni-$RHSiO_2$ (f) 40Ni-$RHSiO_2$

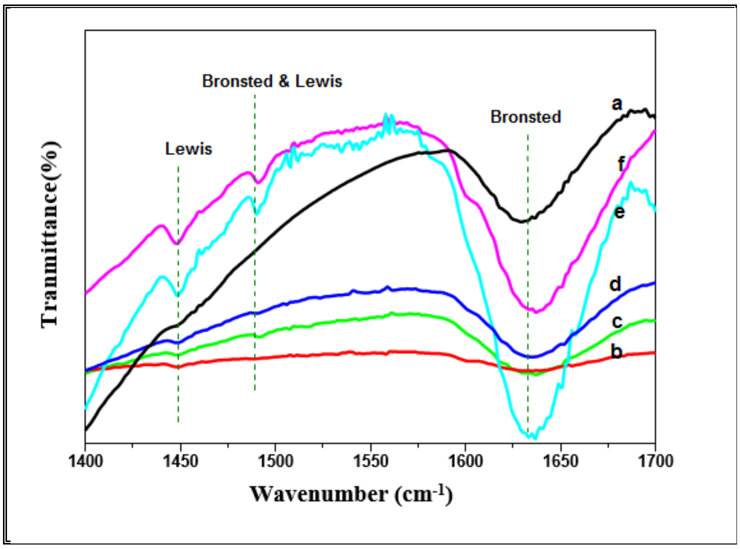


Fig.3 Pyridine absorbed FT-IR patterns (a) $RHSiO_2$ (b) 5Ni-$RHSiO_2$ (c) 10Ni-$RHSiO_2$ (d) 20Ni-$RHSiO_2$ (e) 30Ni-$RHSiO_2$ (f) 40Ni-$RHSiO_2$

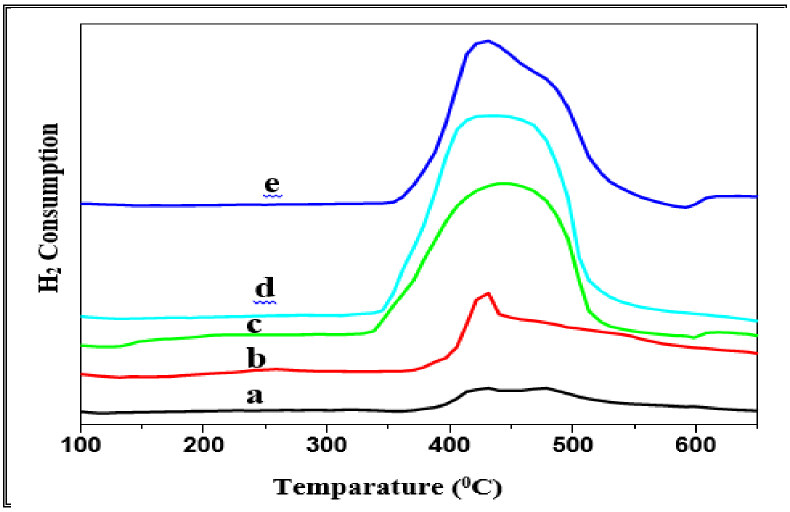
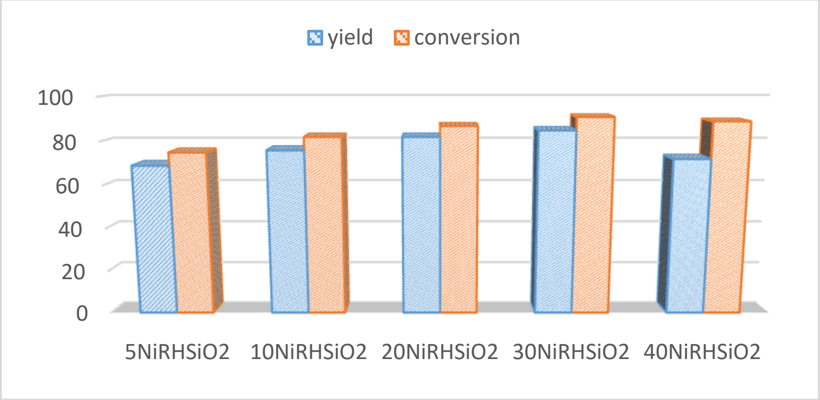


Fig.4 TPR profiles of (a) 5Ni-$RHSiO_2$ (b) 10Ni-$RHSiO_2$ (c) 20Ni-$RHSiO_2$ (d) 30Ni-$RHSiO_2$ (e) 40Ni-$RHSiO_2$



(Reaction Conditions: Weight of the catalyst=1 g, Temperature = 250 °C, Pressure=1 atm, Levulinic acid = 1 ml h^{-1}, carrier gas (H_2) =1800 ml h^{-1})

Fig.5 Effect of Ni loading on the activity of the levulinic acid hydro-cyclisation over Ni-$RHSiO_2$ catalysts.

