Comparison of Acidity Test Method of Nickel Phosphate Silica Catalyst for Production Levulinic Acid from Glucose

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Abstract

The reaction of Levulinic acid production from glucose has a reaction stage that requires a high temperature and high activation energy so that in this Levulinic acid production reaction a catalyst is needed. The required catalyst must have a lewis acid site and a bronsted acid site so that the acidity of the catalyst is very influential for the successful production of Levulinic acid. Silica nickel phosphate catalysts have lewis acid sites from Ni metal and bronsted acid sites from phosphoric and silica groups. The acidity of the catalyst was measured using the pyridine and ammonia adsorption method and the acidity center strength method using the TGA-DTA base adsorption-desorption. The adsorption of ammonia and pyridine uses the gravimetric method so that it can easily obtain the amount of total acidity of the catalyst and the acidity of the catalyst surface while the TGA-DTA method shows the acid strength of the actual catalyst, which is the real state of the catalyst when catalyzing a reaction and shows the catalyst's resistance to high temperatures. These two methods of measuring acidity have the same disadvantage that they cannot show and know the number of lewis acid sites and bronsted acid sites.

Keywords: Nickel Phosphate Silica, Acidity Catalyst, Adsorption-desorption base, Gravimetric, TGA-DTA

Abstrak (Indonesian)

Reaksi produksi asam levulinat dari glukosa memiliki tahapan reaksi yang membutuhkan suhu yang tinggi dan energi aktivasi yang tinggi sehingga dalam reaksi produksi asam levulinat ini dibutuhkan katalis. Katalis yang dibutuhkan harus memiliki situs asam lewis dan situs asam bronsted sehingga keasaman katalis sangat berpengaruh untuk keberhasilan produksi asam levulinat. Katalis nickel fosfat silika memiliki situs asam lewis dari logam Ni dan situs asam bronsted dari Gugus fosfat dan silika. Keasaman katalis diukur menggunakan metode adsorpsi piridin dan ammonia dan metode kekuatan pusat keasaman menggunakan adsorpsi-desorbsi basa TGA-DTA. Adsorpsi ammonia dan piridin menggunakan metode gravimetri sehingga dapat dengan mudah mendapatkan jumlah keasaman total katalis dan keasaman permukaan katalis sedangkan metode TGA-DTA memperlihatkan kekuatan asam dari katalis yang sebenarnya yaitu keadaan nyata katalis saat mengkatalisis suatu reaksi dan memperlihatkan ketahanan katalis terhadap suhu tinggi. Kedua metode pengukuran keasaman ini memiliki kelemahan yang sama yaitu tidak dapat menunjukkan dan mengetahui jumlah situs asam lewis dan situs asam bronsted.

Kata Kunci: Nikel fosfat silika, Keasaman katalis, Adsorpsi-desorpsi basa, Gravimetri, TGA-DTA

INTRODUCTION

Levulinic acid is a flatform chemical compound in the chemical industry for the manufacture of polymers, organic chemical compounds and the pharmaceutical industry [1]. Levulinic acid can be produced from several raw materials such as biomass, glucose and fructose [2]. The production of Levulinic acid from glucose raw materials in the reaction through

several intermediate reactions, namely glucose isomerase into fructose, dehydration reaction to 5-HMF and rehydration reaction to Levulinic acid [3]. A very long reaction makes the process of producing Levulinic acid from glucose requires a large activation energy so that a catalyst is needed [4].

The catalysts needed in the Levulinic acid production process have distinctive characteristics because each intermediate reaction requires different acidity properties of the catalyst [5]. In the process of isomerase glucose into Levulinic acid requires lewis acid properties and the dehydration process becomes 5-HMF and the process of rehydration into Levulinic acid requires the acidity properties of Bronsted [6]. The silica nickel phosphate catalyst in its structure has both acidity properties, namely lewis acid from Nickel metal [4] and Bronsted acid from SiO_2 and $-HPO_4$ [7].

The acidity value of a catalyst can be analyzed by analysis of the acidity of the catalyst. Catalyst acidity analysis can be determined in several ways, namely acid strength determination methods, determination of acids strength and acid number of acids center, base adsorption method, titration methods and temperature programmed desorption method [8]. Comparison of the methods of measuring the acidity of the silica nickel phosphate catalyst that will be discussed in this text is adsorption with ammonia to find out the total acidity of the catalyst and adsorption using pyridine to find out the amount of acidity of the catalyst surface and the TGA method.

