

FULL PAPER

Synthesis of silica nanoparticles and study of its catalytic properties in the preparation of carboxylic esters

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Silica nanoscale powders were obtained by heat treatment on the waste of laboratory silica gel HF₂₅₄ available at the warehouse. That white solid was thermally treated at optimal conditions at 700 °C for 4 h. After decomposition of all of the materials, it was refluxed with HCl (6 M) for 24 h. The prepared catalyst was characterized using the scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET) analysis. The average nanoparticle size was found to be 25 nm. The purpose was to investigate the attributes of the catalyst supported by chloro sulfuric acid and its application in the Fisher esterification reaction as an acid solid catalyst under solvent-free conditions. According to this, different parameters such as the types of alcohols and phenols and carbon chain length were studied using both nano-silica sulfuric acid (NSSA) and silica sulfuric acid (SSA) at the same conditions. In this case, the findings illustrated esterification at the presence of NSSA was performed at reaction time less than SSA and the production yield of NSSA was higher than SSA. The obtained results in the mentioned method proved silica from the wastes of silica gel HF₂₅₄ can be employed as a catalyst at the more reaction.

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KEYWORDSSilica nanoparticles; silica gel HF₂₅₄; nano silica sulfuric acid; esterification.**Introduction**

In the field of catalytic knowledge, achieving high activity and selectivity for performing a catalytic reaction is a challenging issue. Nanocatalysts based heterogeneous catalytic systems have a high surface-to-volume ratio which guarantees high activity of the catalytic system. Also, these catalysts, can be easily separated from the reaction media. These features make nanocatalysts based on heterogeneous catalytic systems as a great option for both industrial and academic chemists [1-8].

Nowadays, one of the most important and necessary tasks assigned to chemists,

especially organic chemists are the protection of the environment and also develops methods that are both environmentally and economically acceptable. One major objective is therefore to simplify and accommodate in a modern way the classical procedures with the aim of keeping pollution effects to a minimum, together with a reduction in energy and raw materials consumption. Solvent-free techniques are one of the most promising ways to reach this aim, because in this approach often removed the expensive, problematic, and toxic solvent. The solvent-free synthesis has a lot of advantages than with the other methods, such as higher yield of product, easier workup, safer reaction profile,

higher selectivity in many reactions, shorter reaction time [9-16].

Production of esters from alcohols, phenols, and carboxylic acids, usually carried out according to the Fisher method is called esterification reaction [17-21]. In literature, a transformation of alcohol to the corresponding acetate is carried out by various methods and mechanisms such as acetylation [17], Yamaguchi esterification [19], Steglich esterification [22], oxidative esterification of aldehydes [23], monoesterification [24], nitration and so on [25]. Since esterification is a very slow and reversible reaction and besides, plays an important role in various backgrounds [26-28] such as utilization in perfumes, flavors, adhesives, paint, cosmetic and hygienic, pharmaceuticals industries, and also as a plasticizer and insect propulsive, it is absolutely necessary to apply an appropriate catalyst for the industrial synthesis [18, 21].

Formerly, most commonly used catalysts for the synthesis of esters employed H_2SO_4 , HCl, and HI as the homogenous catalyst [29]. These catalysts produced exorbitant acid waste which is dangerous to environment whereas heterogeneous solid acid as a catalyst could be eventuated better than early catalysts in recent years [30-34]. While most of the reported results revealed disadvantages such as large reaction time, high cost, inaccessibility of the reagents, provision of new proper catalysts, and routes are still necessary for esterification.

Silica gel supported sulfuric acid is used in many organic chemical synthesis and transformations. It shows good results as a new, efficient, cheap, accessible, and recyclable catalyst [30-33].

In this work, we investigated the immobilization of sulfuric acid on silica nanoparticles for the preparation of carboxylic acid esters from alcohols and phenols which conducted to develop esterification reaction as a side reaction by attracting water.

Materials and methods

General

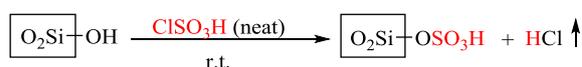
Commercially available chemicals were used without purification. The progress of the reaction was controlled by TLC. Separation of products determined the yield. Silica sulfuric acid and nano-silica sulfuric acid were prepared according to the reported literature. Nano-silica was produced from laboratory waste and was characterized using the spectroscopy methods and the obtained esters were characterized by the 1H NMR (250 MHz), ^{13}C NMR (62 MHz) in $CDCl_3$.

