# Nano-TiO$_2$ on Dodecyl-Sulfated Silica: As an Efficient Heterogeneous Lewis Acid−Surfactant-Combined Catalyst (HLASC) for Reaction in Aqueous Media

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ABSTRACT: A reusable Lewis acid−surfactant-combined catalyst (LASC), using immobilization of nano-TiO$_2$ on dodecyl-sulfated silica support (NTDSS), has been developed. To obtain this catalyst system, sodium dodecyl sulfate (SDS) was reacted with silica chloride (SC) to generate a dodecyl-sulfated silica (DSS) substrate. Subsequently, the addition of TiCl$_4$ to a water solution of DSS resulted in the immobilization of nano-TiO$_2$ on the surface of a DSS substrate. The NTDSS catalyst was characterized using different techniques such as TEM, SEM, XRD, ICP, and FT-IR. The catalyst was successfully used for the synthesis of coumarin derivatives via Pechmann condensation in water as a green solvent. High catalytic activity of the catalyst in water media can be a result of colloidal particle formation on the surface of the NTDSS catalyst due to the grafted DS moieties on the surface of silica, which act as a surfactant. It seems that the generation of emulsion droplets containing nano-TiO$_2$ on the surface of the catalyst would function as an effective reaction reactor to accelerate the rate of the reaction in water media.

KEYWORDS: *Lewis Acid−surfactant-combined catalyst (LASC), TiO$_2$ nanoparticles, Water, Pechmann condensation, Coumarin*
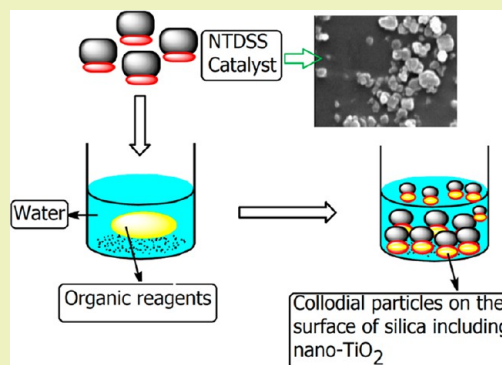
INTRODUCTION

Water is a safe, benign, green, and cheap solvent compared with other solvents for organic transformations.[1] However, common uses of water as a solvent in both industrial and academic researches is restricted because of two important limitations: (1) insolubility of most organic substances "in water" and (2) distribution or deactivation of many reactive substrates, reagents, and catalysts by water molecules.[2] Although some of the reactions have been conducted "on water", these reactions also have their limitations.[3] To overcome these constraints, there are some strategies that facilitate the use of water as a solvent for a wide range of reactions. Along this line, the use of organic co-solvents,[4,5] surfactants,[6,7] water-stable Lewis acids,[8−12] and Brønsted/Lewis acid−surfactant-combined catalysts[13−16] are the most important reported strategies to date. Among them, Lewis acid−surfactant-combined catalysts (LASC) are interesting because they act both as a catalyst to activate the substrate molecules and as a surfactant to form colloidal particles. The formed colloidal particles in water media function as an effective reaction reactor.[2] Several organic reactions including aldol, Diels−Alder, dehydration, allylation, Mannich-type, multicomponent, and cationic polymerization have been performed using LASC catalysts.[17−19] In the structure of LASC catalysts, there is a metal Lewis acid, and LASC catalysts of the following metals have been synthesized: Sc, Cu, Zr, Al, Ag, Zn, Yb, Mn, and Co.[13−19] It is noteworthy that in the most reported LASC catalysts the surfactant part is dodecyl sulfate (DS). According to previous studies, DS can

create a good combination with Lewis acids to form an efficient LASC catalyst.[20,21]

On the other hand, titanium (Ti) catalysts are well known as efficient and applicable catalysts in many organic transformations.[22−24] One of the reactive catalysts based on Ti is nano-TiO$_2$, which has been used as a catalyst in several reactions due to its unique surface properties.[25−30] High activity, reusability, strong oxidizing power, easy availability, nontoxicity, and long-term stability are other advantages of nano-TiO$_2$ catalysts.[31]

In the current study, our goal is to develop a novel heterogeneous catalytic system based on nano-TiO$_2$ that enables the use of water as a solvent for organic reactions. To achieve this aim, we used a mixture of nano-TiO$_2$ and DS as catalyst in a Pechmann reaction[32] (as an acid catalyst process). It was not effective in the reaction and also was not reusable. To improve the catalytic activity and heterogeneity of the nano-TiO$_2$ catalyst with regard to LASC catalyst concepts, we decided to graft the DS chains on silica to obtain a reusable substrate for immobilization of nano-TiO$_2$. For this purpose, SDS was reacted with SC to generate a DSS substrate. Following addition of TiCl$_4$ to a water solution of DSS substrate, generation of nano-TiO$_2$ on the substrate occurred. Herein, we disclose the preparation of immobilized nano-crystalline TiO$_2$ on a dodecyl-sulfated silica support (NTDSS)

as a reusable Lewis acid—surfactant-combined catalyst for application in organic transformations.

■ EXPERIMENTAL SECTION

General. Chemicals were purchased from Fluka and Aldrich chemical companies and used without further purification. The known products were characterized by comparison of their spectral and physical data with those reported in the literature. ^{1}H (250 MHz) and ^{13}C NMR (62.9 MHz) spectra were recorded on a Bruker Avance spectrometer in CDCl$_3$ and DMSO-d_6 solutions with tetramethylsilane (TMS) as an internal standard. X-ray diffraction (XRD, D8, Advance, Bruker, axs) and FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) were employed for characterization of the NTDSS catalyst and products. ICP analysis was determined using an inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro). The scanning electron micrograph (SEM) for the NTDSS catalyst was obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). Transmission electron microscopy (TEM) was obtained using a TEM apparatus (CM-10-Philips, 100 kV) for characterization of the NTDSS catalyst. Melting points were determined in open capillary tubes in a Barnstead electro-thermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70−230 mesh).