MATERIALS AND METHODS
Materials
The equipment used in the study included a set of standard glassware, furnace, analytical balance sheet, 200 mesh sieve, mortar, hot plate, oven, filter paper, regular funnel, vacuum filter, magnetic stirrer, Stative, Centrifugation, TGA-DTA Hitachi STA200RV. The ingredients used in the study include Ammonia liquid Merck, Pyridine Merck, $AgNO_3$ Merck, Ammonium dihydrogen phosphate Merck, Diammonium hydrogen phosphate Merck, Absolute Ethanol Merck, Ammonia Merck, Demin Water, Nickel Chloride Hexahydrate Merck, Nickel Nitrate Hexahydrate Merck, TEOS Merck, Tributyl phosphate Merck.

Methods
Preparation of Nickel Phosphate Solution
Synthesis of $Ni_3(PO_4)_2$ reactants was started by mixing 0.002 mol $NiCl_2.6H_2O$ and 0.0013 mol $(C_4H_9)_3PO_4$ then dissolved with aqueous afterwards into a 100 mL measuring flask and then diluted with aqueous [9]. The manufacture of nickel phosphate solution with mole from nickel solution is made the same, namely 0.002 mol and three different phosphate sources based on the reaction below:

$$3Ni^{2+} + 2(C_4H_9)_3PO_4 \rightarrow Ni_3(PO_4)_2 + 6(C_4H_9)^+$$
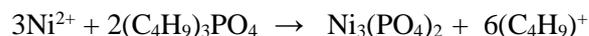
Preparation of Silica Nickel Catalyst and Nickel Phosphate Silica
Preparation of silica nickel phosphate was done by mixing 50 mL of absolute ethanol with 5 mL of water. A mixture of water and ethanol is stirred using a magnetic stirrer for 15 minutes. Then 5.6 mL of TEOS and 1 mL of 28% liquid ammonia were added to the mixture of water and ethanol. The mixture is then stirred using a magnetic stirrer using room temperature for 3 hours. After 30 minutes the solution will turn a turbid color then 2 mL of liquid ammonia is added by dripping it slowly with a state of remaining sorted for 30 minutes. After 30 minutes silica will form in the form of a gel. The silica gel obtained is ventilated for 24 hours with a temperature of 85 °C until it becomes silica powder. The obtained silica powder is dispersed into 100 mL of nickel phosphate silica solution and for silica nickel catalyst by dispersing silica gel into 100 mL of nickel nitrate solution 0.02 M for 30 min [9]. After 30 minutes the solution is put in the oven for 24 hours with a temperature of 120°C. Then the catalyst is calcined with a temperature of 700 °C for 4 hours then smoothed and sifted 200 mesh.

Adsorption using pyridine and ammonia
The acidity of the catalyst is carried out by gas adsorption ammonia. The empty crucible was weighed and recorded as W_1 then added with a catalyst of 0.5 g in the crucible then weighed and recorded as W_2 and put into the desiccator. The desiccator used must be closed and have 2 valves one connected with a vacuum pump and one connected with a closed erlenmeyer containing liquid ammonia or liquid pyridine.

The desiccator that has contained the catalyst, the valve connected to liquid ammonia or liquid pyridine is closed, while the valve connected to the vacuum pump is opened to vacuum the desiccator's circumference. Steaming is carried out for 1 hour. After 1 hour the vacuum pump valve is closed, the valve connected with ammonia or liquid pyridine is opened, then left for 24 hours. After that the Crucible was removed from the desiccator then weighed and recorded as W_3[10].

Strength Analysis of catalyst acidity with TGA-DTA
The sample to be analyzed by the TGA-DTA method of the sample is prepared by being adsorbed first using ammonia and pyridine. This procedure of adsorbing ammonia and pyridine is carried out the same as doing adsorption using pyridine and ammonia.