Preparation of Nano-Silica

Some of the HF_{254} wastes were retrieved by heat-treatment at $700\text{ }^\circ\text{C}$ for 4 h and all the additional materials were completely removed. The SiO_2 obtained from the waste was refluxed with HCl (6M) for 24 h, then the nano-particles were filtered and washed by distilled water for several times until reaching the pH of 7.

Preparation of Silica Sulfuric Acid (SSA)

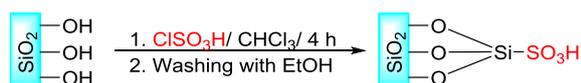
SSA was synthesized from the reaction silica gel with neat chlorosulfonic acid at room temperature (Scheme 1) [29].



SCHEME 1 Synthesis of SSA

Preparation of Nano-silica Sulfuric Acid (NSSA)

Nano-silica sulfuric acid was synthesized from the reaction of nano-silica extracted from the laboratory waste that was employed instead of silica gel with neat chlorosulfonic acid in $CHCl_3$ at room temperature for 4 h (Scheme 2) [29].

**SCHEME 2** Synthesis of NSSA*Synthesis of Esters from Alcohols and Carboxylic Acids*

A mixture of alcohol (1.5 mmol), benzoic acid (1 mmol) and SSA or NSSA (0.02 g) were stirred at 55-95 °C for the specified time (Table 1). The reaction was monitored by TLC. After completion of the reaction, the mixture was extracted with CH_2Cl_2 (20 mL), and filtered to recover the catalyst.

Synthesis of Esters from Phenols and Carboxylic Acids

A mixture of phenol (1.5 mmol), benzoic acid (1 mmol) and SSA or NSSA (0.02 g) were stirred at 100-200 °C (Table 2). The reaction was monitored by TLC. After completion of the reaction, the mixture was extracted with CH_2Cl_2 (30 mL) and filtered to recover the catalyst.

Butyl Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 0.982 (t, 3H, CH_3), 1.41 (m, 2H, CH_2), 1.76 (p, 2H, CH_2) 4.328 (t, 2H, $\text{CH}_2\text{-O}$), 7.2-7.583 (m, CH), 8.05 (d, 2H, CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 13.77, 19.27, 30.76, 64.83, 128.3, 129.52, 130.5, 132.78, 166.7.

Sec-butyl Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 0.98 (t, CH_3), 1.308 (d, CH_3), 1.7 (m, CH_2), 5.1 (m, CH), 7.42 (q, CH), 7.53 (CH), 8.05 (CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 9.7, 19.5, 28.9, 72.8, 128.2, 129.4, 130.9, 132.6, 166.2.

Cyclohexyl Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 1.434 (m, CH_2), 1.863 (m, CH_2), 2.2 (m, CH_2), 5.1 (m, CH), 7.25-7.56 (m, CH), 8.05 (CH). ^{13}C NMR (CDCl_3 , 62.5

MHz): δ 23.6, 25.4, 31.6, 73, 128.2, 129.5, 130.9, 132.6, 165.9.

Allyl Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 4.82 (d, 2H, CH_2), 5.30 (q, CH_2), 5.44 (q, CH_2), 6.029 (m, CH), 7.2-7.56 (m, CH), 8.1 (d, 2H, CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 65.53, 118.2, 128.36, 129.62, 130.13, 132.22, 132.98, 166.24.

Prop-2-yn-1-yl Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 2.50 (s, CH), 4.92 (s, 2H, CH_2), 7.12-7.75 (m, 3H, CH), 8.05 (m, 2H, CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 52.45, 75, 77.02, 128.43, 129.8, 133.35.

2, 2, 2-Trichloroethyl Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 4.98 (CH_2), 7.46 (CH), 7.628 (2 CH), 8.13 (2 CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 74.44, 95.08, 128.63, 128.7, 130.08, 133.83, 164.91.

Naphthalene-5-yl- Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 7.243 (d, CH), 7.335-8.071 (m, 10H, CH), 8.55 (d, CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 112.58, 117.93, 118.3, 121.3, 124.5, 127.35, 127.48, 128.37, 128.77, 129.13, 131.69, 133.83, 137.33, 138.19, 163.96, 201.14.

