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# Selective conversion of glycerol to acrolein over supported nickel sulfate catalysts

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## ABSTRACT

Supported nickel sulfate was proved to be an efficient catalyst for gas-phase dehydration of glycerol to acrolein at 340 °C in the presence of oxygen. At a GHSV of glycerol of 873 h<sup>-1</sup>, glycerol conversion over 17NiSO<sub>4</sub>-350 was still higher than 90% even after 10 h of reaction, with selectivity to acrolein always higher than 70 mol.%. It was demonstrated that Lewis acid sites were responsible for heavy compounds formation, and that Brønsted acid sites with medium and high strength were active sites for acrolein production from glycerol dehydration. The acidity of supported nickel sulfate was associated with one meta-stable structure, NiSO<sub>4</sub>·xH<sub>2</sub>O (0 < *x* < 1). Furthermore, not only nickel cations but also sulfate groups exhibited oxidizability during reactions, and loss of sulfur was the main reason for irreversible deactivation of supported nickel sulfate.

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#### 1. Introduction

As the main by-product of biodiesel production, glycerol should be processed efficiently in order to achieve sustainability of the biodiesel industry. The significantly increasing production of glycerol has been targeted as a feedstock for several chemical and biochemical conversions to produce value-added chemicals [1–4]. One promising route to glycerol valorization is its catalytic dehydration to produce acrolein, which is an important industrial intermediate for the chemical and agrochemical industries [5,6]. Various acid catalysts have been tested for the conversion, including zeolites [7–11], heteropolyacids [12–18], phosphates [19,20], and metal oxides [21–27].

Recently, Cavani et al. reported the application of sulfated zirconia catalyst to the dehydration of glycerol to acrolein [28,29]. They found that the conversion of glycerol suffered from extensive deactivation and that selectivity to acrolein was restricted by concomitant formation of several by-products derived from both parallel reactions on glycerol and consecutive reactions upon acrolein. The principal by-product—heavy compounds, which were precursors for coke formation—contributed to the fast catalyst deactivation.

It was well known that the formation of heavy compounds mainly occurred under mass transfer limitation conditions, which were greatly influenced by the porosity and surface area of the support [8,11,12,14]. However, it was extremely difficult to synthesize specific zirconia with high surface area and well-developed channel network. Another reason for the intensive deactivation may be the strong acid property of sulfated zirconia, which was more inclined to catalyze bimolecular condensation reactions to coke [9,23]. One further important factor affecting coke formation was probably the insufficient oxidation ability of THE metal promoter— $Zr^{4+}$ , which could only be reduced at a relatively high temperature [30].

Additionally, in sulfated zirconia, the most basic  $OH^-$  and coordinatively unsaturated  $O^{2-}$  sites over the bare zirconia surface were consumed by the sulfation process. However, the remaining moderate basic sites may still be active to catalyze some side reactions of glycerol, especially when the number of sulfate groups was lower than that required for complete "monolayer" coverage of the zirconia surface [23,25,26,31].

To overcome the disadvantages of sulfated zirconia, we decided to conduct the reaction over nickel sulfate supported on inert mesoporous silica with high surface area and large pore diameter, which could reduce mass transfer resistance substantially in a much easier way. As a classic acid catalyst, nickel sulfate could provide a large quantity of moderately acid sites and a strong oxidation ability as well, with the latter probably being derived from the existence of nickel cations [32,33]. Furthermore, fewer and weaker basic sites were supposed to be detected over the catalyst, due to its higher sulfate content.

Although water was reported to be necessary for the generation of Brønsted acid sites in nickel sulfate and the maintenance of surface hydroxylation at high temperature, it was also essential to dilute glycerol for superior catalytic performance, which made nickel sulfate extremely suitable for the reaction. Therefore, supported



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nickel sulfate might, in theory, be a perfect catalyst for this reaction under aerobic conditions, owing to the combination of moderate acid sites and enhanced oxidation properties.

### 2. Experimental

#### 2.1. Catalyst preparation

Supported nickel sulfate catalysts were prepared by conventional impregnation of mesoporous silica (specific surface area =  $386.8 \text{ m}^2/\text{g}$ , average pore diameter = 9.6 nm) with an aqueous solution of NiSO<sub>4</sub>·6H<sub>2</sub>O, followed by calcination at various temperatures for 2 h in air. A prescribed amount of NiSO<sub>4</sub>·6H<sub>2</sub>O was dissolved in deionized water, and silica with particle size ranging from 100 to 150 µm was added into the solution. The slurry was stirred vigorously and evaporated at 65 °C until dryness. Then, the obtained solid was dried at 120 °C overnight before calcination. Hereafter, silica-supported nickel sulfate is denoted as *a*NiSO<sub>4</sub>-T, where "*a*%" indicates the loading amount and "*T*" represents the calcination temperature. Supported ammonium sulfate and nickel oxide catalysts were prepared following the procedures described above.

The modification of ammonium sulfate (AS) and cesium carbonate was conducted over 29NiSO<sub>4</sub>-550 through an incipient wetness method. The required amount of promoter was dissolved in a volume of deionized water corresponding to the pore volume of 29NiSO<sub>4</sub>-550, which was then added dropwise to the 29NiSO<sub>4</sub>-550 sample during intensive mixing. The resulting catalyst precursor was dried at 120 °C overnight and subsequently calcined in air at 550 °C for 2 h.

