Effect of organic template removal approaches on physiochemical characterization of Ni/Al-SBA-15 and eugenol hydrodeoxygenation

Xiangping Li, Han Yin, Jianguang Zhang, Juping Liu, Guanyi Chen

PII: S0022-4596(19)30568-7

DOI: https://doi.org/10.1016/j.jssc.2019.121063

Reference: YJSSC 121063

To appear in: Journal of Solid State Chemistry

Received Date: 17 September 2019

Revised Date: 12 November 2019

Accepted Date: 12 November 2019

Please cite this article as: X. Li, H. Yin, J. Zhang, J. Liu, G. Chen, Effect of organic template removal approaches on physiochemical characterization of Ni/Al-SBA-15 and eugenol hydrodeoxygenation, *Journal of Solid State Chemistry* (2019), doi: https://doi.org/10.1016/j.jssc.2019.121063.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier Inc.





Effect of organic template removal approaches on physiochemical characterization of Ni/Al-SBA-15 and eugenol hydrodeoxygenation

Xiangping Li^{1, 2}, Han Yin¹, Jianguang Zhang^{3,*}, Juping Liu¹, Guanyi Chen^{1, 4}

¹ China-Australia Centre for Sustainable Urban Development/School of Environmental Science and

Engineering, Tianjin University, Tianjin 300072, China;

²Qingdao Institute for Ocean Technology of Tianjin University, Qingdao 266235, China;

³ School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong

266580, China;

⁴ Tianjin Key Lab of Biomass/Wastes Utilization, Tianjin 300354, China *Corresponding authors.. E-mail addresses: <u>eduzjg@163.com</u>

Abstract

Template removing approaches can significantly impact the physiochemical properties of mesoporous molecular sieve materials. In order to better understand the relationship between template removing approaches and the properties of Ni/Al-SBA-15, four kinds of template removing approaches were introduced to remove the organic template from Al-SBA-15, respectively. The structural characteristics of these materials were analyzed by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray fluorescence (XRF), powder X-ray diffraction (XRD), N₂-sorption, Fourier transform infrared spectra (FT-IR), infrared spectra of pyridine adsorption (Py-FTIR), magic angle spinning-nuclear magnetic resonance (MAS-NMR), X-ray photoelectron spectroscopy (XPS) and gas chromatography-mass spectrometry (GC-MS). Ni/Al-SBA-15 of which the organic template was removed by two-step calcination method had the maximum specific surface area (619 m²/g). In contrast, Ni/Al-SBA-15 of which the organic template was

removed using solvent extraction approaches had the lowest specific surface area (555 m^2/g). The mesopore diameter of Ni/Al-SBA-15, using electric heating digestion method to remove the template, was significantly increased and the wall thickness was significantly decreased to 11.62 nm in comparison with the other samples. The selectivity of products during the process of eugenol hydrodeoxygenation was investigated. High hydrocarbons were obtained during catalytic hydrodeoxygenation over Ni/Al-SBA-15 of which the organic template was removed by using solvent extraction approaches. Compared with direct calcination process, two-step calcination was more effective in removing template and the corresponding catalyst was much more suitable for the hydrodeoxygenation process.

Keywords:

Ni/Al-SBA-15, template removing approaches, hydrodeoxygenation, eugenol

1. Introduction

In recent years, materials with different structure have attracted extensive attention, especially for mesoporous materials [1-5]. With high specific surface area, regular and tunable pore size, large pore volume, as well as stable and interconnected framework, mesoporous materials have great potential to be applied in heterogeneous catalysis [6], bio-adsorption [7], separation [8], drug delivery [9], sensing [10, 11] as well as optical and electronic uses [12]. Since MCM-41 was synthesized by BECK using quaternary ammonium supramolecular surfactant as template, mesoporous materials entered a new stage of development, especially in the field of catalysis [13, 14]. Mesoporous materials has been widely used in aromatization [15, 16], hydrodesulfurization and hydrodeoxygenation [17, 18]. The pore structure and hydrothermal properties of mesoporous material can be improved by changing the synthesis method and post-treatment method [19].