4-Benzoyl-3-hydroxyphenyl Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 6.9-8.23 (m, 13CH aromatic), 12.05 (OH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 118.4, 118.66, 121.72, 125.89, 128.35, 128.57, 129.16, 129.49, 130.17, 131.94, 133.59, 133.62, 150.96, 163.23, 165.19, 201.66.

4-Bromophenyl Benzoate

^1H NMR (CDCl_3 , 250 MHz): δ 7.127 (CH), 7.549 (CH), 8.17 (CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 119, 123.54, 128.64, 129.13, 130.20, 132.53, 133.82, 150.02, 199.

(3-chloro-4-hydroxyphenyl)(phenyl)methanone

^1H NMR (CDCl_3 , 250 MHz): δ 5.375 (OH), 7.298 (CH), 7.513 (CH), 7.67 (CH), 8.243 (CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 113.92, 120.7, 123.87, 127.06, 127.77, 128.64, 130.37, 133.85, 163, 207.

1-(1-hydroxynaphthalen-2-yl)ethan-1-one

^1H NMR (CDCl_3 , 250 MHz): δ 2.707 (s, CH_3), 7.26-7.986 (m, 5H, CH), 8.45 (m, CH). ^{13}C NMR (CDCl_3 , 62.5 MHz): δ 26.92, 118, 124.44, 124.92, 125.94, 127.40, 130.06, 140, 164, 202.

Results and discussion

The successful preparation of SSA and NSSA catalyst were investigated and confirmed by

applying several skills such as SEM, TEM, XRD and BET analysis. In the following, the obtained data were investigated in detail. In the beginning, HF_{254} wastes included all of the organic and inorganic substances which decomposed and obtained a white solid powder after thermal treatment at 700 °C for 4 h.

Catalyst Characterizations

In order to investigate the crystallographic features of the prepared nanocatalyst, X-ray Diffraction (XRD) analysis of the samples was performed. XRD diagram shows that silica nanoparticles have amorphous shape, and the SEM image confirms that their size are about 38-42 nm.

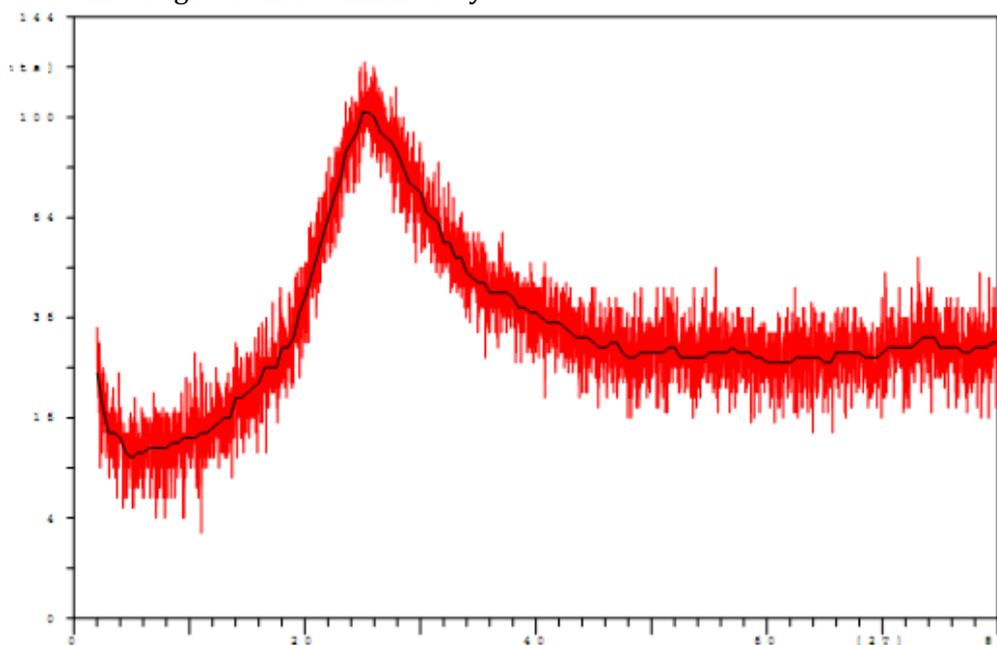


FIGURE 1 XRD pattern of recycled silica gel HF_{254} waste

In order to evaluate the morphology and particle size of the NSSA, SEM and TEM techniques were used (Figure 2 and 3). On the basis of SEM and TEM images, the catalytic particles in the NSSA sample has a round-shaped particles with diameters of about 20-

25 nm. That is a fact we succeeded to synthesize nanoparticles from harmful and useless waste. This project will be worth investigating more extensively for more improved outcomes in the future.