#### 2.2. Characterization

Several characterization techniques, including nitrogen adsorption, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT–IR), temperature-programmed desorption of  $CO_2$  ( $CO_2$  TPD), temperature-programmed desorption of ammonia (NH<sub>3</sub> TPD), temperature-programmed reduction of H<sub>2</sub> with mass spectroscopy (H<sub>2</sub> TPR–MS), and thermogravimetric analysis with mass spectroscopy (TG–MS), were used to determine the structure and acid–base properties of nickel sulfate catalysts.

BET surface area, average pore diameter, and pore volume were measured by an Autosorb-iQ Automated Surface Area and Pore Size Analyzer using the nitrogen adsorption method. Prior to measurement, all samples were evacuated at 200 °C for 4 h at a pressure of  $1.0 \times 10^{-3}$  kPa to ensure complete removal of adsorbed moisture. XRD was used to identify the crystalline structure of catalysts using an X'pert PRO MPD diffractometer (PANalytical Company, Netherlands) with Cu K $\alpha$  radiation (40 kV, 40 mA). The X-ray diffractograms were recorded from 5° to 75° at a speed of 5°/min. The morphology of different catalysts before and after reaction was studied by S-4800 SEM (Hitachi Company, Japan).

The acidity (basicity) of supported nickel sulfate was evaluated by TPD of ammonia (carbon dioxide). Detailed operation procedures have been described previously [8]. Nevertheless, pretreatment temperature was adjusted to catalyst calcination temperature. Consequently, all TPD profiles were baseline-corrected to remove the contribution of impurities emitted at temperatures higher than the pretreatment temperature. The acidity measurements were also performed by FT–IR after pyridine adsorption. All spectra were collected using a diffuse reflectance accessory connected to an infrared spectrometer (Nicolet NEXUS 670) that was equipped with a Mercury Cadmium Telluride (MCT) detector. Each spectrum involved the accumulation of 64 scans at a resolution of 4 cm<sup>-1</sup>. Brønsted and Lewis acid sites were identified by bands at around 1540 and 1450 cm<sup>-1</sup>, respectively.

FT–IR in transmission mode was employed to identify the conformation of nickel sulfate, for which a DTGS detector was used. Prior to analysis, the sample was ground together with pure, dry spectroscopic grade KBr to a fine powder, and then, the mixture was transferred to a compression die, in which it was converted to a wafer transparent to infrared light through high pressure. The thickness of the thin wafers was kept constant through controlling preparation parameters. The spectrum of a KBr wafer was collected initially as a background reference. All spectra in this section were obtained by subtraction of the corresponding background reference.

The oxidation properties of  $29NiSO_4$ -550 were investigated by means of H<sub>2</sub> TPR–MS. The sample (about 0.1 g) was pretreated at 550 °C for 2 h under flowing helium to ensure complete removal of impurities. After cooling down to 80 °C, the carrier gas was switched to a mixture of 10 vol.% H<sub>2</sub>/N<sub>2</sub> (30 mL/min) and the system kept at 80 °C till stability of TCD signals. A 10 °C/min temperature ramp was then started from 80 °C up to the final isotherm at 360 °C, kept for 1.5 h, during which TCD signals were recorded as a function of temperature, and the effluent gas was analyzed by means of MS. The mass numbers (*m*/*z*) 2, 18, 32, 34, 64, and 80 were used for H<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, and SO<sub>3</sub>, respectively.

To understand the difference in catalytic performance of catalysts calcined at various temperatures, TG–DTA–MS was employed to study structural changes of nickel sulfate during calcination. The sample (approximately 20 mg) was heated in alumina crucibles from room temperature to 750 °C at a rate of 10 °C/min, under high-purity helium (100 mL/min), during which evolved gases were introduced to a mass spectroscope to obtain evolution curves. The gas lines between TG and MS were kept at 100 °C to avoid condensation of gaseous products.

Nickel content in the liquid product was determined by atomic absorption spectrometry (AAS) in order to ascertain loss of active component attributed to flushing with high-temperature steam.

XPS data were obtained using an ESCALab250 electron spectrometer from Thermo Scientific Corporation with monochromatic 150 W Al K $\alpha$  radiation. Pass energy for the narrow scan was 30 eV. The base pressure was about  $6.5 \times 10^{-11}$  kPa. The binding energies were referenced to the Si2*p* line at 103.6 eV or the Al2*p* line at 74.7 eV from the carrier.

#### 2.3. Catalytic reaction

Gas-phase dehydration of glycerol was conducted in a vertical fixed-bed reactor (8 mm i.d.) under atmospheric pressure using 1 g of catalyst. A preheater was located on top of the reactor to vaporize the feed (vaporization temperature 250 °C). In the meantime, the reactor had provided an additional preheating zone (spiral chute, about 10 cm in length) to ensure complete vaporization.