Experimental Procedure for Synthesis of NTDSS Catalyst.
Synthesis of Silica Chloride (SC). In a three-necked flask (100 mL) that was equipped with a dropping funnel containing thionyl chloride (SOCl$_2$, 40 mL), a condenser, and a gas inlet tube for conducting HCl gas over an adsorbing solution (10% NaOH) 10 g of silica was charged. Thionyl chloride was added dropwise over a period of 30 min at room temperature. When the addition was completed, the mixture was stirred for 24 h at the refluxing temperature of SOCl$_2$. Then, the untreated SOCl$_2$ was removed by distillation. The silica chloride was dried in a vacuum at 90 °C, and the resulting greyish powder was stored in a desiccator under vacuum.

Synthesis of Dodecyl-Sulfated Silica (DSS). A solution of 2 g SC, SDS (0.5 g), and triethylamin (0.5 mL) were refluxed in chloroform for 24 h. The resulting white precipitate was filtered through a Celite pad, washed with water, and dried in vacuum to afford the DSS substrate.

Synthesis of NTDSS Catalyst. For synthesis of the NTDSS catalyst, 0.55 mL of TiCl$_4$ (dropwise) was added in to a freshly prepared aqueous solution of DSS containing 5 g of DSS in 20 mL water. Then, the mixture was sonicated for 1 h and stirred at room temperature for 24 h. The resulting precipitate was filtered through a Celite pad, washed with water, and dried in vacuum to afford the NTDSS as a white solid.

General Procedure for the Pechmann Reaction Catalyzed by NTDSS. Into a canonical flask (25 mL), a mixture of phenol (1 mmol), β-ketoester or lactone (1.2 mmol), and NTDSS (0.05 g, 5 mol % Ti) were refluxed in H$_2$O (5 mL) for an appropriate time, which is specified in Scheme 2. After completion of the reaction, as indicated by TLC, 50 mL CHCl$_3$ was added, and the suspension was filtered to remove the catalyst. The obtained solution was then washed with water (2 mL × 50 mL) and evaporated. Finally, the residue was recrystallized from EtOH or EtOH−H$_2$O to obtain the pure compounds.

1-Methyl-3H-benzo[f]-chromen-3-one (3b). Yield: 96%, light pink solid, mp 177−179 °C. IR (KBr): ν = 1690 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.97 (s, 3H), 6.42 (s,1H), 7.51 (d, J = 9.0, 1H), 7.55−7.68 (m, 2H), 7.94 (d, J = 8.7, 1H), 8.00 (d, J = 9.0, 1H), 8.63 (d, J = 8.7, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS): 25.5, 113.8, 115.7, 117.3, 125.1, 125.3, 127.9, 129.4, 129.5, 130.8, 133.7, 153.9, 154.5, 159.1. Anal. Calcd for C$_{14}$H$_{10}$O$_2$ (210.23): C, 79.98 ; H, 4.79. Found: C, 79.95; H, 4.85.

7-Hydroxy-4-methyl-2H-chromen-2-one (3c). Yield: 95%, colorless prisms, mp 185−188 °C. IR (KBr): ν = 3500 (s), 1681 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.13 (s, 3H), 5.88 (s, 1H), 6.31 (s, 1H), 6.59 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 8.7 Hz, 1H),

10.32 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 18.0, 102.0, 110.1, 111.9, 112.7, 126.4, 153.4, 154.7, 160.2, 161.1. Anal. Calcd for C$_{10}$H$_8$O$_3$ (176.17): C, 68.18 ; H, 4.58. Found: C, 68.13; H, 4.60.

5,7-Dihydroxy-4-methyl-2H-chromen-2-one (3d). Yield: 98%, white solid, mp 280−284 °C. IR (KBr): ν = 3252 (s), 1668 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.44 (s, 3H), 5.81 (s, 1H), 6.14 (s, 1H), 6.16 (s, 1H), 10.4 (s, 1H), 10.50 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 23.4, 94.4, 98.0, 102.0, 108.7, 154.92, 156.42, 157.87, 160.04, 160.98. Anal. Calcd for C$_{10}$H$_8$O$_4$ (192.17): C, 62.50; H, 4.20. Found: C, 62.45; H, 4.24.

4,6,8-Trimethyl-2H-chromen-2-one (3e). Yield: 94%, white solid, mp 129−132 °C. IR (KBr): ν = 1708 (s) cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$/TMS) δ (ppm): 2.30 (s, 3H), 2.36 (s, 6H), 6.18 (s, 1H), 7.12 (s, 2H). ^{13}C NMR (62.9 MHz, CDCl$_3$/TMS) δ (ppm): 15.6, 18.8, 20.9, 114.7, 119.4, 122.0, 126.0, 133.1, 134.1, 150.1, 152.6, 161.2. Anal. Calcd for C$_{12}$H$_{12}$O$_2$ (188.22): C, 76.57; H, 6.43. Found: C, 76.51; H, 6.40.