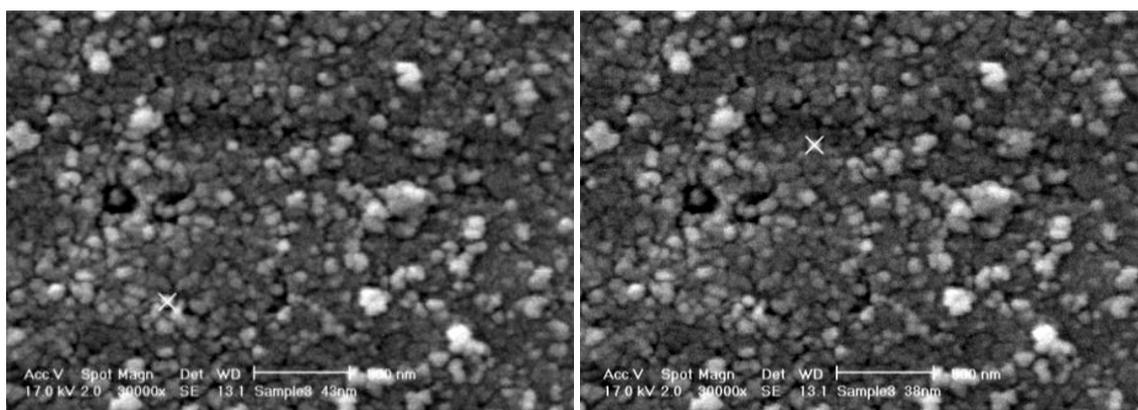


FIGURE 2 SEM micrographs of synthesized silica nanoparticles using silica gel HF₂₅₄ waste.

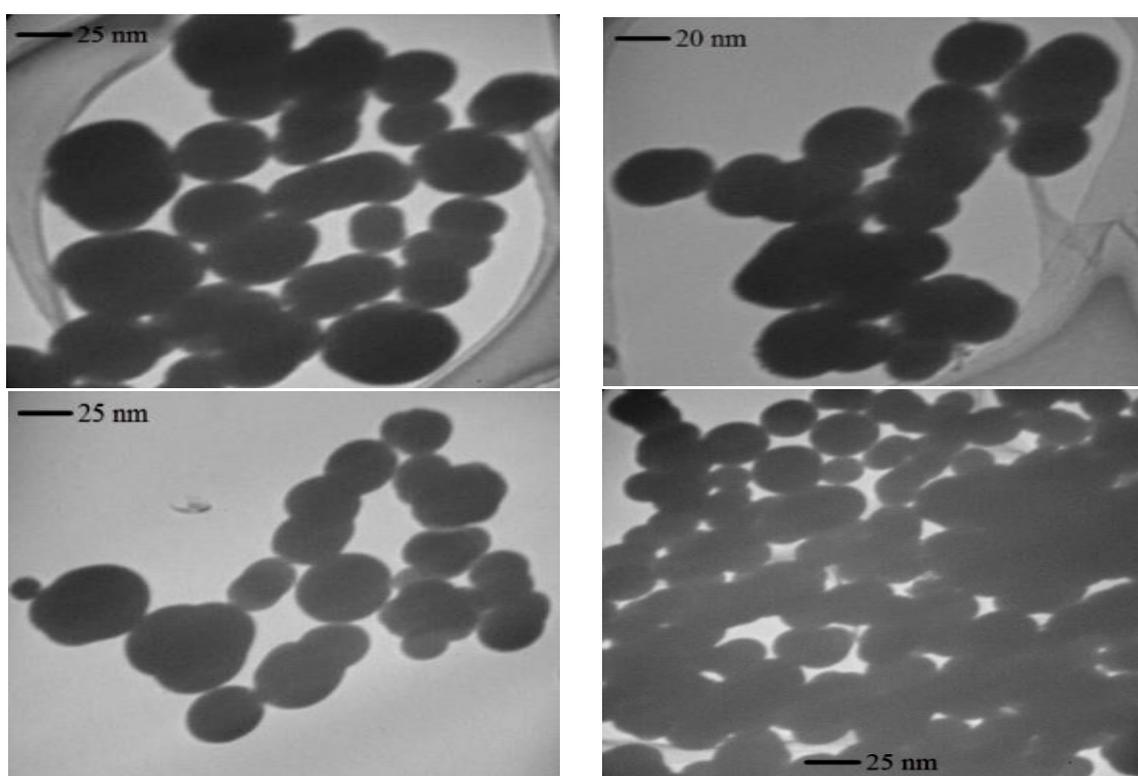


FIGURE 3 TEM micrographs of synthesized silica nanoparticles using silica gel HF₂₅₄ waste