Prior to reaction, catalysts were pretreated at reaction temperature (340 °C) in flowing nitrogen for about 1 h. The reaction feed, an aqueous solution with 20 wt.% glycerol, was then introduced into the system with carrier gas (20 mL/min) from the top of the preheater by an HPLC pump at a fixed flow rate of 0.13 mL/min. The reaction was carried out at a gas hourly space velocity (GHSV) of glycerol of 873 h<sup>-1</sup>, which was much higher than in previously published experiments. And the GHSV was defined as the gaseous volume flow rate of vaporized glycerol at 340 °C and 101.325 kPa divided by the volume of catalyst (ca. 1 mL). During reaction, the effluent was collected in a receiver located at the exit of the reactor, which was kept at 0 °C by means of a mixture of water and ice. A certain amount of ethanol was loaded into the receiver to ensure efficient capture of products. The reaction was carried out for several hours, and products were collected every hour for analysis.



Fig. 1. Catalytic performance of 29NiSO<sub>4</sub>-550 for gas-phase dehydration of glycerol at 340  $^\circ\text{C}$  under different carrier gas atmospheres.

The sample obtained during the first hour was disregarded, considering its poor material balance.

The composition of the reaction gases was determined by a Bruker 450-GC gas chromatograph equipped with three detectors, two TCDs for analyzing H<sub>2</sub> and CO/CO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>, separated on a 2-m molecular sieve 5A column and a 2.5-m molecular sieve 13X column, respectively, and a flame ionization detector (FID) for light hydrocarbons, separated on a 50 m Plot/Al<sub>2</sub>O<sub>3</sub> column. Liquid products were analyzed on an Agilent 6820 gas chromatograph equipped with an HP-INNOWAX capillary column (30 m × 0.32 mm × 0.25 µm) and an FID. A known amount of internal standard (ethylene glycol) was mixed within the sample prior to analysis for quantitative determination. The amount of coke deposition was calculated by subtracting the weight loss of fresh catalyst between 200 and 550 °C in flowing air from that of spent catalyst determined by the TG analyzer.

Glycerol conversion, product selectivity, and yield are defined as follows:

glycerol conversion(mol.%) = 
$$\left(1 - \frac{\text{moles of glycerol in the sample}}{\text{moles of glycerol in feed}}\right) \times 100;$$

product yield(mol.%) = 
$$\frac{\text{moles of carbon in a defined product in the sample}}{\text{moles of carbon in glycerol in feed}}$$
  
× 100;

product selectivity(mol.%) = 
$$\frac{\text{product yield}}{\text{glycerol conversion}} \times 100.$$

#### 3. Results and discussion

3.1. Catalytic performance of supported nickel sulfate catalyst in air or under nitrogen

The catalytic dehydration of glycerol was first conducted over  $29NiSO_{4}$ -550 with either nitrogen or air as carrier gas. Glycerol

Table 2

Acid pro	perties	of	various	supported	catalysts.
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Catalysts	Acid amount (mmol/g)					
	Weak acid <sup>a</sup>	Strong acid <sup>a</sup>	Total acid			
29NiSO <sub>4</sub> -350	1.984	1.080	3.064			
29NiSO <sub>4</sub> -450	1.251	0.721	1.972			
17NiSO <sub>4</sub> -550	0.305	0.111	0.416			
29NiSO <sub>4</sub> -550	0.776	0.321	1.097			
38NiSO <sub>4</sub> -550	0.481	0.179	0.660			
29NiSO <sub>4</sub> -650	0.391	0.214	0.605			
29NiSO <sub>4</sub> -750	0.096	0.035	0.129			
29NiSO <sub>4</sub> -550-AA <sup>b</sup>	0.135	0.039	0.174			
29NiSO <sub>4</sub> -550-AN <sup>c</sup>	0.113	0.006	0.119			
16NiO-550	0.052	0.008	0.060			
$20 SO_4^2 - 350^d \\$	0.552	0.249	0.801			

 $^{\rm a}$  The moles of ammonia desorbed in the range of 100–300 °C represented the amount of weak acid, while those above 300 °C indicated the amount of strong acid.

<sup>o</sup> After 7 h of reaction in air.

After 5 h of reaction under nitrogen.

<sup>d</sup> Supported ammonium sulfate catalyst.

conversion and product selectivity are shown in Fig. 1 and Table 1. Under inert atmosphere, glycerol conversion dropped sharply from 84.1 mol.% at TOS = 2 h to 50.8 mol.% at TOS = 5 h, while selectivity to acrolein increased significantly from 58.3 mol.% to 69.8 mol.%. After reaction, the catalyst color became pitch black, indicating that substantial carbon deposits were formed on the catalyst surface. The coke deposition determined by the TG analyzer was 121 mg/g-cat, confirming that severe coke formation was probably responsible for the intensive deactivation.

Although no oxygen was introduced, some oxidation products,  $CO_2$  and acids, were detected, which were attributed to the oxidation properties of nickel sulfate. Distribution of products changed during catalyst deactivation, resulting in more acrolein and less  $CO_x$  and heavy compounds (Table S1), which implied a variation of active sites participating in the reaction. According to  $NH_3$  TPD characterization results (Table 2), the acid amount of fresh 29NiSO<sub>4</sub>-550 reached 1.097 mmol/g, which was notably larger than that of zeolite catalysts [8]. However, after 5 h of reaction under nitrogen, it decreased to almost nil, especially the strong acid amount. Thus, the variation of product distribution with TOS could be attributed to the disappearance of very strong acid sites.