After that samples that had adsorbed ammonia and pyridine were analyzed with TGA-DTA with Simultaneous differential scanning calorimetry and thermogravimetric analysis of used nickel phosphate silica catalyst were carried out in a flow of air (20 mL/min) at a heating rate of 1 °C /min with a DSC-TGA STA449F3 thermal analyzer. The DSC-TGA data was obtained at the temperature ranging from 40 to 600 °C. The sample loading was typically 10–15 mg

Data Analysis

The acidity of the catalyst using the Adsorption using pyridine and ammonia method can be calculated using the formula below:

Formula Adsorption Ammonia Total Acidity catalyst:

$$\frac{w_3 - w_2}{Mr\ NH_3\ (w_1 - w_2)} \times 1000\ mmol \qquad (1)$$

Formula Absorption Pyridine Surface Acidity:

$$\frac{w_3 - w_2}{Mr\ N_5H_3(w_1 - w_2)} \times 1000\ mmol \qquad (2)$$

RESULTS AND DISCUSSION

Adsorption using pyridine and ammonia

Catalyst acidity analysis using ammonia gas is used to calculate the total acidity of the catalyst. This is because ammonia is able to be adsorbed on the surface and into the pores of the catalyst. The size of molecule ammonia is smaller than pyridine molecule size so that it can be adsorbed into the catalyst pore and bind to the active site in the catalyst pore [11]. Ammonia will bind to the active site owned by the catalyst. The results obtained from the analysis of the total acidity of the catalyst using ammonia gas are shown in **Table** 1.

The $Ni(H_2PO_4)_2$-SiO_2 catalyst has the highest total acidity of the other three silica nickel phosphate catalysts at 8,275 mmol/g. This can be due to the presence of lewis acid sites from nickel metals and Bronsted acid sites from OH^- groups based on H_2PO_4 and SiO from catalyst support, namely silica [12]. The most important thing that increases the acidity of the $Ni(H_2PO_4)_2$-SiO_2 catalyst is the number of Hydrogen atoms that are the site of the Bronsted acid[11].

The difference in the total acidity of the catalyst between the catalysts is influenced by the number of hydrogen atoms because the surface hydroxy groups can act as Brønsted acid or base sites. the catalyst $Ni(H_2PO_4)_2$-SiO_2 has two hydrogen atoms from the $(H_2PO_4)^-$ group and $NiHPO_4$-SiO_2 has one hydrogen atom from $(HPO_4)^{2-}$ and the catalysts $Ni_3(PO_4)_2$-SiO_2 and Ni-SiO2 do not have hydrogen atoms because there is no group $(H_2PO_4)^-$ or $(HPO_4)^{2-}$, so from Table 1 it can be seen that the decrease in the number of Hydrogen atoms from the catalyst is directly proportional to the decrease in the total acidity of the catalyst. This is also confirmed by the results of the analysis of the total acidity of the catalyst from the $Ni_3(PO4)_2$-SiO_2 and Ni-SiO_2 catalysts which have a total acidity value that is not too far away.

Table. 1 Acidity analysis using ammonia

Sample	W_1 (g)	W_2 (g)	W_3 (g)	Total acidity (mmol/g)
$Ni(H_2PO_4)_2$-SiO_2	12.6340	13.1379	13.2089	8.275
$NiHPO_4$-SiO_2	15.7022	16.2039	16.2651	7.166
$Ni(PO4)_2$-SiO_2	14.4015	14.9061	14.9061	1.501
Ni-SiO_2	15.1900	15.6924	15.7048	1.450

Acidity analysis using pyridine absorption is performed to analyze the acidity of the catalyst surface. Pyridine gas will be absorbed on the surface of the catalyst and bind to the active site that is on the surface of the catalyst. It is characterized by pyridine being larger in size than ammonia so that the pyridine only binds to the site active on the surface of the catalyst [11]. The results of the catalyst surface acidity analysis can be seen in **Table** 2. The $Ni(H_2PO_4)_2$-SiO_2 catalyst has the highest acidity value of the other three nickel phosphate catalysts. The advantage of the gravimetric acidity analysis method using ammonia and pyridine in the gas phase is that it can determine the total acidity or acidity of the surface and the equipment needed is easy to obtain and cheap, and the results are also can be obtained in a short time. Weakness this method is unable to see the strength of the acidity of the catalyst on the reaction and unable to determine the number of sites of lewis acid and Bronsted acid.