Figure 4a illustrates the N₂ adsorption-desorption isotherms of the nanosilica powders with large hysteresis. This type of isotherm is characteristic of an open interpenetrating pore system with a cage structure. At higher pressures, the slope shows increased uptake of adsorbate as pores become filled, inflection point typically occurs near completion of the first monolayer. In fact, the initial loop is created mono-multilayer

adsorption and the second loop is created due to the desorption. This type of hysteresis loops has been observed with certain mesoporous ordered silicas after hydrothermal treatment. According to the literature, it occurs on porous adsorbents with pores at the range of 1.5-100 nm [35]. So, over 80% of particles were between the particle voids less than 10 nm (Figure 4b). So, it confirmed the mesoporous structure for the silica nanoparticles.

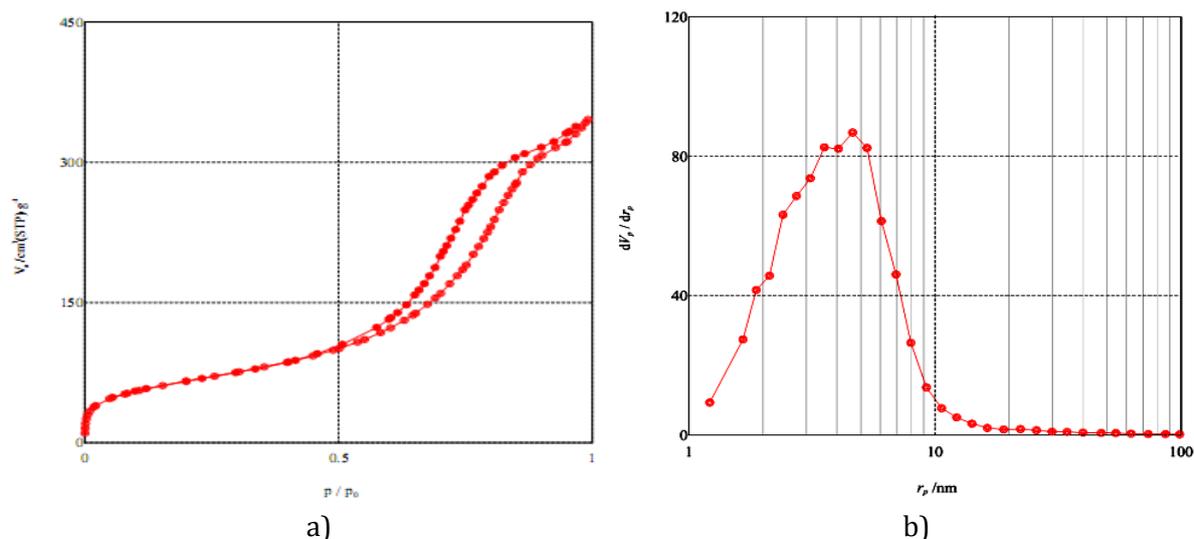


FIGURE 4 a) BET image and b) BJH image of the synthesized silica nanoparticles using silica gel HF254 waste

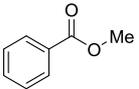
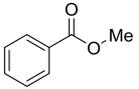
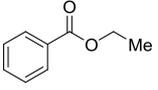
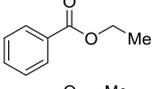
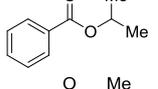
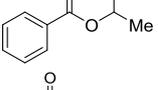
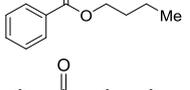
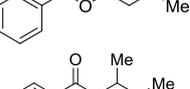
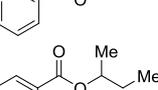
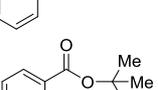
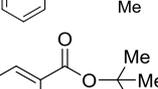
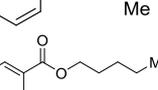
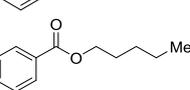
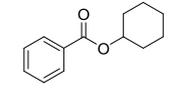
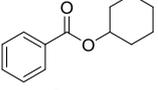
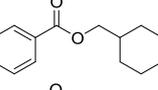
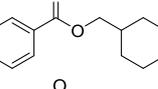
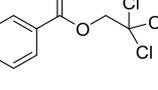
Effect of Catalyst