As expected, the catalytic activity declined much slower, and selectivity to acrolein remained almost constant with TOS in the presence of air, suggesting that addition of oxygen could efficiently inhibit intensive deactivation without pronounced impact on acrolein selectivity. By comparison, the carbon deposit decreased to 94 mg/g-cat in spite of the fact that TOS under aerobic conditions was 2 h longer than under anaerobic conditions, resulting in a relatively larger quantity of acid sites remaining after reaction (Table 2).

Moreover, significant differences were found in selectivity to acetol,  $CO_x$ , acids, and heavy compounds (Table 1). After the introduction of oxygen, nearly half of acetol was converted to excessive oxidation product  $CO_x$ , indicating that as a primary product from glycerol dehydration, acetol was much more reactive than acrolein

Table 1

Product distribution over 29NiSO<sub>4</sub>-550 for gas-phase dehydration of glycerol at 340 °C under different carrier gas atmospheres (TOS = 3 h).

Carrier gas	Conversion (mol.%)	Product selectivity	Product selectivity (mol.%)				Carbon balance (%)
		Acetaldehyde	Acrolein	Acetol	COx	Others <sup>a</sup>	
Air N <sub>2</sub>	89.2 65.5	6.1 7.4	62.1 62.6	8.2 16.5	7.1 0.3	13.0 10.9	96.5 97.7

<sup>a</sup> Selectivity for others = carbon balance – total selectivity for all products listed. The others included propionaldehyde, acetone, methanol, propenol, acetic acid, propionic acid, acrylic acid, light olefins, coke, and heavy compounds with unknown structure, all of which were present in minor amounts. The selectivity to unknowns was estimated using the correction factor and molecular formula of glycerol.

[9]. Minor amounts of acetic acid, acrylic acid, and propionic acid were also detected, which were probably formed from partial oxidation of acetaldehyde, acrolein, and propionaldehyde, respectively [19,27]. Propionic acid could be produced from isomerization of acetol as well [9].

As shown in Fig. 2a and b, nickel sulfate exhibited a wellcrystallized structure with a particle size of ca. 10  $\mu$ m<sup>2</sup> on the surface of silica, which was formed by aggregation of several rod-like crystals (approximately 0.5 × 2.5  $\mu$ m). The surface of the crystals was quite smooth and clean. After reaction under nitrogen, nickel sulfate crystals were almost completely covered by numerous layers of substances, appearing as quite compact entities, which were supposed to be graphite-like coke (Fig. 2c). However, the SEM image of 29NiSO<sub>4</sub>-550-AA revealed a much smaller surface roughness than for 29NiSO<sub>4</sub>-550-AN, indicating that oxygen could inhibit the formation of more highly condensed carbon deposits [14,15]. It was because of this that co-feed oxygen may help in accelerating the removal of heavy compounds incipiently formed on the catalyst surface through in situ combustion.

It was noteworthy that the catalytic performance was dramatically enhanced over that of sulfated zirconia with either nitrogen or air as carrier gas [28]. In order to make clear this phenomenon, 16NiO-550 and  $20SO_4^2$ -350 were prepared intentionally, which had the same contents of nickel and sulfate ions, respectively, as 29NiSO<sub>4</sub>-550 did. However, glycerol conversion at the initial stage of reaction over both catalysts was negligible under either aerobic or anaerobic conditions.

Through characterization, it could be deduced that deficiency of acid sites was responsible for the low catalytic activity of supported nickel oxide catalysts (Table 2). Surprisingly, supported ammonium sulfate catalyst exhibited insufficient ability for glycerol conversion despite its large numbers of Brønsted acid sites with high strength, evidenced by characterization results of FT–IR after pyridine adsorption and  $NH_3$  TPD. It was probably because of this that the carbon deposition after 2 h of reaction under inert atmosphere was about 104 mg/g-cat, indicating that coke was preferentially formed over acid sites in the absence of nickel cations. Based on the series of experiments above, it could be concluded that both sulfate groups and nickel cations were indispensable for dehydration of glycerol.

#### 3.2. Effect of catalyst preparation parameters on catalytic performance

#### 3.2.1. Calcination temperature

A series of supported nickel sulfate catalysts were prepared in order to investigate the influence of catalyst calcination temperature on catalytic performance. After calcination at 350 °C, numerous poorly crystallized nanocrystals of nickel sulfate with particle size ranging from tens to hundreds of nm were observed on the surface of silica, indicating fine dispersion of active component on mesoporous silica (Supplementary Material, Fig. S1a). This was confirmed by the complete absence of all diffraction peaks characteristic of nickel sulfate in the XRD pattern of 29NiSO<sub>4</sub>-350 (data not shown). As calcination temperature went up, diffraction peaks of nickel sulfate emerged and became sharper gradually, which was consistent with the increasing particle size and surface smoothness of nickel sulfate crystals. Obvious sintering phenomena were perceived when calcination temperature rose to 650 °C (Supplementary Material, Fig. S1b). Over 29NiSO<sub>4</sub>-750, a large amount of nickel oxide, due to the decomposition of nickel sulfate, was generated, as evidenced by strong diffraction peaks characteristic of nickel oxide in the XRD pattern.

NH<sub>3</sub> TPD profiles revealed that all catalysts exhibited one low-temperature desorption peak of ammonia, maximized at about



Fig. 2. SEM images of 29NiSO<sub>4</sub>-550 catalyst (a) and (b) before reaction, (c) after reaction under N<sub>2</sub>, and (d) after reaction under aerobic conditions.