Table 2. Acidity Analysis using pyridine

Sample	W_1 (g)	W_2 (g)	W_3 (g)	Total acidity (mmol/g)
$Ni(H_2PO_4)_2$-SiO_2	16.2540	16.8038	16.8894	0.126
$NiHPO_4$-SiO_2	16.5439	17.0447	17.4495	0.070
$Ni(PO4)_2$-SiO_2	15.7832	16.3144	16.3269	0.017
Ni-SiO_2	15.6463	16.1493	16.1343	0.015

Analysis of the strength of the catalyst using the base adsorption-desorption method

The acidity of the catalyst can also be determined using the base adsorption-desorption method, which is where the catalyst is fed with ammonia gas and

pyridine gas which is the process of adsorption of the base by the catalyst. The alkaline desorption process in this method and analyzed using TGA-DTA [13]. TGA charts for each catalyst that has adsorbed ammonia gas can be seen in **Figure** 1. Ni-SiO$_2$ catalyst and Ni$_3$(PO$_4$)$_2$-SiO$_2$ there was a significant decrease in temperatures below 150°C which were identified as desorption of ammonia gas with the catalyst acid site. The bonding of the acid site with ammonia is relatively weak so that it is easy to break at a temperature of 150 °C [14].
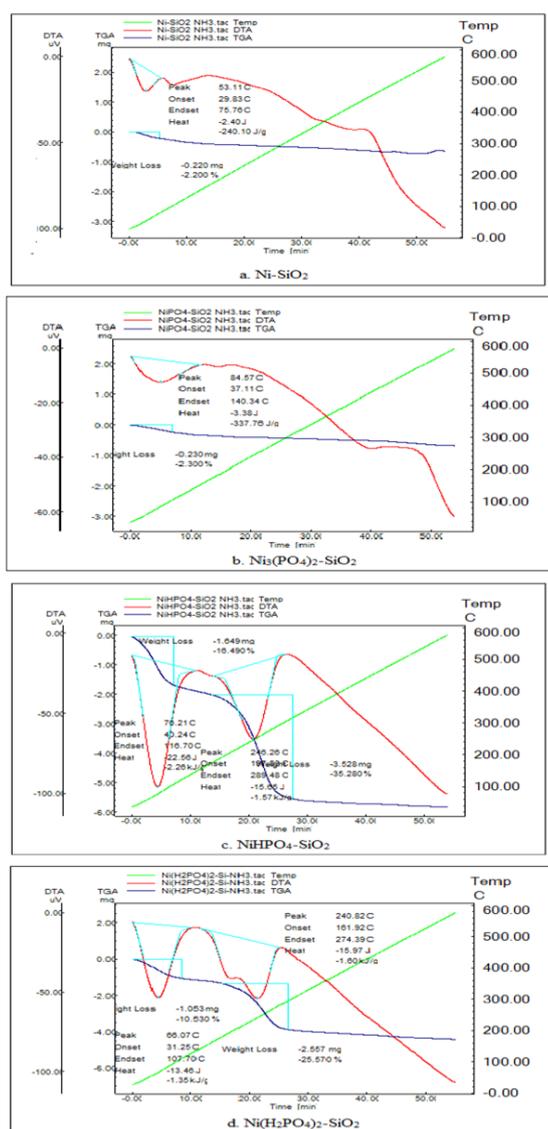
Figure 1. TGA-DTA from ammonia adsorbed Nickel phosphate catalyst a) Ni-SiO$_2$ b) Ni$_3$(PO$_4$)$_2$-SiO$_2$ c) NiHPO$_4$-SiO$_2$ d) Ni(H$_2$PO$_4$)$_2$-SiO$_2$

The Ni-SiO$_2$ catalyst curved can be seen in **Figure** 1a, shows only one peak of the TGA-DTA which shows at a temperature of 53.11 °C with a lost mass of 2.2% of the mass lost from the catalyst identified as

ammonia release, after which there is no significant mass reduction, this also shows that the catalyst is stable at high temperatures.

Figure 1b has only one peak.at a temperature of 84.57 °C and there is a significant mass reduction of 2.3%. The mass reduction is identified as the release of ammonia absorbed by the catalyst. The Ni$_3$(PO$_4$)$_2$-SiO$_2$ catalyst in **Figure** 1b shows stability in high temperatures as there is no longer a significant mass change at 300°C. Ni-SiO$_2$ and Ni$_3$(PO$_4$)$_2$-SiO$_2$ catalysts did not experience significant weight loss this is due to no catalyst decomposition, Ni$_3$(PO$_4$)$_2$ and Ni-SiO$_2$ will be decomposed at a temperature of about 600°C[15].