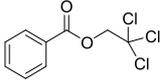
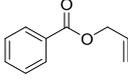
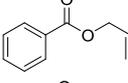
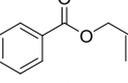
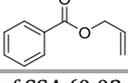
An acid catalyst such as SSA which has reliability in recent researches was prepared for investigation of the catalyst ability of such nano-particles. Esterification of the alcohols and phenols with benzoic acid and acetic acid at the presence of NSSA versus SSA as the catalyst was compared in the absence of a solvent (Tables 1 and 2).

As shown in Table 1 and 2, higher yields were obtained for NSSA compared to SSA at the same temperatures and conditions. Water, the by-product at the Fisher esterification, was always present at the reaction medium, so the reaction went on by absorbing water by the solid catalysts; however, the NSSA absorbed more water than SSA. This was due to its larger surface and consequently developed the side reaction and led to a much better yield than SSA. In entry 11 and 12 in Table 1, no products were formed except in an instant so we did not get any yield after performing about 30 h. We guessed it might have converted to alkenes at the presence of an acid catalyst via an elimination reaction.

It is important to pay more attention to the esterification of phenols with benzoic acid and acetic acid. As demonstrated in Table 2, we managed to prepare esters of phenols by NSSA and SSA and the observations were very wonderful. During the reaction process, several spots were observed on the TLC, which even continued by the end of the reaction. So we obtained several products and the results did not change with the repetition of reactions. It was supposed most likely that; rearrangement or dimerization reactions had taken place along the esterification. Conditions and workup were hard as all of the spots were very close to each other. We just separated the spots available in Table 2. One of them related to Fries rearrangement (Scheme 3) and the rest were not identified. Since the contents of other products were very low, we couldn't extract them. For this reason, no reliable results were reported for yields at entries 7, 8, 17, and 18. This experiment was also repeated at microwave irradiation conditions. Despite it took a very short time, since the spots were located more closely compared to the previous state, no product was separated.

TABLE 1 Esterification of alcohols using benzoic acid in the presence of SSA and NSSA

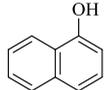
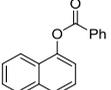
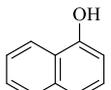
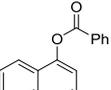
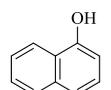
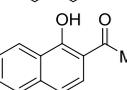
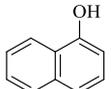
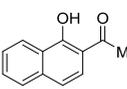
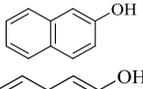
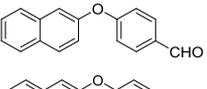
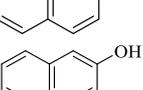
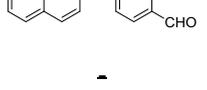
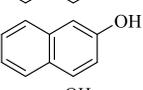
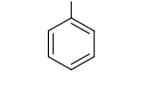
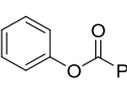
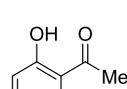
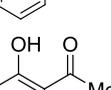
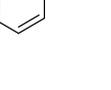
Entry	Alcohol	Catalyst	T (°C)	Time (h)	Ester	Yield% ^a
1	Methanol	NSSA	55	20		56
2	Methanol	SSA	85	21		28
3	Ethanol	NSSA	74	64		28
4	Ethanol	SSA	75	138		16
5	2-propanol	NSSA	75	47		22
6	2-propanol	SSA	75	93		11
7	1-butanol	NSSA	95	23		49
8	1-butanol	SSA	74	47		22
9	2-butanol	NSSA	75	97		36
10	2-butanol	SSA	74	175		27
11	Tertiary butanol	NSSA	80-90	28:15		-b
12	Tertiary butanol	SSA	74	240		-b
13	1-hexanol	NSSA	55	89		47
14	1-hexanol	SSA	85	95		35
15	Cyclohexanol	NSSA	95	23		83
16	Cyclohexanol	SSA	75	84		65
17	Benzyl alcohol	NSSA	75	9:30		80
18	Benzyl alcohol	SSA	95	47		33
19	Trichloro ethanol	NSSA	75	162		80