**Fig. 3.** FT-IR spectra of supported nickel sulfate catalysts calcined at different temperatures after pyridine adsorption. Absorbance peaks characteristic of hydrogen-bound pyridine (H), Brønsted (B), weak Lewis (WL), and strong Lewis (SL) sites are indicated.

190 °C, with a medium-temperature shoulder (Supplementary Material, Fig. S2a). The acid amount dropped significantly as the calcination temperature ascended (see Table 2), suggesting that the acidity of nickel sulfate was probably associated with one metastable structure, which was sensitive to the calcination temperature. It could be deduced from the shift of both desorption peaks to lower temperatures that the strength of weak and strong acid sites declined slightly with increasing calcination temperature, which could be attributed to the variance of chemical circumstances around acid sites caused by calcination.

The FT-IR spectra of silica-supported nickel sulfate exhibited one band at around 1595 cm<sup>-1</sup> (see Fig. 3), attributed to pyridine being physisorbed through the hydrogen bond [34,35], and a strong band at approximately 1450 cm<sup>-1</sup>, ascribed to the chemisorption of pyridine on Lewis acid centers. The two bands at around 1610 and 1575 cm<sup>-1</sup> indicated the existence of strong and weak Lewis acid sites, respectively [36,37]. Also, some Brønsted acid sites were detected, the amount of which decreased gradually with increasing calcination temperature, confirming the poor thermal stability of acid sites.

At a GHSV of glycerol of  $873 h^{-1}$ , glycerol conversion was always higher than 85% at 7 h on stream, and selectivity to acrolein remained at ca. 70 mol.% over  $29NiSO_4$ -350 (Fig. 4). The fascinating catalytic performance implied the participation of tremendous Brønsted acid sites in the glycerol dehydration reaction. Thus, it could be hypothesized that transformation of Lewis acid sites into Brønsted ones with the existence of steam during reaction was non-negligible [38]. Both catalytic activity and acrolein selectivity decreased with elevated calcination temperature, especially above  $550 \,^{\circ}$ C, which was consistent with the significantly diminishing acid amount [7,24]. The intensified sintering phenomenon could also make some contribution to the inferior reactivity over  $29NiSO_4$ -650. The extremely low catalytic activity of  $29NiSO_4$ -750 was caused by decomposition of nickel sulfate to inactive nickel oxide.

#### 3.2.2. Loading amount

The loading amount of the active component was an important factor influencing catalytic performance [12,16–18]. Several nanocrystal clusters were obtained over  $17NiSO_4$ -550, indicating that nickel sulfate was finely dispersed in pores as well as on the surface of mesoporous silica (Supplementary Material, Fig. S1c). Evident agglomeration phenomena were discovered as the loading amount increased, especially over 38NiSO\_4-550, where large chunks of nickel sulfate were deposited on the surface of silica



**Fig. 4.** (a) Glycerol conversion and (b) acrolein selectivity over supported nickel sulfate catalysts calcined at different temperatures. All reactions were conducted at 340 °C under aerobic conditions.

(Supplementary Material, Fig. S1d), blocking numerous pores, as proved by the declining surface area and pore volume (data not shown). The acid amount increased with the loading amount initially, but it decreased to some extent when too much nickel sulfate was introduced, probably due to the agglomeration phenomenon (Supplementary Material, Fig. S2b and Table 2).

In comparison with 29NiSO<sub>4</sub>-550, relatively lower catalytic activity was found over  $17\text{NiSO}_4$ -550 on account of less acid sites (Fig. 5), while the nanoparticles of nickel sulfate exhibited promoted catalytic activity, proved by higher selectivity to CO<sub>x</sub> and acetaldehyde at the cost of lower selectivity to acrolein and acetol. In the case of 38NiSO<sub>4</sub>-550, both glycerol conversion and acrolein selectivity dropped to a lower level as a result of insufficient acid sites and enhanced diffusion resistance caused by agglomeration of nickel sulfate.

Based on the investigation in Section 3.2, it could be concluded that supported nickel sulfate with lower calcination temperature and moderate loading was more suitable for the reaction. Therefore,  $17NiSO_4$ -350 was prepared intentionally and tested at 340 °C in air (GHSV = 873 h<sup>-1</sup>). Glycerol conversion was still higher than 90% even after 10 h of reaction, with selectivity to acrolein always higher than 70 mol.% (see Supplementary Material, Fig. S3), which was superior to most of the results reported previously [7,15,21,24,26,28].

#### 3.3. Modification of ammonium sulfate and cesium carbonate

According to Section 3.1, severe carbon deposition was probably the major reason for intensive deactivation of supported nickel



Fig. 5. Glycerol conversion and acrolein selectivity over supported nickel sulfate catalysts with different loadings. All reactions were conducted at 340 °C under aerobic conditions.

sulfate catalyst. It was believed that coke formation occurred on strong acid sites, and that polyglycerols or acetalization products of glycerol were formed and remained adsorbed on basic sites [31,39]. Both types of sites could be involved in the catalyst deactivation. For this reason, it was hard to identify the predominant factor, catalyst acidity or basicity. To make it clear, two series of catalysts with different acid and base properties were prepared by modification of 29NiSO<sub>4</sub>-550 with cesium carbonate and ammonium sulfate. Cesium carbonate was reported previously to modify the Brønsted acidity of supported heteropolyacids [13,15,18], while ammonium sulfate modification was considered to be an efficient approach to suppress basic sites over metal oxides through a sulfation process [40].