SBA-15 with stable skeleton structure is one kind of silica-based mesoporous material. For SBA-15, the specific surface area can reach to 1000 m²/g, the pore wall thickness is about 6 nm, and the molecular surface contains a large number of silanol groups make SBA-15 become an ideal catalyst carrier [20]. Al-SBA-15 with large specific surface area, large pore diameter and pore volume can be obtained by adding aluminium source during synthesis process. The unique structure, surface characteristics, good thermal stability and mechanical strength make Al-SBA-15 have higher catalytic activity than those of traditional alumina catalysts during the reaction. It is effective to prepare Al-SBA-15 using hydrothermal synthesis process by adding organic template agent.

However, organic templates which occluded within the pores of Al-SBA-15 should be removed before application [21]. Only the template agent is removed from the original network structure, can the ideal ordered mesoporous materials be obtained [22]. Various methods have been explored to remove organic template from the precursor of the synthesized porous materials. The most commonly used organic templates removing methods are calcination and solvent extraction (by conventional solvent) [23, 24]. The organic template can be completely removed by using calcination method, but the structure of materials can also be contracted or collapsed after calcination. Moreover, a large amount of CO₂ and organic amine mixture are produced [25]. He et al. reported that when two-step calcination method was used to remove the organic template, MCM-41 with a better long-range structure and larger quantities of acid sites was obtained in comparison with MCM-41 prepared by directly calcination process at high temperature [26]. Solvent extraction can preserve the skeleton structure of the material to a great extent while recycling expensive organic agents, however the removal of the organic template was not complete [27].

Ultraviolet decomposition method [28] and ozone oxidation method [29] were also used to remove the organic template from porous materials, which can remove the template at a relatively low temperature, and the damage to the hole is less. But the processing amount is very limited at a time, thus long processing time is needed, and the operating conditions are complex [27]. Supercritical carbon dioxide extraction is another method, which is high-efficiency and environment-friendly [30]. However, due to the harsh operation, high operating cost and requirement for expensive equipment, the wide application of this method is limited. Microwave-assisted method has also been used in removing templates [21, 31]. This method can quickly remove the templating agent from mesoporous materials. But the removal conditions of the microwave-assisted method are difficult to control for some mesoporous materials [31]. Template removing method have a great influence on the structural stability of the mesoporous material and the silanol groups on the surface of the mesoporous material. However, the impact of these methods on the physiochemical properties of Al-SBA-15 and the corresponding catalytic activity of Al-SBA-15 supported catalysts has not been deeply investigated.

Nickel as one kind of transition metal with unique properties has been widely used in catalysts [32-34]. Ni/Al-SBA-15 is regarded as one of the most promising catalysts to be used in bio-oils refining processes such as hydrodeoxygenation (HDO), cracking and so on [35, 36]. Due to the complex composition of bio-oil and its instability, investigation of bio-oil upgrading by HDO directly is challenged. Eugenol as one of the model compounds of bio-oil has been used to develop highly active and selective hydrodeoxygenation catalysts [35, 37].

In this study, four kinds of template removing methods were introduced to remove the template existing in Al-SBA-15 precursor. Ni/Al-SBA-15 is synthesized

and used as catalyst for eugenol hydrodeoxygenation. Nickel species were loaded onto Al-SBA-15 by using incipient wetness impregnation method. The effects of different template removing methods on the physiochemical characteristics of Al-SBA-15 and Ni/Al-SBA-15, and on the eugenol hydrodeoxygenation activity in liquid phase over Ni/Al-SBA-15 were investigated.

2. Materials and methods

2.1. Materials

Pluronic P123 (EO20-PO70-EO20) was purchased from Sigma-aldrich company. Tetraethyl orthosilicate (TEOS, AR) was purchased from Sinopharm Chemical Reagent company. Aluminium nitrate 9-hydrate (AR, Al(NO₃)₃·9H₂O), nickel nitrate hexahydrate (98 %), *p*-cresol (\geq 99.7 %) and eugenol (99 %) were purchased from Aladdin Chemical company. *n*-dodecane (AR) was purchased from Tianjin Kermel Chemical company. All the chemicals were used as received.