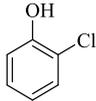
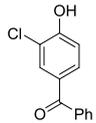
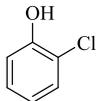
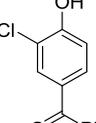
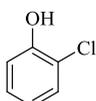
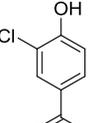
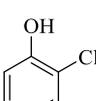
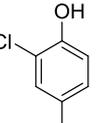
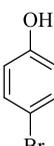
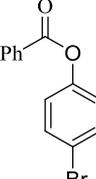
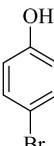
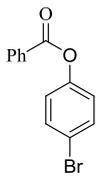
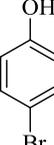
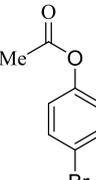
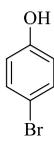
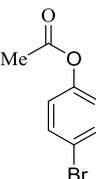
20	Trichloro ethanol	SSA	75	224		41
21	Alyl	NSSA	82	8		68
22	Alyl	SSA	75	18		40
23	Propargil	NSSA	92	5		25
24	Propargil	SSA	92	7		17

^a Esterification of alcohols (1.5 mmol) using benzoic acid (1 mmol) in the presence of SSA (0.02g) and NSSA (0.02g)

^b Ester was not formed

TABLE 2 Esterification of phenols (1.5 mm) using benzoic acid (1 mm) and acetic acid (1 mm) in the presence of SSA (0.02 g) and NSSA (0.02 g)

Entry	Phenol	Catalyst	Acid	T(°C)	Time(h)	Product	Yield (%) ^b
1		NSSA	Benzoic acid	180	15		74
2		SSA	Benzoic acid	180	21		56
3		NSSA	Acetic acid	180	22		62
4		SSA	Acetic acid	180	22		48
5		NSSA	Benzoic acid	200	8		34
6		SSA	Benzoic acid	200	8		12
7		NSSA	Acetic acid	200	17	-	- ^b
8		SSA	Acetic acid	200	17	-	- ^b
9		NSSA	Benzoic acid	100	10		39
10		SSA	Benzoic acid	100	10		24
11		NSSA	Acetic acid	180	18		10
12		SSA	Acetic acid	180	21		1

13		NSSA	Benzoic acid	200	15		25
14		SSA	Benzoic acid	200	15		10
15		NSSA	Acetic acid	180	19		12
16		SSA	Acetic acid	180	21		2
17		NSSA	Benzoic acid	200	7		- ^c
18		SSA	Benzoic acid	200	11		- ^c
19		NSSA	Acetic acid	180	2		28
20		SSA	Acetic acid	180	3		11

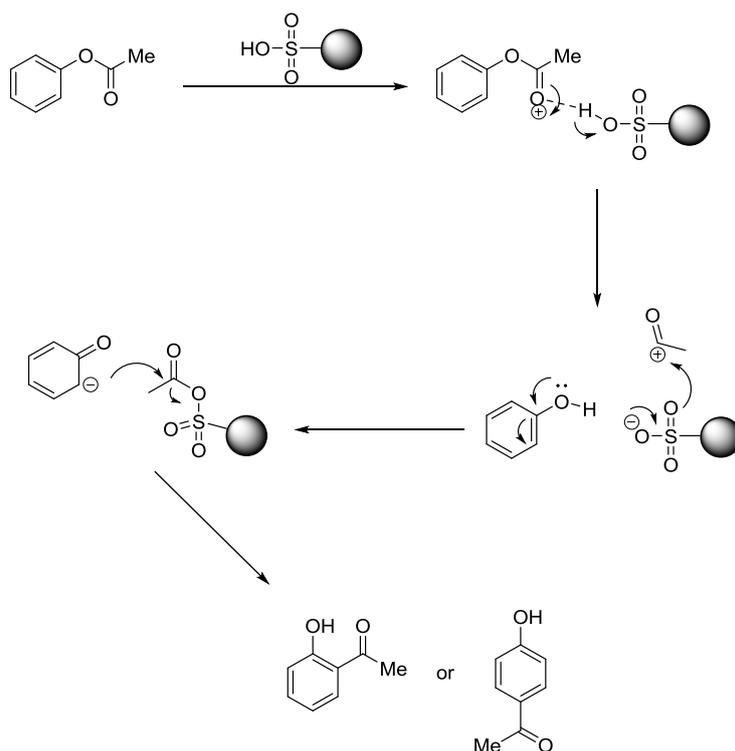
^a Esterification of phenols (1.5 mmol) using benzoic acid (1 mmol) and acetic acid (1 mmol) in the presence of SSA (0.02 g) and NSSA (0.02 g)

^b More than one product was formed which was impossible to separate

^c These products are the only one of several products which were produced during the reaction, there were ester and isomers of ortho and para.