The acid and base properties of modified  $29NiSO_4$ -550 were obtained by means of NH<sub>3</sub> TPD and CO<sub>2</sub> TPD techniques, respectively. The acid amount with high as well as medium strength decreased gradually with increasing cesium content due to the replacement of protons by cesium cations (Supplementary Material, Fig. S2c), which implied that Brønsted acid sites were the major component of strong acid. No additional basic sites were generated from introduced cesium cations, as evidenced by CO<sub>2</sub> TPD characterization (data not shown).

A broad desorption peak of  $CO_2$  was observed in the range of 130–550 °C over 29NiSO<sub>4</sub>-550, and the calculated density of basic sites was only 0.196 mmol/g-cat. After introduction of 1 wt.% ammonium sulfate, most of the basic sites disappeared (Supplementary Material, Fig. S4); meanwhile, the acid amount increased slightly (Supplementary Material, Fig. S2d). What is more, the acid

and base properties remained almost unchanged with the everincreasing loading of ammonium sulfate. This was probably because extra ammonium sulfate was removed during the calcination process due to its weak interaction with the catalyst. The AS modification did not create any new category of acid sites either, as evidenced by the peak position in NH<sub>3</sub> TPD profiles (Supplementary Material, Fig. S2d), indicating that introduced sulfate ion interacted with coordinately unsaturated nickel cation in the same way as nickel sulfate.

Glycerol conversion, together with selectivity to acrolein, decreased significantly with increasing cesium carbonate loading, while the selectivity to acetol and heavy compounds increased dramatically (see Fig. 6 and Table 3). This was probably because much more glycerol was supposed to be converted on remaining Lewis acid sites when strong Brønsted acid sites were neutralized by cesium cations, leading to preferential formation of acetol through monodehydration at either terminal carbon of glycerol [13,41]. Fairly large quantities of heavy compounds, quantitatively evaluated as unknowns, were detected at the initial stage of the reaction when the Cs/Ni ratio was 12 mol.%, which was exactly the reason for its extremely low activity for glycerol conversion.

The severe formation of heavy compounds and descending selectivity to acrolein after cesium carbonate modification suggested that Lewis acid sites should be responsible for the low catalytic stability of supported nickel sulfate under inert atmosphere [22,23], and that Brønsted acid sites with medium and high strength were active sites for the production of acrolein from glycerol dehydration [13].

In comparison with  $29NiSO_4$ -550, both glycerol conversion and acrolein selectivity were improved slightly after the introduction of 1 wt.% AS, and maintained at a similar level as AS loading increased further (Fig. 6). The improvement of catalytic performance by AS modification through suppression of basic sites on the surface of nickel sulfate indicated that catalyst basicity may also contribute like Lewis acid sites, but to a lesser extent, to the deactivation of catalyst. As reported previously, the number of basic sites directly affected the selectivity to acrolein in the gas-phase dehydration of glycerol [26]. Consequently, relatively high acrolein selectivity was achieved after AS modification.

# 3.4. Characterization of acid and oxidation property over nickel sulfate catalyst

#### 3.4.1. TG–DTA–MS and FT–IR analysis

29NiSO<sub>4</sub>-350 could provide remarkably large quantities of acid sites, which dropped apparently with calcination temperature, implying that acid sites of nickel sulfate were possibly associated with one metastable structure. The issue above would remain confusing unless the structure of acid sites was determined. Thus, TG– DTA–MS characterization was employed. In order to exclude the disturbance of silica, unsupported analytical pure nickel sulfate hexahydrate was chosen for investigation. Instead of air, high-purity helium was used as the carrier gas for the purpose of detecting oxygen concentration variation during heating.

Three obvious weight-loss steps were discovered at temperatures lower than 280 °C, corresponding to three endothermic peaks in the DTA curve and three weight-loss peaks in the DTG curve (Fig. 7). Between 280 and 500 °C, there was one slow weight-loss step. They were all derived from removal of water, either coordinated or adsorbed one, as proved by the fact that no release of sulfur species was detected before 600 °C (see Fig. 8).

The XRD pattern of nickel sulfate hexahydrate calcined at 500 °C for 2 h showed characteristic peaks of anhydrous nickel sulfate. Through calculation, it was found that the ratio of weight loss between 280 and 500 °C to the mass remaining at 500 °C was 2.37:20.75, which was similar to the ratio of molar mass of water



Fig. 6. (a) Glycerol conversion and (b) acrolein selectivity over cesium carbonate-modified 29NiSO<sub>4</sub>-550 under aerobic conditions; (c) glycerol conversion and (d) acrolein selectivity of ammonium sulfate-modified 29NiSO<sub>4</sub>-550 in inert atmosphere.

Tab	le 3

Product distribution of cesium carbonate-modified 29NiSO₄-550 for gas-phase dehydration of glycerol at 340 °C under aerobic conditions (TOS = 3 h).