The NiHPO$_4$-SiO$_2$ and Ni(H$_2$PO$_4$)$_2$-SiO$_2$ catalysts shown in **Figure** 1c and **Figure** 1d. NiHPO$_4$-SiO$_2$ catalysts have the first two peaks of TGA-DTA at temperature of 76.21°C, with a mass decrease of 16.49% this peak is identified as ammonia release, so this number is considered the total number of active sites of the catalyst. The second peak was at a temperature of 246.26°C and a mass decrease of 35.28% this peak was identified as degradation from the catalyst indicating that the catalyst was unstable at high temperatures. Ni-SiO$_2$ and Ni$_3$(PO$_4$)$_2$-SiO$_2$ catalysts have the same results as Ni-SiO$_2$ and Ni$_3$(PO$_4$)$_2$-SiO$_2$ catalysts that adsorb ammonia, which does not experience significant weight loss, this is because there is no catalyst decomposition, Ni$_3$(PO$_4$)$_2$ and Ni-SiO$_2$ will decompose at a temperature of around 600°C [15].

The Ni(H$_2$PO$_4$)$_2$-SiO$_2$ catalyst has two TGA-DTA peaks. The first peak is at a temperature of 66.07°C with a mass change of 10.53%. This is identified as the release of ammonia gas adsorbed by the catalyst active site, this value is identified as the total acidity of the catalyst. The second peak was at a temperature of 240.82°C with a mass decrease of 25.57%. The second peak is identified as degradation of the catalyst or a change in the structure of the catalyst so that the catalyst is unstable at high temperatures. All catalysts have peaks at temperatures below 100°C which are identified as ammonia releases adsorbed by the catalyst's active site [16] so that the strength of the catalyst acid is determined from the amount of mass lost at temperatures below 100°C. The catalyst that has the highest acid strength is NiHPO$_4$-SiO$_2$ but this catalyst is also the most unstable at high temperatures. The decomposition of Ni(H$_2$PO$_4$)$_2$-SiO$_2$ and NiHPO$_4$-SiO$_2$ catalysts due to the release of hydrogen and oxygen atoms [17].

Acidity analysis of alkaline adsorption-desorption was also carried out using pyridine gas. In this method, pyridine gas is used as an adsorbent and adsorption is

carried out on the catalyst and the desorption process is carried out using TGA-DTA analysis. The TGA-DTA graph for catalysts that adsorb pyridine gas can be seen in **Figure** 2.
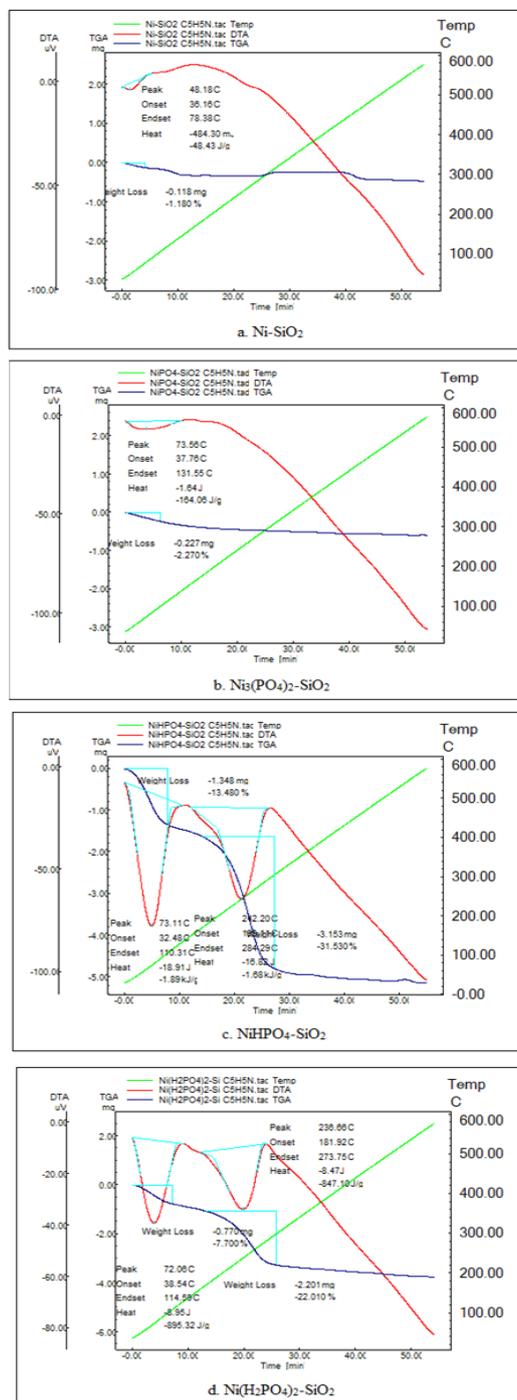
Figure 2. TGA-DTA graph of pyridine adsorbed nickel phosphate catalysts a) Ni-SiO$_2$ b) Ni$_3$(PO$_4$)$_2$-SiO$_2$ c) NiHPO$_4$-SiO$_2$ d) Ni(H$_2$PO$_4$)$_2$-SiO$_2$