7,8-Dihydroxy-4-phenyl-2H-chromen-2-one (3f). Yield: 90%, colorless oil. IR (KBr): ν = 3300 (broad), 1690 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 6.1 (s, 1H), 6.2 (s, 1H), 6.24 (s, 1H), 6.75−7.53 (m, 5H), 8.7 (s, 1H), 9.4 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS): 112.3, 117.2, 118.3, 126.4, 127.2, 128.5, 135.4, 142.8, 143.8, 146.2, 149.6, 155.9, 160.1. Anal. Calcd for C$_{15}$H$_{10}$O$_4$ (254.24): C, 70.86; H, 3.96. Found: C, 70.82; H, 4.11.

5,7-Dihydroxy-4-phenyl-2H-chromen-2-one (3g). Yield 93%, yellow solid, mp 236−238 °C. IR (KBr): ν = 3350 (broad), 1720 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 5.72 (s,1H), 6.14 (d, J = 2.5, 1H), 6.25 (d, J = 2.5, 1H), 7.29−7.32 (m, 5H), 10.1−10.39 (s, 2H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS): 94.6, 99.0, 100.5, 110.1, 127.2, 127.3, 127.7, 139.5, 155.9, 156.7, 157.0, 159.8, 161.7. Anal. Calcd for C$_{15}$H$_{10}$O$_4$ (254.24): C, 70.86 ; H, 3.96. Found: C, 70.82; H, 4.10.

7-Hydroxy-3-(2-hydroxyethyl)-4-methyl-2H-chromen-2-one (3h). Yield: 91%, white solid, mp 206−208 °C. IR (KBr): ν = 3400 (broad), 1725 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.34 (s, 3H), 2.68 (t, J = 7.5, 2H), 3.4 (t, J = 5.8, 2H), 4.6 (m, 1H), 6.6−7.6 (m, 3H), 10.38 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 14.8, 30.7, 59.3, 101.7, 112.5, 112.7, 118.3, 126.4, 148.4, 153.2, 160.0, 161.1. Anal. Calcd for C$_{12}$H$_{12}$O$_4$ (220.22): C, 65.45; H, 5.49. Found: C, 65.40; H, 5.55.

5,7-Dihydroxy-3-(2-hydroxyethyl)-4-methyl-2H-chromen-2-one (3i). Yield 94%, white solid, mp 236 °C (decompose). IR (KBr): ν = 3408 (broad), 1672 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.52 (s, 3H), 2.68 (t, J = 7.5, 2H), 3.40 (t, J = 7.5, 2H), 4.6 (m, 1H), 6.1 (d, J = 2.5, 1H), 6.2 (d, J = 2.5, 1H), 10.1 (s, 1H), 10.3 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 18.9, 30.3, 59.3, 94.1, 99.2, 114.9, 116.1, 150.1, 154.7, 159.8, 160.1, 160.8. Anal. Calcd for C$_{12}$H$_{12}$O$_5$ (236.22): C, 61.01; H, 5.12. Found: C, 59.95; H, 5.18.

4,6,7-Trimethyl-2H-chromen-2-one (3j). Yield 89%, white solid, mp 167−169 °C. IR (KBr): ν = 1706 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.27 (s, 3H), 2.36 (s, 3H), 2.49 (s, 3H), 6.24 (s, 1H), 7.13 (s, 1H), 7.46 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 22.8, 23.5, 24.3, 115.0, 121.5, 121.9, 122.5, 129.9, 131.8, 133.4, 140.6, 157.6. Anal. Calcd for C$_{12}$H$_{12}$O$_2$ (188.22): C, 76.57; H, 6.43. Found: C, 76.55; H, 6.47.

6-Benzyl-4-methyl-2H-chromen-2-one (3k). Yield 90%, white solid, mp 107−109 °C. IR (KBr): ν = 1706 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.29 (s, 3H), 3.90 (s, 2H), 6.17 (s, 1H), 7.07−7.31 (m, 8H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 18.6, 41.3, 111.8, 115.1, 117.1, 119.8, 124.5, 126.4, 128.7, 132.5, 137.2, 140.3, 152.03, 152.4, 160.9. Anal. Calc. for C$_{17}$H$_{14}$O$_2$ (250.29): C, 81.58; H, 5.46. Found: C, 81.13; H, 5.59.

Estradiol Coumarin (3l). Yield 88%, white solid. mp 115 °C. IR (KBr): ν = 3450 (broad), 1726 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 0.63 (s, 4H, CH$_3$+OH), 1.04 (m, 1H), 1.07 (m, 1H), 1.17 (m, 2H), 1.24 (m, 2H), 1.28 (m, 1H), 1.52 (m, 1H), 1.78 (m, 1H), 1.83 (m, 1H), 2.02 (m, 1H), 2.16 (m, 1H), 2.46 (m, 1H), 2.54 (s, 3H), 2.66 (t, J = 6.0 Hz, 2H), 3.49 (t, J = 8.5 Hz,

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1H), 6.40 (s, 1H), 6.45 (d, J = 8.5 Hz, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 11.2, 17.9, 22.7, 26.0, 26.9, 29.1, 29.8, 36.5, 38.6, 42.7, 43.5, 49.5, 80.0, 112.6, 114.6, 126.0, 130.4, 136, 137.1, 148.0, 154.8, 161.0. Anal. Calc. for $C_{22}H_{26}O_3$ (338.44): C, 78.07; H 7.74. found: C, 78.06; H, 7.62.