2.2. Preparation of Al-SBA-15 precursors

Al-SBA-15 precursor was synthesized by using P123 as polymeric template according to the method reported [35, 38]. At the first step, 1.0 g of Pluronic P123 was put in a glass beaker with volume of 150 mL. Then, 80 mL of deionized water was added into the above beaker and stirred to dissolve the Pluronic P123. Thirdly, 0.41 g of Al(NO₃)₃·9H₂O was put into the mixture and stirred magnetically until completely dissolved. Afterwards, 7.3 mL of TEOS was added into the above mixture, followed by vigorous magnetic stirring for 15 h at room temperature, and then at 313 K for 24 h. Afterwards, the obtained mixture was transformed into the hydrothermal synthesis reactor at 363 K for 2 days. Finally, the solid product in the bottom of

reactor was filtered, washed with distilled water, and put in an oven for drying at 333 K overnight in air.

2.2. Methods for removing the template of Al-SBA-15 precursors

The template of Al-SBA-15 precursor was removed by different methods, including the direct calcination, two-step calcination, solvent extraction and electric heating digestion method. In direct calcination process, Al-SBA-15 precursor in square crucible was firstly put into a muffle furnace and heated from room temperature to 823 K with a heating rate of 3 K/min, and held at this temperature for 5 h. The obtained Al-SBA-15 was named as SC1 for short in this paper. In two-step calcination process, Al-SBA-15 precursor in square crucible was firstly put into a muffle furnace for heating from room temperature to 373 K with a heating rate of 3 K/min and held at this temperature for 2 h, followed by heating from 373 K to 823 K with a heating rate of 3 K/min and held at this temperature for 5 h. The obtained Al-SBA-15 was named as SC2 for short in this paper. In the solvent extraction process, Al-SBA-15 precursor was dried at 353 K for 24 h to evaporate water. Then, 6 g of Al-SBA-15 precursor was added into a round-bottom flask containing 250 mL of ethanol. The template was removed by using a Soxhlet system for 6 h. After extraction, the samples were filtrated and dried at 353 K for 12 h, resulting in the formation of Al-SBA-15 named as SE for short in this paper. The electric heating digestion process was as follows. (1) 5.83 mL of HNO₃ was solved in 5.17 mL of water, then 4 mL of H_2O_2 (30%) was added to the solution; (2) 1 g of Al-SBA-15 precursor was added into the above solution; (3) the mixture was poured into a PTFE

digestion tube and sealed, then the PTFE digestion tube was put into an electric digestion apparatus (Hanon, SH230) at 600 w and 423 K for 15 min; (4) After filtration, the solid was washed with deionized water until to pH=7; (5) the solid material was put in an oven at 363 K overnight, resulting in the formation of Al-SBA-15 named as SD for short in this paper.

Incipient wetness impregnation method was applied to load nickel species onto Al-SBA-15. The process was proceeded as according to the method reported in reference using ethanol as the impregnant and using nickel nitrate hexahydrate as nickel source [35]. SC1, SC2, SE and SD was respectively named as NSC1-C, NSC2-C, NSE-C and NSD-C after loading nickel species and calcination. Before reaction, Ni/Al-SBA-15 was reduced under H₂ and N₂ atomosphere (3:7) at 100 mL/min and kept at 823 K for 2 h with a heating rate of 3 K/min. Samples after reduction were named as NSC1-R, NSC2-R, NSE-R and NSD-R, respectively.

2.3. Catalyst characterization

Hitachi S-4800 SEM-microscope was used to measure the SEM images of samples. TEM images were taken by a Hitachi FB-2100 FIB apparatus. Before TEM measurement, a drop of an ultra-sonicated methanol-sample mixed suspension was deposited onto a carbon-coated Cu grid. The measurement of nitrogen sorption isotherms of samples were carried out at 77 K by using a physical sorption instrument (Micromeritics ASAP 2460). Samples were outgassed at 423 K for 3 h before adsorption measurements. Brunauer-Emmett-Teller (BET) model was introduced to calculate the total specific surface areas of the samples, and *t*-plot method was used to