The Ni-SiO$_2$ catalyst curved can be seen in **Figure** 2a, there is one peak of TGA-DTA at a temperature of 48.18 °C with a time decrease of 1.18%. This is identified as the release of pyridine gas absorbed by the catalyst. The amount of mass lost is less than that of Ni-SiO$_2$ catalysts that are adsorbed with ammonia gas. The TGA-DTA graph of Ni$_3$(PO$_4$)$_2$-SiO$_2$ is shown in **Figure** 2b, the Ni$_3$(PO$_4$)$_2$-SiO$_2$ catalyst also has one peak at a temperature below 100°C which is at a temperature of 73.56°C. with a lost mass of 2.27%. The pyridine-infused Ni$_3$(PO$_4$)$_2$-SiO$_2$ catalyst has almost the same amount of mass loss as the Ammonia-adsorbed Ni$_3$(PO$_4$)$_2$-SiO$_2$ catalyst.

The TGA-DTA curved of NiH$_2$PO$_4$-SiO$_2$ catalyst in **Figure** 2b has two peaks. The first peak was at 73.11°C with a lost mass of 13.48%. The first peak is identified as the strength of the catalyst acid because this peak is the peak at which the release of pyridine absorbed by the catalyst. The second peak at 242.20°C with a missing mass of 31.53% of the peak was identified as a change in the structure of the catalyst indicating that the catalyst was NiH$_2$PO$_4$-SiO$_2$ unstable at high temperatures. The TGA-DTA curved of Ni(H$_2$PO$_4$)$_2$-SiO$_2$ in **Figure** 2d. It is seen on the chart that Ni(H$_2$PO$_4$)$_2$-SiO$_2$ also has two peaks, namely the first peak at a temperature of 72.06% with a lost mass of 7.70% and the second peak at a temperature of 236.66 °C with a lost mass of 22.01%. The first peak is identified as the acidity strength of the catalyst because at this temperature it is the release of pyridine absorbed by the catalyst while the second peak is a change in the structure of the catalyst which indicates that the catalyst is unstable at high temperatures. The presence of decomposition of the catalyst Ni(H$_2$PO$_4$)$_2$-SiO$_2$ and NiHPO$_4$-SiO$_2$ just like a catalyst that adsorbs ammonia, which is due to the release of hydrogen and oxygen atoms [17].

TGA-DTA analysis using ammonia and pyridine obtained a significant weight lost point was at the same temperature but had a difference in the amount of mass loss. Analysis of the strength of the central acid using base adsorption-desorption analyzed using TGA-DTA has the advantage of this method is that the acidity measurements can be made in the real working conditions of the catalyst and see the catalyst's resistance to temperature and time. The disadvantage of this method of acidity analysis is that it cannot significantly calculate the number of sites of lewis acid and Bronsted acid and must use instruments and results are not obtained directly [16].

CONCLUSION

Each of the silica nickel phosphate catalysts has a lewis acid site and a Bronsted acid site and has a different central acid strength. The total acidity of the

catalyst can be determined using the gravimetric acidity analysis method using gaseous phase ammonia while to see the acidity of the catalyst surface can use the gravimetric acidity analysis method using pyridine. Catalyst Ni(H$_2$PO$_4$)$_2$-SiO$_2$ has the highest total acidity value and surface acidity value of 8.275 mmol/g and 0.126 mmol/g. The TGA-DTA method can be used to measure the central acid strength of a catalyst that represents the strength of the catalyst acid at a real reaction but the catalyst needs to be dosed using ammonia and pyridine with a gas phase first and requires instruments in the measurement. The similarity of these two methods of acidity analysis is that it cannot determine the lewis acid site and the Bronsted acid site.

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