6-Amino-3-(2-hydroxyethyl)-4-methyl-2H-chromen-2-one (**3m**). Yield 90%, light brown solid, mp =213-215 °C. IR (KBr): ν = 3445 (s), 1658 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.14 (s, 3H), 2.67 (brs, 1H), 2.80 (t, J = 7.5 Hz, 2H), 4.1 (t, J = 7.5 Hz, 2H), 4.23 (s, 2H), 6.73 (d, J = 6.2 Hz, 1H), 6.93 (d, J = 6.2 Hz, 1H), 8.00 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 14.2, 29.7, 62.9, 115.2, 126.1, 127.3, 129.9, 130.3, 153.1, 154.5, 154.6, 172.1. Anal. Calc. for $C_{12}H_{13}NO_3$ (219.24): C, 65.74; H, 5.98; N, 6.39. Found: C 66.08; H 6.00; N 6.79.

7-Amino-3-(2-hydroxyethyl)-4-methyl-2H-chromen-2-one (**3n**). Yield 91%, light yellow solid, mp 195−197 °C. IR (KBr): ν = 3420 (broad), 1658 (s) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6/TMS) δ (ppm): 2.29 (s, 3H), 2.48 (brs, 1H), 2.83 (t, 2H, J = 7.5 Hz), 4.25 (t, 2H, J = 7.5 Hz), 6.48 (m, 3H), 7.1 (m, 1H), 8.13 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d_6/TMS) δ (ppm): 14.9, 27.0, 66.9, 101.1, 111.1, 111.3, 115.0, 129.3, 140.4, 151.4, 158.0, 173.0. Anal. Calc. for $C_{12}H_{13}NO_3$ (219.24): C 65.74; H 5.98; N 6.39. Found: C, 65.18; H, 6.00; N, 6.30.

■ RESULTS AND DISCUSSION

Catalyst Preparation and Characterization. The preparation strategy for NTDSS catalyst is shown in Scheme 1.

Scheme 1. Synthetic Route for the Preparation of NTDSS Catalyst
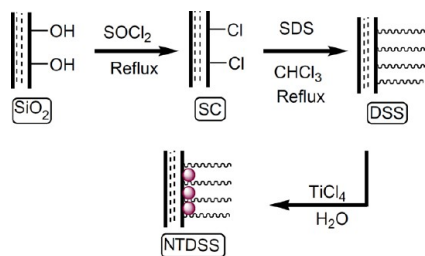
In this study, SC was prepared based on the reported procedure in the literature.[33] It is noteworthy that SC is not soluble in all of the organic solvents, and due to this property it can accept different nucleophiles, particularly hydroxyl groups (due to generation of strong Si−O bond).[34] Considering this issue, SC can react with −SO$_3$ groups of DS conveniently. The NTDSS catalyst was characterized using different techniques

such as TEM, SEM, XRD, EDX, and FT-IR spectroscopy. The TEM images of the NTDSS catalyst (Figure 1) show that the TiO$_2$ nanoparticles with near spherical morphology are assembled onto the DSS support with relatively good monodispersity. The SEM images of the NTDSS catalyst (Figure 2) show that the nano-TiO$_2$ particles possess near cubic morphology with relatively good monodispersity. In this study, the average diameter of the TiO$_2$ particles was estimated ∼58 nm. The histogram (Figure 2d) was proposed according to the results obtained from the TEM and SEM images and revealed the size distributions of TiO$_2$ nanoparticles.

The XRD pattern of the NTDSS catalyst also shows that we have TiO$_2$ nanoparticles in the structure of the NTDSS catalyst (Figure 3a). The peaks are indexed as the (110), (200), (211), (118), and (220) planes of the TiO$_2$ nanoparticles.[25] According to Figure 3a, a sharp peak of TiO$_2$ is observed at ∼2θ = 32°. The size of the TiO$_2$ nanoparticles was also determined from X-ray line broading using the Debye−Scherrer formula[35] given as $D = 0.9 \, L/\beta \cos(\theta)$, where D is the average crystalline size, L is the X-ray wavelength used, β is the angular line width at half-maximum intensity, and θ is the Bragg's angle. For θ = 16°, L = 1.06 Å and β = 0.15 mm, and the average size of the TiO$_2$ nanoparticles on DSS is estimated to be about 64 nm. This value is in good agreement with data obtained from the TEM image.

The EDX spectrum also indicated the presence of Ti in the NTDSS catalyst (Figure 3b). The spectrum also shows other elements such as C, O, S, and Si, which exist in the DSS substrate. To evaluate the Ti content of catalyst, it was treated with concentrated HCl and HNO$_3$ to digest the Ti species and then was analyzed by ICP analysis. The Ti content was determined to be 73.1 ppm (73.1 mg/L), which was equal to 7.31% w/w. In this study, FT-IR spectroscopy was used as an applicable technique for further characterization of the NTDSS catalyst (Figure 4).

In accordance with the FT-IR spectra, the peaks positioned at ∼486 and ∼470 cm^{-1} are related to the formation of TiO$_2$ nanoparticles.[36] The absorbance bands are related to the Ti−O stretching and Ti−O−Ti bending vibration. Also, distinguished peaks at ∼1635, 933, and 803 cm^{-1} confirmed the presence of DS species in the structure of catalyst. The peaks positioned at 933 and 802 cm^{-1} are associated to the stretching of the S=O bond.[37] The band at 1635 cm^{-1} belongs to H−O−H bending during the adsorption of water molecules.[25] Additionally, the strong peak at 3379 cm^{-1} is as a result of the stretching of silica −OH groups caused through the adsorption of H$_2$O
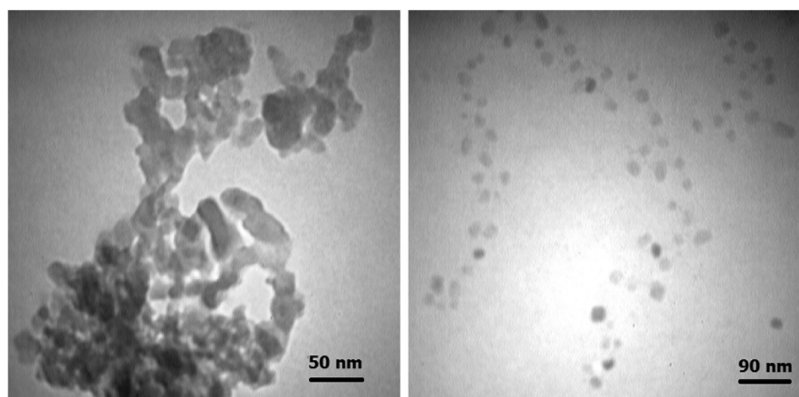