calculate the micropore volume and the external specific surface area of the samples. The non-local density functional theory (NLDFT) was introduced to analyze the mesopore diameter. The crystal structure of samples was analyzed by XRD patterns which were obtained by using a Bruker D8 Advance diffractometer with Cu Ka radiation. The XRD patterns were accumulated within the wide-angle range of 20-70° (20) and small-angle the range of $0-5^{\circ}$ (20). XPS measurements of samples were taken by a X-ray photoelectron spectrometer (ThermoFischer, ESCALAB 250Xi, Al Ka radiation (hv=1253.6 eV)). The binding energies (BE) of elements in samples were calibrated by referring to the BE of C 1s peak at 284.60 eV. XRF spectrometer (Axios PW4400, Panalytical) was used to detect Si to Al ratio and nickel content of the Ni/Al-SBA-15. ²⁹Si MAS-NMR spectra were collected by the solid state nuclear magnetic resonance spectrometer (Infinityplus 300, Varian). FT-IR spectra of samples were collected by a FT-IR spectrometer (Nicolet, Nexus 410) at room temperature. Before detection, samples were mixed with KBr, ground thoroughly and compressed into self-supporting wafers. Then, the FT-IR spectra of samples were collected within wavenumber range of 2000 to 400 cm⁻¹ with resolution of 4 cm⁻¹. The distribution, strength and type of acid sites were calculated by Py-FTIR on a FTIR spectrometer (Thermo Nicolet 380).

2.4. Catalytic conversion of eugenol

Eugenol hydrodeoxygenation over different Ni/Al-SBA-15 in liquid phase was carried out in an autoclave reactor with internal volume of 100 mL. Before reaction, 770 μ L of eugenol, 40 mL of *n*-dodecane and 0.05 g of Ni/Al-SBA-15 were put into the reactor. 0.1 Mpa of H_2 was used to flush the reactor for three times and eugenol hydrodeoxygenation was took place at 513 K for 2 h under stirring speed of 680 rpm. After reaction, the liquid product was separated and put in glass bottles and sealed. The catalyst was dried at 373 K overnight, weighed and recorded. All products were analyzed by GC-MS (Agilent 7890A/5975C) and *p*-cresol was used as an internal standard during the detect process.

3. Results and discussion

3.1. Characterization of the samples

In order to obtain the mesostructure of Ni/Al-SBA-15, small-angle powder XRD was introduced. The XRD patterns of samples are shown in Fig. 1. Three characteristic peaks, namely (100), (110) and (200), appeared in the XRD patterns of all the samples. This indicated that all Ni/Al-SBA-15 samples had an ordered two-dimensional (2D) hexagon structure, which is very consistent with the topology pattern of SBA-15. The (100) plane of NSD-C moved to lower angle of 2 θ due to the increase of lattice spacing(*d*) after removing the organic template [39].



Fig. 1. Small-angle Powder X-ray diffraction patterns after calcination.

The nitrogen sorption isotherms and pore size distribution curves of NSC1-C, NSC2-C, NSD-C and NSE-C are as shown in Fig. 2. All the samples showed typical IV type isotherms of IUPAC classification (Fig. 2a). In addition, due to the capillary condensation phenomenon, hysteresis loops were observed in the IV type isotherms [40]. The hysteresis loops presented in the desorption branch of the calcined samples were divided into two steps. The first step was the desorption process within the range from 0.75 to 0.61 p/p^0 on the desorption branch, which was corresponded to the nitrogen desorption from the "open" mesopores. The second step was the desorption process within the range from 0.61 to 0.47 p/p^0 , which was corresponded to the N₂ adsorption in the "blocked" mesopores [38, 41, 42]. This indicates that NSC2-C and NSE-C had larger ratio of "open" mesopores than the other two samples. The NLDFT pore size distribution curves of samples are shown in Fig. 2b. It could be seen that the pore size distribution of NSD-C was moved to higher diameter. The parameters such as pore diameter, pore volume and specific surface area of samples are as shown in Table 1. The Si to Al ratios maintained within range of 60-64 for NSC1-C, NSC2-C and NSE-C. However, the Si to Al ratio of NSD-C was up to 844, which was caused by aluminum leaching during the template removal process by using electric heating digestion methods. The nickel contents of samples were within the range of 17.6-20.4 %. The specific areas of samples were in the order of NSC2-C>NSC1-C>NSD-C>NSE-C. NSC2-C had the largest specific surface area (619 m²/g); while NSE-C had the lowest (555 m²/g). NSC1-C, NSC2-C and NSE-C had approximately the same mesopore diameter, which was about 6.1 nm. While for NSD-C, the mesopore diameter was up to 6.68 nm. The wall thickness of NSC1-C, NSC2-C and NSE-C was about 12.2 nm. In contrast, the wall thickness of NSD-C was significantly decreased to 11.62 nm. In combined with the shape of hysteresis