Cesium content Conversion (mol.%)		Product selectivity	Product selectivity (mol.%)				
		Acetaldehyde	Acrolein	Acetol	COx	Others <sup>a</sup>	
Cs/Ni = 0%	89.2	6.1	62.1	8.2	7.1	13.0	96.5
Cs/Ni = 3%	74.2	7.4	55.4	11.8	4.6	16.6	95.8
Cs/Ni = 6%	62.8	5.7	39.4	13.3	2.1	37.1	97.6
Cs/Ni = 12%	31.8	7.1	27.9	14.0	0.8	45.5	95.3

<sup>a</sup> The others were mainly composed of heavy compounds with unknown structure, which were precursors for coke.



Fig. 7. TG–DTA curves of analytical pure nickel sulfate hexahydrate.

to that of anhydrous nickel sulfate. It could be inferred that weight loss in this period was attributable to the dehydration of nickel sulfate monohydrate to anhydrous nickel sulfate. The XRD pattern of unsupported nickel sulfate calcined at 350 °C revealed a mixture of nickel sulfate monohydrate and anhydrous nickel sulfate, which confirmed the speculation above.

The DTG curve between 280 and 500 °C could be divided into two overlapping peaks, consistent with two apparent endothermic peaks in the DTA curve. The emergence of a second peak implied that one metastable structure was probably formed during dehydration of nickel sulfate monohydrate. By comparison, weight-loss rate in the second peak was much smaller and remained constant for a long time, which suggested that the structure exhibited relatively better thermal stability than nickel sulfate monohydrate. Thus, the metastable structure was assumed to be NiSO<sub>4</sub>·*x*H<sub>2</sub>O (0 < *x* < 1), which meant part of coordinated water was removed from nickel sulfate monohydrate [33].

To sum up, the decrease in acidity of  $29NiSO_4$ -T (T < 600) with calcination temperature was associated with removal of coordinated water from nickel sulfate monohydrate. The details are



Fig. 8. MS signals in TG-DTA-MS profile of analytical pure nickel sulfate hexahydrate.

described as follows: since sulfate ion was a kind of electron-withdrawing group, the neighboring nickel atom should be electropositive, in which case the coordinately unsaturated nickel ion should be transformed into a Lewis acid site. If one water molecule was coordinated to the nickel cation, the strong interaction between the nickel cation and oxygen in water would free a proton, generating one Brønsted acid site. The loss of coordinated water caused by calcination would lead to disappearance of Brønsted acid sites, while high-temperature calcination would also lead to a decrease in coordinately unsaturated nickel ions through polymerization of nickel sulfate (Scheme 1).

The release of SO<sub>2</sub> together with a small amount of oxygen between 600 and 700 °C was probably due to self-reduction of the sulfate group to a sulfite group followed by decomposition of the latter [29]. When temperature rose to 700 °C, a new weight-loss step showed up, which was ascribed to the decomposition of nickel sulfate, evidenced by the emergence of sulfur dioxide and oxygen in Fig. 8. The evolution curve of SO<sub>2</sub> and O<sub>2</sub> exhibited the same variation trend with time, and no sulfur trioxide was detected during the whole process, which was probably because of the transformation of SO<sub>3</sub> into SO<sub>2</sub> and O<sub>2</sub> in the MS chamber [42].

Thus, it seemed credible that in the case of  $29NiSO_4$ -650, self-reduction of the sulfate group could make some contribution to the further decrease in acidity, while the extremely low acidity of  $29NiSO_4$ -750 was caused by decomposition of nickel sulfate.

It was believed that Brønsted acid site of  $29NiSO_4$ -T (T < 600) could also be supplied by the surrounding physical adsorbed water [33]. All FT–IR spectra of nickel sulfate hexahydrate calcined at different temperatures revealed one band at ~1630 cm<sup>-1</sup> (Fig. 9), which may be assigned to the O–H bending vibration of adsorbed water [43]. The appearance of two overlapping broad peaks in the region between 2800 and 3700 cm<sup>-1</sup>, corresponding to the stretch-



Scheme 1. The speculated structure of acid sites over nickel sulfate catalysts.



Fig. 9. FT-IR spectra in transmission mode of analytical pure nickel sulfate hexahydrate calcined at different temperatures.

ing vibration of water, confirmed the existence of two kinds of water—coordinated and adsorbed [44]. Thus, it could be concluded that water was very likely to be adsorbed on the surface of nickel sulfate, especially when calcined at a lower temperature, which should make some contribution to the Brønsted acidity after being acidified by the inductive effect of the neighboring cationic Lewis acid sites.

The four bands at  $\sim$ 985, 1050, 1165, and 1240 cm<sup>-1</sup> were related to the stretching vibration of the sulfate group. These peak positions revealed that nickel sulfate was constructed in a bidentate mononuclear (chelating) coordination pattern [45], as shown in Scheme 1.

#### 3.4.2. H<sub>2</sub> TPR-MS experiment

The comparatively different catalytic performance of supported nickel sulfate under inert atmosphere and air confirmed the important role of oxidation properties, probably provided by nickel ion, in improving catalytic stability by limiting the formation of heavy compounds. To find out the oxidative sites,  $H_2$  TPR–MS was conducted over 29NiSO<sub>4</sub>-550. In view of the fact that glycerol could be transformed into a variety of products during heating, which would make detection extremely difficult,  $H_2$  was chosen as a probe molecule to investigate the reducibility instead.