Table-1 Surface area and pore size of Ni-$RHSiO_2$ catalysts

S.No.	**Catalyst**	**Surface area(m^2/g)**	**Pore Size (nm)**
1	$RHSiO_2$	595.2	3.12
2	5Ni-$RHSiO_2$	474.2	3.04
3	10Ni-$RHSiO_2$	452.1	2.98
4	20Ni-$RHSiO_2$	411.8	3.11
5	30Ni-$RHSiO_2$	398.6	3.05
6	40Ni-$RHSiO_2$	345.6	2.87

IV. Conclusions

- The manufacture of silica from rice husk ash works out to be very cheap and cost effective as the main raw material, the rice husk can be obtained at low cost. Activated carbon obtained as the byproduct has a good market value.
- A general procedure is outlined for silica precipitation and activated carbon from rice husk.
- Ni-$RHSiO_2$ is the inexpensive and environmentally benign catalyst for the production of gamma velerolactonefrom hydrogenation of levulinic acid at atmospheric pressure under solvent free conditions.
- The present results disclose that Ni-based catalysts on rice husk extracted silica are economically viable and alternative to the expensive noble metal catalysts for the hydrogenation of levulinic acid.

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References

[1]. K. S. Deffeyes, Beyond Oil: The View from Hubbert's Peak, Farrar, Straus and Giroux, New York, 2005.
[2]. J.J.Bozell, L.Moens, D.C.Elliott, Y.Wang, G.G.Neuenscwander, S.W.Fitzpatrick, R.J.Bilski,J.L.Jarnefeld, Resour.,Cons.Recycl.,28, 2000, 227.
[3]. P.Gullon, A.Romani, C.Vila, G.Garrote and J.C.Parajo, Biofuels,Bioproducts and Biorefining, 6, 2012, 219.
[4]. (a) D.J. Hayes, S. Fitzpatrick, M.H.B. Hayes, J.R.H. Ross, in: B. Kamm, P.R. Gruber,M.Kamm (Eds.), Biorefineries—Industrial Processesand Products, Wiley- VCH,Weinheim, 1, 2006, 139. (b) D.J. Hayes, Catal. Today, 145, 2009, 138
[5]. Z. Zhang, K. Dong, Z. Zhao, Chem. Sus. Chem, 4, 2011, 112.
[6]. Z.S.He,Chemical Industry and Engineering, 2, 1999, 163
[7]. a) A. P. Dunlop, S. Smith, US Patent 2676186, 1955; b) N. Sonoda, S. Tsutsumi, Bull.Chem. Soc. Jpn. 36, 1963, 1311.
[8]. a) H. A. Schuette, R. W. Thomas, J. Am. Chem. Soc. 52, 1930, 3010; b) A. P. Dunlop,J.Madden, US Patent 2786852, 1957; c) L. E. Manzer,
[9]. K. W. Hutchenson, US Patent2004254384, 2003; d) L.E.Manzer, WO Patent 2002074760, 2002; e) L.E.Manzer, US Patent20030055270,2003.
[10]. a) A. A. Bader and A. B. Kontowicz, J. Am. Chem. Soc. 1954, 76, 4465; b) Y. Isoda,M.
[11]. Azuma, JP Patent 08053390, 1994; c) H. Itsuda, M. Kawamura, JP Patent 61186346, 1986;
[12]. d) R. E. W. Romeo, Z. G. Gardlund, US Patent 3567686, 1971; e)K.Tabayashi, N. Yamamoto,JP Patentb62070338, 1987; f) G. J. Willems, J. Liska, EP Patent 933348, 1999.