loops appearing in the adsorption-desorption isotherms, it can be deduced that the part of the ordered pore structure in NSD-C was destroyed after removal of organic templates by using electric heating digestion methods.



Fig. 2. (a) nitrogen adsorption-desorption isotherms at 77 K determined on calcined Ni based Al-SBA-15 samples with different organic template removal approaches and (b) NLDFT pore size distribution curves calculated from adsorption branches of calcined Ni based Al-SBA-15 samples with different organic template removal approaches.

Table 1 The structural properties of Ni/Al-SBA-15 samples with different organic templateremoval approaches from N_2 sorption and XRD data.

Journal Pre-proof									
Sample	Si/Al ^a	Ni/%ª	A_{BET}	V_p	V_{mic}	V _{mes}	a_0	D_p	t (nm)
			(m ² /g)	(cm ³ /g)	(cm ³ /g)	(cm ³ /g)	(nm)	(nm)	
NSC1-C	64	17.6	574	0.552	0.103	0.448	18.3	6.12	12.18
NSC2-C	60	18.4	619	0.584	0.118	0.465	18.3	6.11	12.19
NSE-C	63	20.4	555	0.568	0.091	0.477	18.3	6.11	12.19
NSD-C	844	20.2	571	0.687	0.048	0.640	18.3	6.68	11.62

a, the Si to Al ratios and the nickel content were obtained by XRF. A_{BET} - total specific surface area obtained by the BET method. V_p -total pore volume of single point adsorption at $p/p_0= 0.995$. A_{ext} and V_{mic} -external specific surface area and micropore volume obtained by the t-plot method. V_{mes} -mesopore volume, calculated as $V_{meso}=V_{total}-V_{micro}$. a_0 - unit cell parameter determined by XRD. D_p -mesopore diameter corresponding to the maximum of PSD calculated by NLDFT method from ads orption branch; *t*-wall thickness, calculated as $t=a_0-D_p$.

Powder X-ray diffraction patterns of NSC1, NSC2, NSD and NSE after calcining and reduction are shown in Fig. 3. The broad peak appearing at about 20° - 30° for all samples was attributed to amorphous silica in framework [43]. NiO diffraction peaks at ~ 37° , ~ 43° and ~ 63° were observed in the XRD spectra of NSC1-C, NSC2-C, NSD-C and NSE-C [44]. As shown in Fig. 3b, Ni diffraction peaks at ~ 44.5° and ~ 52° were observed in the XRD spectra of NSC1-C, NSC2-C, NSD-C and NSE-C [45]. Moreover, the diffraction peaks of NiO were still can be observed in the XRD spectra of reduced samples, which indicated that NiO was partially converted to Ni after reduction at 823 K. The chemical states of Ni in the NSD-C and NSD-R were also

analyzed by the Ni 2p XPS (Fig.S1). Spin-orbit doublets peaks at ~856 and ~873 eV were observed for NSD-C and NSD-R, which were ascribed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively [46]. Peak at 852.6 eV appearing at the XPS spectra of NSD-R was attributed to $2p_{3/2}$ of Ni⁰ [47]. Two satellite peaks of Ni were appeared at ~862.0 eV and ~880.3 eV for both NSD-C and NSD-R [48]. The presence of Ni²⁺ at the XPS spetra of NSD-R was mainly due to the strong interactions between the Ni particles and the support. The XPS results show that both Ni⁰ and Ni²⁺ existed on the surface of NSD-R.



Fig. 3. Powder X-ray diffraction patterns of nickel based Al-SBA-15 samples: (a) nickel based Al-SBA-15 samples after reduction.