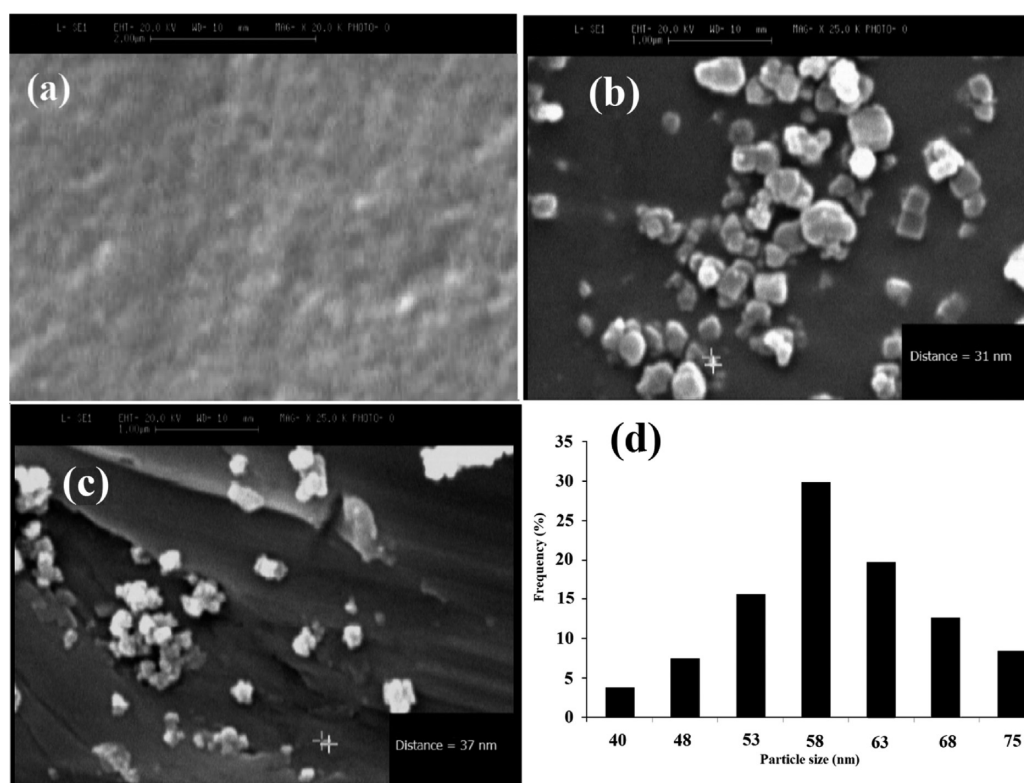**Figure 1.** TEM images of two different position of NTDSS catalyst.

Figure 2. SEM image of (a) DSS substrate, (b) NTDSS catalyst in fresh form, and (c) NTDSS catalyst after 5 times of reusability. (d) Histogram representing the size distribution of synthesized TiO_2 nanoparticles on DSS substrate.
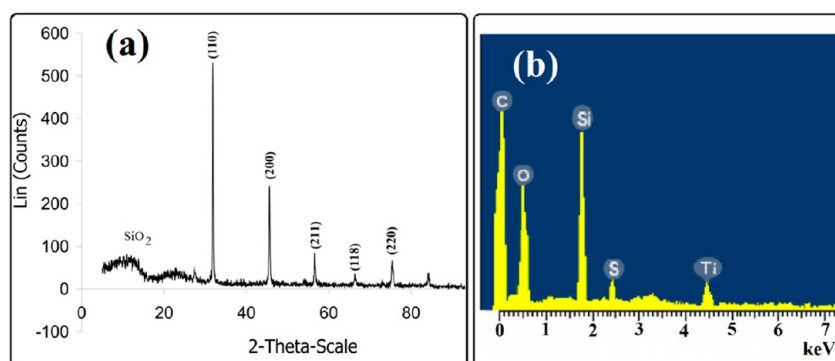

Figure 3. (a) XRD spectrum of the NTDSS catalyst. (b) EDX spectrum of NTDSS catalyst.

molecules.[38] The weak bands at 2924 and 2862 cm^{-1} are due to the stretching vibration of C–H and C–C bonds.

After characterization of the catalyst, formation of emulsion droplets on the surface of the catalyst in the presence of water was confirmed by optical microscopy (Figure 5).

The colloidal particle formation in the NTDSS catalyst is attributed to the property of grafted DS as a surfactant on the surface of silica. The generation of emulsion droplets containing nano-TiO_2 on the surface of the catalyst function as an effective reaction reactor to accelerate the rate of organic reaction in water media (Figure 6).