[13]. W. L. Shilling, US Patent 32355562, 1996.
[14]. L. R. Crook, B. A. Jansen, K. E. Spencer, D. H. Watson, GB Patent 1036694, 1996
[15]. a) H. J. Bart, J. Reidetschlager, K. Schatka, A. Lehmann, Ind. Eng. Chem. Res. 33,1994,21
[16]. b) P. M. Ayoub, WO Patent 2005070867, 2005; c) L. E. Manzer, US Patent 2005210738, 2005; d) L.E.Manzer, WO Patent 2005097723, 2005
[17]. J.C.Serrano-Ruiz, D.J.Braden, R.M.West, J.A. Dumesic, Appl. Catal., B, 2010, 100,184
[18]. D. Kopetzki and M. Antonietti, Green Chem., 12, 2010, 656
[19]. L. Deng, Y. Zhao, J. Li, Y. Fu, B. Liao and Q. X. Guo, ChemSusChem, 3,2010, 1172
[20]. H. Heeres, R. Handana, D. Chunai, C. B. Rasrendra, B. Girisuta and H. J. Heeres, Green Chem., 11, 2009, 1247
[21]. R. J. Haan, J.-P. Lange and L. Petrus, US Pat. 20070208183, 2007
[22]. H. Mehdi,V.Fabios, R.Tuba, A.Bodor, L.T.Mika and I.T.Horváth, Top.Catal. 48, 2008, 49
[23]. J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke and H. Gosselink, Angew.Chem., Int. Ed., 49, 2010, 4479
[24]. L. E. Manzer, US Pat. 6617464 B2, 2003
[25]. R. A. Bourne, J. G. Stevens, J. Ke and M. Poliakoff, Chem. Commun., 2007, 4632.
[26]. Z. P. Yan, L. Lin and S. Liu, Energy Fuels, 23, 2009, 3853
[27]. F. Joo and M. T. Beck, React. Kinet. Catal. Lett., 2, 1975, 257
[28]. F. Joo, Z. TothandM. T. Beck, Inorg. Chim.Acta, 25, 1977, L61.
[29]. K. Osakada, S. Yoshikawa and T. Ikariya, J. Organomet. Chem., 231,1982, 79
[30]. W.R.H.Wright,R.Palkovits, chem.sus.chem, 5, 2012,1657
[31]. I. T. Horváth, H. Mehdi, V. Fábos, L. Boda and L. T. Mika, Green Chem., 10, 2008, 238
[32]. B.L.Oser, S.Carson,M.Oser,Food cosmet.toxicol, 3,1965, 563
[33]. L. E. Manzer, Appl. Catal., A, 272, 2004, 249
[34]. a) D. Fegyverneki, L. Orha, G. Lang and I. T. Horvath, Tetrahedron, 66,2010, 1078– 1081
[35]. b) I. T. Horváth, Green Chem., 10,2008, 1024
[36]. J.P.Lange,J.Z.Vastering,R.J.Haan,chem.comm, 2007, 3488
[37]. A.P.Dunlop, J.W.Madden.,(Quakers oats Co), US2786852,1957.
[38]. M.Widebmeyer,; S. Grasser, K. Khler, R. Anwander, Micro. Meso. Mat. 44-45, 2002, 327
[39]. Y. H. Hsien,C. F. Chang, Y. H. Chen, S. Sheng, Appl. Catal. B 31, 2001, 241
[40]. A. Tuel, L. G. Hubert-Pfalzgraf, J. Catal. 217, 2003, 343
[41]. F. Chicker, J. Ph. Nogier, F. Launay, J. L. Bonarder, Appl. Cata. A 243,2003, 309
[42]. M.V. Landau, L. Vradman, X. Wang, L. Titelman, Micro. Meso. Mat. 78, 2005, 117
[43]. R. Srivastava,D. Srinivas, P. Ratnasamy, Micro. Meso. Mat. 90, 2006, 314.
[44]. R.Gmez-Reynoso, J.Ramrez, R.Nares, R. Luna, F.Murrieta, Catal. Today 107-108, 2005, 926
[45]. Liou TH, Chang FW, Lo JJ, Pyrolysis Kinetics Of Acid-Leached Rice Husk. IndustrialEngineering & Chemical Research. 1997
[46]. Chakraverty A, Mishra P, Banerjee HD ,Investigation Of Combustion Of Raw AndAcid-Leached Rice Husk For Prod. Of Pure Amorphous White Silica. J Mat.Sci 23, 1988, 21-24.
[47]. J. Q. Wang, L. Huang, M. Xue, Y. Wang, L. Gao, J. H. Zhu, Z. Zou, J. Phys. Chem. C,112,2008, 5014.
[48]. T. Kang, Y. Park, K. Choi, J. S. Lee, J. Yi,J.Mater. Chem, 14,2004, 1043
[49]. A. Rahman, S. B. Jonnalagadda, Catal. Lett, 123, 2008, 264
[50]. M. Zhu, Z. Li, Q. Wang, X. Zhou and X. Lu, Ind. Eng. Chem. Res., 51,2012, 11659
[51]. M. Akcay, Appl. Catal., A, 294,2005, 156.
[52]. B. Mile, D. Steriling, M. A. Zammitt, J. Mol. Catal, 62,1990, 179
[53]. T. Wu, Q. Yan, H. Wan, J. Mol. Catal. A: Chem, 226, 2005, 41

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