SEM and TEM images of NSC1-C, NSC2-C, NSE-C and NSD-C are as shown in Fig. 4. All the samples exhibited aggregated morphology like wheat. But for NSD-C, part of the long rod-like particles were damaged. All the samples showed regular long ordered pore structure. The TEM images of samples demonstrated that particles of nickel species were existed on the surface of samples and the ordered



2D-hexagonal symmetry is observed.

Fig. 4. SEM and TEM image of calcined nickel based Al-SBA-15 samples with different organic template removal approaches.

The FTIR spectra of NSD, NSE, NSC2 and NSC1 after calcination or reduction are shown in Fig. 5. All samples after calcination exhibited peaks at 1630, 962, 800, 575, 466 cm⁻¹, as well as broad bands at 1091 and 1221 cm⁻¹. The peak appearing at 1630 cm⁻¹ was attributed to the vibration of hydroxyl bands for adsorption water [49]. A broad band appearing at 1091 cm⁻¹ coupling with a shoulder peak at 1221 cm⁻¹ was due to the asymmetric stretching vibration of Si-O-Si [49]. The reason for the appearance of the band at about 962 cm⁻¹ is still in dispute. It was reported that this peak was caused by the part asymmetry of the framework due to the existence of defects [50]. A strong shoulder peak indicated the symmetry of the framework was decreased. The peak appearing at 962 cm⁻¹ in NSD-C and NSD-R was significantly stronger than that in the other three samples. The peak appearing at ~800 cm⁻¹ was caused by the intrinsic symmetric stretching vibration of the TO₄ containing Al and Si [35, 49, 51]. The band appearing at 575 cm⁻¹ and 466 cm⁻¹ was attributed to the bending vibration of Si-O [49]. It can be seen from Fig.5 that the band appearing at 1630 cm⁻¹ was significantly decreased after reduction of sample, which indicated that adsorption water in samples was further removed after reduction. No other difference was observed for these samples before and after reduction.



Fig. 5. FT-IR spectra of 16 % Ni based Al-SBA-15 obtained with different organic template removal approaches: (a) represents Ni/Al-SBA-15 samples after calcination and (b) represents Ni/Al-SBA-15 after reduction.

The ²⁹Si MAS-NMR spectra of SC1, SC2, SE and SD are shown in Fig. 6. In the ²⁹Si MAS-NMR spectra, three resonances at about -90, -100 and -110 nm were obtained for all the samples, which can be ascribed to Q_2 , Q_3 and Q_4 sites, respectively. n in Q_n represents the number of the adjacent silicon atoms which are

linked with oxygen bridge. The chemical shift of Q_3 ranged from -100 to -106 nm, which was probably resulted from two structure units including Si(OSi)₃(OAl) and Si(OSi)₃(OH) for Al-SBA-15 [43]. The chemical shift of Q_2 at around -90 nm was corresponded to structure units including Si(OSi)₂(OH)₂, Si(OSi)₂(OAl)₂ or Si(OSi)₂(OAl)(OH) [52]. The ²⁹Si MAS-NMR spectra of NSC1 and NSC2 are very similar. However, for sample SE and sample SD, the concentration of Q_2 sites was increased. Based on the Si/Al ratios obtained by XRF, it can deduced that much more Si(OSi)₃(OH) and Si(OSi)₂(OAl)(OH) or Si(OSi)₂(OAl)₂ existed in SE. Moreover, part of SD structure was destroyed and much more Si(OSi)₃(OH) was formed.



Fig. 6. ²⁹Si MAS-NMR spectra of Al-SBA-15 samples after removal of template.

3.2. Performance of eugenol hydrodeoxygenation over Ni/Al-SBA-15

The reaction results of eugenol hydrodeoxygenation over Ni/Al-SBA-15 with different organic template removal approaches are shown in Fig. 7. The conversion of eugenol after reaction was nearly 100 % for all the reaction. Four products, including