Pechmann Condensation in the Presence of NTDSS Catalyst. The NTDSS catalyst was applied in the Pechmann condensation for the synthesis of coumarin derivatives to evaluate catalytic performance. Coumarins are important in the viewpoint of natural products and synthetic organic chemistry.[39] Enormous efforts have been made by chemists for developing different synthetic routes to coumarins, which is

apparent evidence indicating their great importance.[40] Among the methods applied, the Pechmann reaction is the most widely applied method for the synthesis of coumarins, as it involves the condensation of phenols with β-ketoesters in the presence of a variety of acid condensing agents.[41,42] Because of several synthetic problems associated with this transformation, there is still an urgent need to develop more efficient catalysts for the Pechmann reaction under green conditions.[43−46] Therefore, in view of the importance of coumarins, we report NTDSS as a novel, reusable, and efficient LASC catalyst for the synthesis of structurally diverse coumarins via the Pechmann condensation in water. To evaluate the catalytic activity of the NTDSS catalyst, the Pechmann reaction between 4-methoxyphenol (**1a**) and ethyl acetoacetate (**2a**) was selected as a simple model substrate, and optimization studies are shown in Table 1.

First, the model reaction was checked in the absence of the catalyst in water, and no product was detected even after 24 h (Table 1, entry 1). We used silica in H_2O for the reaction
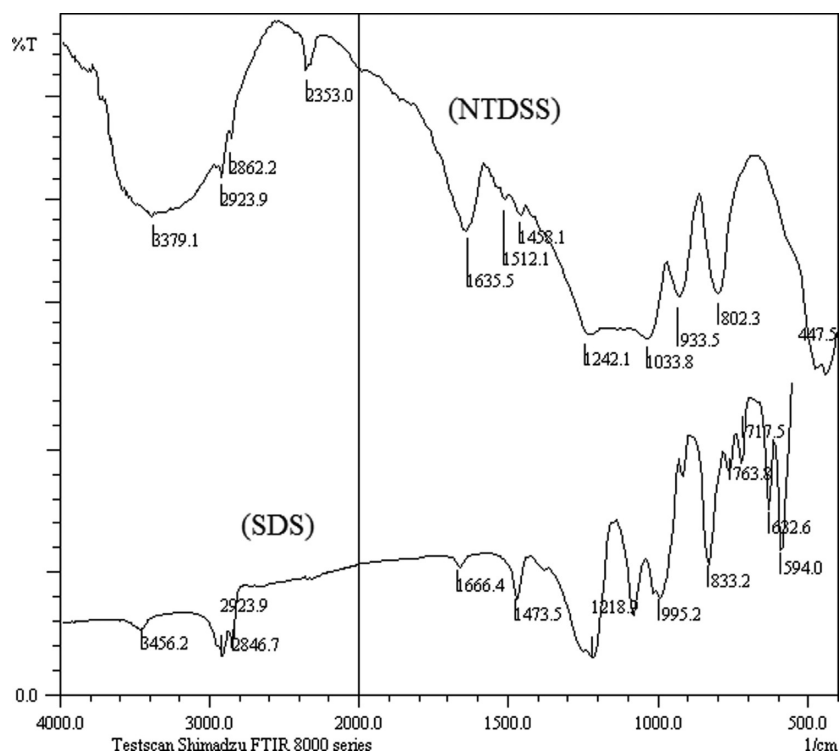
Figure 4. Comparison between the FT-IR spectra of SDS and the NTDSS catalyst.
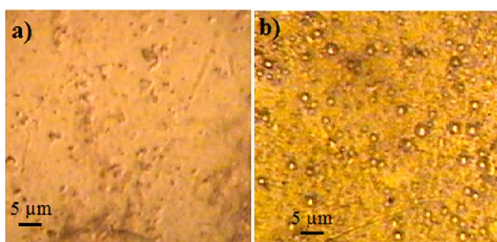

Figure 5. Optical micrograph of (a) NTDSS catalyst and (b) NTDSS catalyst in the presence of water.
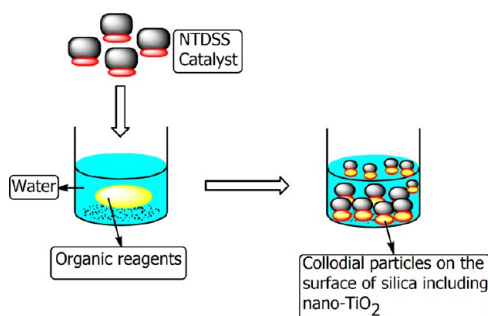

Figure 6. Portrayal of the formation of the colloidal particles on the surface of the NTDSS catalyst in the presence of organic reagents in water.

Table 1. Studies of Various Conditions for the "Pechmann Reaction" between 4-Methoxy Phenol and Ethyl Acetoacetate Using NTDSS Catalyst[a]

entry	catalyst	solvent[b]	time (h)	yield (%)[c]
1	–	H_2O	24	0
2	SiO_2	H_2O	24	trace
3	TiO_2	H_2O	24	18
4	nano-TiO_2	H_2O	24	45
5	SDS	H_2O	24	15
6	nano-TiO_2/SDS	H_2O	24	75
7	NTDSS	H_2O	8	95
			24	96
8	NTDSS	–	12	51[d]
9	NTDSS	EtOH	12	53
10	NTDSS	toluene	12	44
11	NTDSS	H_2O	24	35[e]
12	NTDSS	H_2O	8	95[f]
13	NTDSS	H_2O	12	85[g]
14	NTDSS	H_2O	12	78[h]