From the  $H_2$  TPR curve (Fig. 10), it was obvious that nickel sulfate could be reduced at a temperature higher than 220 °C, merely at a low rate. When temperature rose to 320 °C, the hydrogen consumption rate rocketed with temperature, indicating superior oxidation properties at elevated temperatures, which was probably the reason for the relatively higher reaction temperature needed for supported nickel sulfate.



Fig. 10. H<sub>2</sub> TPR profile of 29NiSO<sub>4</sub>-550.



Fig. 11. MS signals in H<sub>2</sub> TPR-MS profile of 29NiSO<sub>4</sub>-550.



Scheme 2. Proposed pathways for reduction of nickel sulfate in hydrogen atmosphere. Products enclosed in boxes were detected.



Fig. 12. XPS spectra of 29NiSO<sub>4</sub>-550 after 5 h of reaction in nitrogen atmosphere.

Fig. 11 exhibited the MS signals in the  $H_2$  TPR–MS profile of 29NiSO<sub>4</sub>-550. The decrease in oxygen content at 25–35 min was probably owing to the existence of oxygen vacancies on the surface of nickel sulfate [46]. Sulfur dioxide and water were released at the same time, which proved that decomposition of nickel sulfite occurred immediately after its formation (Scheme 2).  $H_2S$  was detected shortly after the emission of SO<sub>2</sub>, which was indicative that  $H_2S$  was derived from sulfur dioxide reduction instead of direct reduction of nickel sulfate.

The concentration of nickel in liquid product detected by AAS was only  $0.12 \mu g/g$ , implying that few of the nickel cations were washed off by flushing with high-temperature steam. The XRD pat-

tern of nickel sulfate after treatment at 360 °C in hydrogen for 6 h showed the peaks characteristic of  $Ni_3S_2$ , so it could be deduced that one-third of sulfur was removed in the form of  $SO_2$  and  $H_2S$ , and that two-thirds of nickel cation was reduced from bivalent to monovalent during treatment in hydrogen, which was probably the reason for poor catalytic performance under nitrogen.

XPS characterization was conducted over 29NiSO<sub>4</sub>-550 after 5 h of reaction in nitrogen atmosphere. As shown in Fig. 12, a large quantity of Ni<sup>+</sup> ions were generated on detriment of Ni<sup>2+</sup>, as evidenced by a strong peak at ~856.5 eV and a weak one at ~858.5 eV, which confirmed the intensive reduction of nickel (II) ions by glycerol molecules under inert atmosphere [47].

It was noteworthy that some  $SO_3^{2^-}$  species were detected together with  $SO_4^{2^-}$  groups after reaction [48]. No signals assigned to  $S^{2^-}$  complexes were found, probably because of the insufficient reduction ability of glycerol in comparison with hydrogen and the relatively low temperature of reaction (340 °C). Consequently, it could be speculated that the loss of sulfur was mainly in the form of sulfur dioxide. The appearance of  $SO_3^{2^-}$  species confirmed that the oxidation properties of nickel sulfate could also be supplied by the sulfate group, but to a lesser extent.

In conclusion, not only nickel cations but also sulfate groups exhibited oxidation characteristics during reactions, and loss of sulfur was the main reason for irreversible deactivation of supported nickel sulfate. The challenge for the future is therefore the retardation of sulfur loss.

#### 4. Conclusions

Supported nickel sulfate was proved to be a selective catalyst for glycerol dehydration to acrolein under anaerobic conditions. Addition of oxygen could efficiently inhibit the intensive deactivation by limiting the formation of higher condensed carbon deposits without pronounced impact on acrolein selectivity. The reference experiments over supported nickel oxide and ammonium sulfate catalysts implied that both sulfate groups and nickel cations were indispensable for dehydration of glycerol.

Based on the investigation of the effect of catalyst preparation parameters, it was obvious that supported nickel sulfate with lower calcination temperature and moderate loading was more suitable for the reaction. At a GHSV of glycerol of 873  $h^{-1}$ , glycerol conversion over 17NiSO<sub>4</sub>-350 was still larger than 90% even after 10 h of reaction with selectivity to acrolein always higher than 70 mol.%, which was superior to most of the results reported previously.

Through cesium carbonate modification, it could be concluded that Lewis acid sites should be responsible for the deactivation of supported nickel sulfate, and that Brønsted acid sites with medium and high strength were active sites for acrolein production from glycerol dehydration. The improvement in catalytic performance after AS modification indicated that catalyst basicity may also contribute like Lewis acid sites, but to a lesser extent, to catalyst deactivation.

TG–DTA–MS and H<sub>2</sub> TPR–MS were employed to speculate on the nature of acid and oxidative sites on supported nickel sulfate. The acidity of  $29NiSO_4$ -T (T < 600) was associated with one metastable structure,  $NiSO_4$ · $xH_2O$  (0 < x < 1), in which part of the coordinated water was removed from nickel sulfate monohydrate. The coordinately unsaturated nickel cations were the main source of Lewis acid sites, and Brønsted acid sites were supplied by coordinated water as well as surrounding physically adsorbed water. Furthermore, not only nickel cations but also sulfate groups exhibited oxidizability during reactions, and loss of sulfur was the main reason for irreversible deactivation of supported nickel sulfate.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.01.019.

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