4-propyl-guaiacol, propylbenzene, 4-propyl-hexane and methanol, were obtained over NSC1-R, NSC2-R, NSE-R and NSD-R, respectively. Moreover, the selectivity of each product varied significantly with the type of catalysts. The selectivity of 4-propyl-hexane was in the order of NSE-R>NSC2-R>NSC1-R>NSD-R. The highest selectivity of 4-propyl-hexane was obtained when using NSE-R as catalyst, which was about 89.87 %. The lowest selectivity of 4-propyl-hexane was 3.96 %, which was obtained when using NSD-R as HDO catalyst. The selectivity of 4-propyl-guaiacol was in the order of NSD-R>NSC1-R>NSC2-R>NSE-R. Only few propylbenzene was produced for all the reactions over different Ni/Al-SBA-15 catalysts. The results showed that high hydrocarbons were obtained during hydrodeoxygenation process by using NSE-C as catalyst. A higher hydrocarbon selectivity was obtained by the hydrodeoxygenation over NSC2-R than that over NSC1-R. This indicated that two-step calcination was more effective than the direct calcination process in template removal and was much more suitable for the hydrodeoxygenation process. Through physiochemical analysis, it can be concluded that electric heating digestion method was not suitable for the template removal of Al-SBA-15.



Fig. 7. Eugenol hydrodeoxygenation on Ni/Al-SBA-15 with different organic template removal approaches.

4. Conclusions

Three kind of template removing methods were introduced, including calcination, solvent extraction and electric heating digestion. The effects of these template removing methods on the physiochemical characterization of Ni/Al-SBA-15 and the corresponding hydrodeoxygenation activities were investigated. In terms of specific area, samples were in the order of NSC2-C>NSC1-C>NSD-C>NSE-C. NSC2-C had the largest BET specific surface area, which was about 619 m²/g. NSC1-C, NSC2-C and NSE-C had similar mesopore diameter, which was about 6.1 nm. While for NSD-C, the mesopore diameter was increased to 6.68 nm. NSC1-C, NSC2-C and NSE-C had similar wall thickness, which was about 12.2 nm, while NSD-C had a decreased wall thickness, which was about 11.62 nm. Part of the ordered pore structure in NSD-C was destroyed after removal of the organic templates by using

electric heating digestion method. The selectivity of each product varied with the type of catalyst. Results showed that the selectivity of 4-propyl-guaiacol was in the order of NSD-R>NSC1-R>NSC2-R>NSE-R. The results showed that high hydrocarbons were obtained during hydrodeoxygenation process by using NSE-C as catalyst. Two-step calcination was more effective than the direct calcination process in template removal and was much more suitable for the hydrodeoxygenation process. Electric heating digestion method was not suitable for the template removal of Al-SBA-15.

Acknowledgment

This work is financially supported by National Natural Science Foundation of China Through Project (grant number 51602215), the Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development (Y807s41001), the Fundamental Research Funds for the Central Universities (18CX02101A), the Independent Innovation and Entrepreneurship projects of Qingdao Institute for Ocean Technology of Tianjin University (20190201-8) and the National Science and Technology Major Project (grant number 2016ZX05014-004-007).

References

[1] K.E. Bremmell, C.A. Prestidge, Enhancing oral bioavailability of poorly soluble drugs with mesoporous silica based systems: opportunities and challenges, Drug Dev. Ind. Pharm. 45 (2019) 349-358.

[2] M. Fattahi, M. Kazemeini, F. Khorasheh, A.M. Rashidi, Vanadium pentoxide catalyst over carbon-based nanomaterials for the oxidative dehydrogenation of propane, Ind. Eng. Chem. Res. 52 (2013) 16128-16141.

[3] M. Fattahi, M. Kazemeini, F. Khorasheh, A.M. Rashidi, Morphological investigations of nanostructured V2O5 over graphene used for the ODHP reaction: from synthesis to physiochemical evaluations, Catal. Sci. Technol. 5 (2015) 910-924.

[4] S. Kumaravel, S. Thiripuranthagan, R. Radhakrishnan, E. Erusappan, M. Durai, A. Devarajan, A. Mukannan, Liquid Phase Esterification of Levulinic Acid into Ethyl Levulinate Over Sulphobenzylated Nanoporous Al-SBA-15 Catalyst, J. Nanosci. Nanotechnol. 19 (2019) 6965-6977.