[a]Reaction condition: **1a** (1 mmol), **2a** (1.2 mmol), catalyst: SiO_2 (0.1 g), TiO_2 (10 mol %), nano-TiO_2 (10 mol %), DSS (0.1 g), nano-TiO_2/SDS (10 mol %/0.1 g), NTDSS (0.05 g, 5.0 mol % TiO_2) and solvent (5 mL). [b]Reflux condition. [c]Isolated yield. [d]100 °C. [e]rt. [f]Catalyst: 0.075 g (7.5 mol % TiO_2). [g]Catalyst: 0.03 g (3.0 mol % TiO_2). [h]Catalyst: 0.025 g (2.5 mol % TiO_2).

between **1a** and **2a**, while **3a** was obtained with trace isolated yield (Table 1, entry 2). The reaction was also checked in the presence of TiO_2 (bulk) as the catalyst, but no remarkable reactivity differences were observed (Table 1, entry 3). When nano-TiO_2 was used as the catalyst for the reaction, compound **3a** was obtained with 45% isolated yield (Table 1, entry 4). This is probably due to increasing the catalyst surface in the nano-TiO_2 rather than in the bulk-TiO_2. Also, in the presence

of SDS, no reaction improved (Table 1, entry 5). In the presence of the TiO_2/SDS mixture in boiling water, the yield of product was increased to 75% (Table 1, entry 6). Regarding this point, we decided to prepare the NTDSS catalyst for use in this reaction. This catalyst shows very interesting results in the Pechmann reaction, which is not comparable with the other tested catalysts (Table 1, entry 7). Then, the effect of solvent was investigated for this reaction, and water as the best solvent

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Scheme 2. Results of Pechmann Reaction with Phenol Derivatives[a]
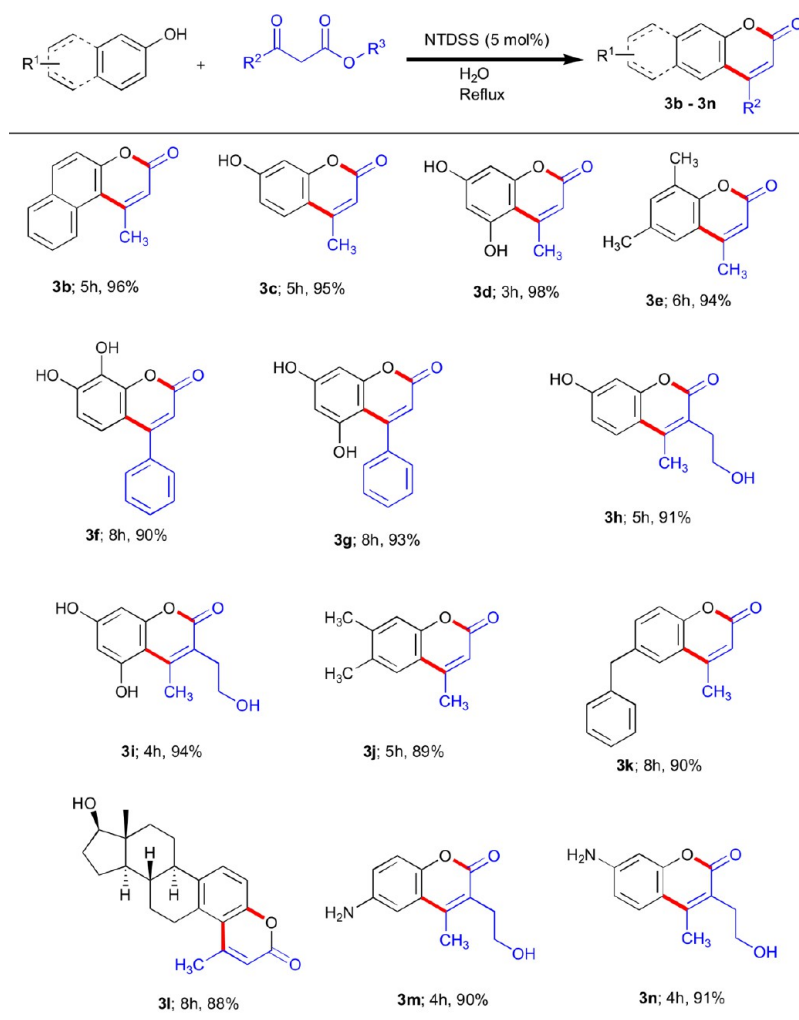
[a]Reagents and conditions: phenol (1 mmol), β-ketoesters (1.2 mmol), catalyst (0.05 g, 5.0 mol % TiO₂), H₂O (5 mL), and reflux. All yields are isolated yields.

was tested (Table 1, entries 7–10). The reaction was checked at rt, but only 35% yield was obtained after 24 h. Subsequently, the catalyst quantity was also optimized, and 5.0 mol % of catalyst was selected as optimum amount (Table 1, entries 12–14). According to the data, which were obtained from optimizing study, the Pechmann reaction was properly carried out in boiling water in the presence of 5 mol % NTDSS catalyst (entry 7). It is noteworthy that the NTDSS catalyst is a heterogeneous catalyst and can easily be separated from the reaction mixture by simple filtration. After the optimizing reaction conditions and in view of the fact that the NTDSS catalyst was an efficient and reusable catalyst for the Pechmann reaction, the catalyst was used with other substrates (Scheme 2).

As shown in Scheme 2, the Pechmann reaction of a variety of aromatic phenols proceeded smoothly to furnish the desired products with good to excellent yields. The generality of this protocol was observed by the application of a wide range of phenols under the same reaction conditions. Also, the functional group compatibility of this reaction was highlighted using 2-acetyl-γ-butyrolactone (4) as the β-ketoester source; it resulted in the synthesis of 3-(2-hydroxy-ethyl)-chromen-2-one derivatives (Schemes 2 and 3, compounds **3h, i, m**, and **n**).