As observed in Table 2, the yields of NSSA surpassed SSA again. Intention to discover the role of catalyst in the preparation of esters by Fisher method led to study the operation of the benzyl alcohol (1.5 mmol) and benzoic acid (1 mmol) with and without various kinds

of silica catalysts. The highest yield and the least time were observed for NSSA catalyst to other catalysts. It is necessary to explain that, the ester was just formed at the presence of silica gel after 100 h in similar conditions, as indicated in Table 3.

**SCHEME 3** Plausible mechanism for reactions**TABLE 3** Study the esterification of benzyl alcohol using benzoic acid in the presence of different catalysts (0.02 g) of silica

Entry	Catalyst	Time (h)	Temperature (°C)	Yield (%)
1	NSSA	19	75	80
2	SSA	46	75	33
3	NS	135	75	12
4	Silica	100	75	Low
5	None	53	75	Low
6	NSSA	166	25	15

We also evaluated the esterification of benzyl alcohol using the acetic acid at the same conditions with benzoic acid (Table 4). After 22 h at 75 °C, we obtained the glue of the reaction benzyl alcohol and acetic acid in the presence of NSSA which was not separated from the catalyst due to insoluble in any

solvent (Table 4, entry 1). Acetic acid might react with the nano-silica, forming ketene. Meanwhile, the content of the catalyst was slightly considered for the synthesis of esters. The rate of NSSA was larger and the yield of reaction was higher, which impressed the speed of the esterification.

TABLE 4 Study the esterification of benzyl alcohol using acetic acid in the presence of different catalysts (0.02 g) of silica

Entry	Catalyst	Time (h)	Temperature (°C)	Yield (%)
1	NSSA	22	75	-
2	NSSA	91	25	Low
3	Silica	168	75	low
4	SSA	62	75	15
5	-	168	75	No reaction

Effect of Carbon Chain Length in Types of Alcohol

Carbon chain length affected the rate of esterification. The sterical hindrance was a factor for this phenomenon and reduced the reaction rate (Table 5). The sterical hindrance effect in butanol and hexanol were more rather than methanol or ethanol. Furthermore, the sterical hindrance effect for cyclohexanol was less than 1-hexanol

regardless of the OH either at the axial or equatorial position. So it was a function for diminution of time of synthesis. However, trichloro ethanol (Table 1, entry 19) with short carbon chain length indicated more time for reaction due to the electron-withdrawing chlorides that donated acid specifications to alcohol. So its reactivity decreased compared with that of the ethanol.

TABLE 5 Study the effect of carbon chain length in esterification

Entry	Alcohol	Time (h)	Temperature (°C)	Yield (%)
1	Methanol	20	55	56
2	Ethanol	64	75	68
3	1-Butanol	43	75	49
4	1-Hexanol	89	75	47

Effect of Alcohol Type

According to the literature, the tendency rate of the esterification for alcohols will be $3^\circ < 2^\circ < 1^\circ <$ methanol. As seen in Table 6, we found that the tertiary butanol did not lead to producing the ester and 2-butanol required

more time and temperature than 1-butanol for the reaction. It confirmed that, the esterification speed at the presence of methanol is more than that of all other alcohols and tertiary butanol is the least. This method is not a favorable method for the synthesis of butyl benzoate.

TABLE 6 Study the type of alcohol in esterification

Entry	Alcohol	Time (h)	Temperature (°C)	Yield (%)
1	Methanol	20	55	56
2	1-butanol	43	75	49
3	2-butanol	55	75	35

Conclusions

Preparation of the NS from laboratory waste plays a significant role in green chemistry and reduction of the chemical pollution enters the environment. It can be a suitable acid catalyst to subject to chemical reactions. NSSA has a large and favorable surface for surface absorption, the reaction yield improves toward non-nano catalyst. It also is a green, clean, non-toxic, recyclable, cheap, and available catalyst just like SSA. As the above data confirms, Fisher esterification with NSSA attains better results than SSA. However, the yield of fisher esterification is

lower than that of the other approaches; however, the reaction was faster at the presence of the NSSA.

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