Scheme 3. 2-Acetyl-γ-butyrolactone as β-Ketoester Source in Pechmann Reaction in the Presence of NTDSS Catalyst
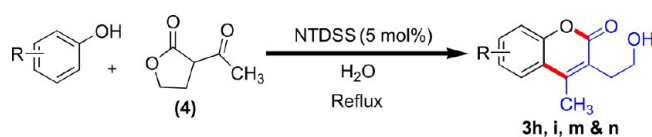
The structural diversity of this reaction was further increased using estradiol as the phenol component, leading to the formation of a new steroid derivative with a coumarin moiety (Scheme 2, compound **3l**). Evidence shows that our environmentally benign catalyst system is comparable with the reported homogeneous and heterogeneous catalysts in efficiency.[41−46] However, this LASC catalyst is more reactive than other counterpart catalysts that have been reported so far for Pechmann reactions in a water solvent. The mechanism shown in Scheme 4 is proposed for the Pechmann condensation between phenols and the β-ketoester in the presence of the NTDSS catalyst in water media.

For practical applications of this heterogeneous catalyst, the level of reusability was also evaluated. The recycled catalyst

Scheme 4. Proposed Mechanism for the Pechmann Condensation of Phenols and β-Ketoester in the Presence of NTDSS Catalyst in Water
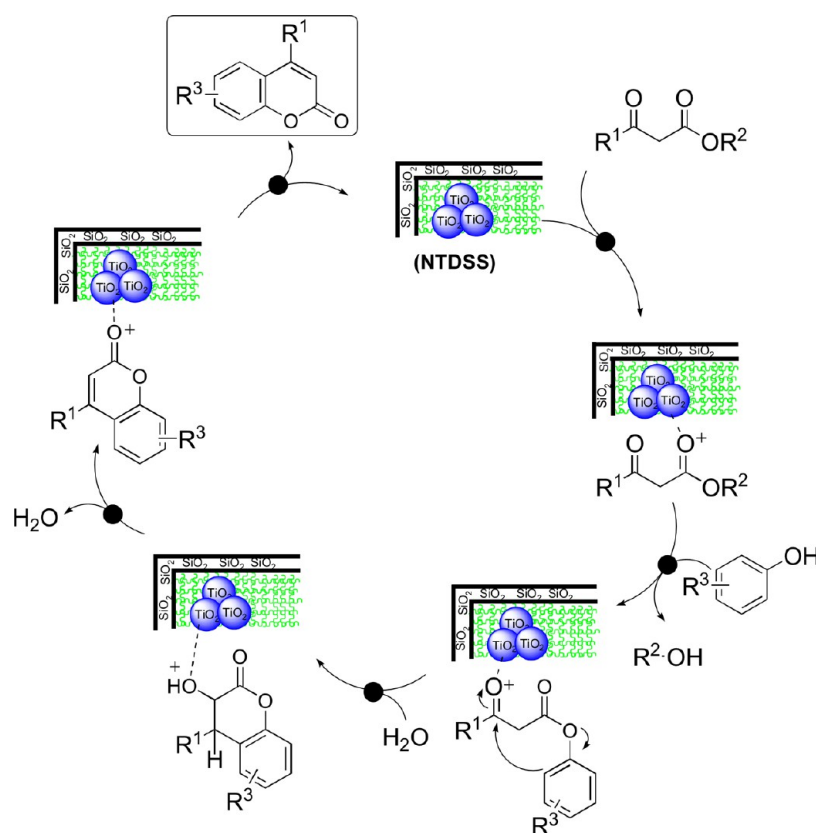
could be reused for at least four times without any treatment (Table 2).

Table 2. Reusability of NTDSS Catalyst in the Pechmann Reaction[a]

entry	yield of product (%)	recovery of NTDSS (%)
fresh	96	>99
1	94	99
2	92	98
3	92	97.5
4	91	97

[a]Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), NTDSS (0.05 g), H_2O (5 mL) and reflux. Reaction time: 8h.

The ICP analysis of the catalyst after five cycles of reusability has shown that only a very small amount (less than 1%) of the Ti metal was removed from the substrate. The results confirmed that the supported TiO_2 on the DSS substrate provides the high catalytic activity without leaching of a significant quantity of TiO_2.

CONCLUSION

In conclusion, the dodecyl-sulfated silica support as a new supported surfactant was synthesized and used for immobilization of nano-TiO_2 in order to prepare a NTDSS catalyst. In DSS support, dodecyl sulfate moieties are directly connected to the silica via an O-linker. We also reported preparation, characterization, and utilization of a new and high performance catalyst system for the Pechmann reaction in water media. In this new catalyst, colloidal particles are produced on the surface

of silica in water media and generate a highly reactive LASC catalyst. Reusability and easy workup are two other advantages of this catalyst system. Also, the NTDSS catalyst provides great promise toward further useful applications in other organic transformations in the future.

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Notes
The authors declare no competing financial interest.

ABBREVIATIONS

LASC, Lewis acid−surfactant-combined catalyst; SDS, sodium dodecyl sulfate; SC, silica chloride; DSS, dodecyl-sulfated silica; NTDSS, nano-TiO_2 on dodecyl-sulfated silica support; TMS, tetramethylsilane; XRD, X-ray diffraction; ICP, inductively coupled plasma; SEM, scanning electron microscopy; TEM, transmission electron microscopy; EDX, energy dispersive X-ray spectra; TLC, thin layer chromatography

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