[5] X. Feng, J. Liu, J. Li, L.F. Ma, L.Y. Wang, S.W. Ng, G.Z. Qin, Series of coordination polymers based on 4-(5-sulfo-quinolin-8-yloxy) phthalate and bipyridinyl coligands: Structure diversity and properties, J. Solid State Chem. 230 (2015) 80-89.

[6] L. Kleiner, L. Vazquez, C.C. Akoh, Lipase-catalyzed concentration of stearidonic acid in modified soybean oil by partial hydrolysis, J. Am. Oil Chem. Soc. 89 (2012) 1999-2010.

[7] M. Hartmann, Ordered mesoporous materials for bioadsorption and biocatalysis, Chem. Mater. 17 (2005) 4577-4593.

[8] M.J. Davis, S.J. Klippenstein, Geometric investigation of association/dissociation kinetics with an application to the master equation for $CH_3+CH_3 <-> C_2H_6$, J. Physic. Chem. A 106 (2002) 5860-5879.

[9] E. Aznar, R. Martinez-Manez, F. Sancenon, Controlled release using mesoporous materials containing gate-like scaffoldings, Expert Opin. Drug Del. 6 (2009) 643-655.

[10] B.J. Melde, B.J. Johnson, Mesoporous materials in sensing: morphology and functionality at the meso-interface, Anal. Bioanal. Chem. 398 (2010) 1565-1573.

[11] B.J. Melde, B.J. Johnson, P.T. Charles, Mesoporous silicate materials in sensing, Sensors 8 (2008) 5202-5228.

[12] Y. Klichko, M. Liong, E. Choi, S. Angelos, A.E. Nel, J.F. Stoddart, F. Tamanoi,J.I. Zink, Mesostructured silica for optical functionality, nanomachines, and drug delivery, J. Am. Ceram. Soc. 92 (2009) S2-S10.

[13] C.E. Song, S.G. Lee, Supported chiral catalysts on inorganic materials, Chem.Rev. 102 (2002) 3495-3524.

[14] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, Synthesis and characterization of molybdenum complexes with bidentate Schiff base ligands within nanoreactors of MCM-41 as epoxidation catalysts, J. Mol. Catal. A-Chem. 248 (2006) 53-60.

[15] Y. Lv, X. Wang, D. Gao, X. Ma, S. Li, Y. Wang, G. Song, A. Duan, G. Chen, Hierarchically porous ZSM-5/SBA-15 zeolite: Tuning pore structure and acidity for enhanced hydro-upgrading of FCC gasoline, Ind. Eng. Chem. Res. 57 (2018) 14031-14043.

[16] Z. Zhang, Z. Chen, X. Gou, H. Chen, K. Chen, X. Lu, P. Ouyang, J. Fu, Catalytic decarboxylation and aromatization of oleic acid over Ni/AC without an added hydrogen donor, Ind. Eng. Chem. Res. 57 (2018) 8443-8448.

[17] F.J. Mendez, O.E. Franco-Lopez, X. Bokhimi, D.A. Solis-Casados, L. Escobar-Alarcon, T.E. Klimova, Dibenzothiophene hydrodesulfurization with NiMo and CoMo catalysts supported on niobium-modified MCM-41, Appl. Catal. B-environ. 219 (2017) 479-491.

[18] X. Li, G. Chen, C. Liu, W. Ma, B. Yan, J. Zhang, Hydrodeoxygenation of lignin-derived bio-oil using molecular sieves supported metal catalysts: A critical review, Renew. Sust. Energ. Rev. 71 (2017) 296-308.

[19] W. Ding, H. Gao, D. Wang, D. Zhao, G. Song, Y. Dai, Removal of macromolecule template in macropores alumina nano material, Speciality Petrochemicals 34 (2017) 20-25.

[20] L. Deng, T. Arakawa, T. Ohkubo, H. Miura, T. Shishido, S. Hosokawa, K. Teramura, T. Tanaka, Highly active and stable Pt-Sn/SBA-15 catalyst prepared by

direct reduction for ethylbenzene dehydrogenation: Effects of Sn addition, Ind. Eng. Chem. Res. 56 (2017) 7160-7172.

[21] L. Xiao, J. Li, H. Jin, R. Xu, Removal of organic templates from mesoporous
SBA-15 at room temperature using UV/dilute H₂O₂, Micropor. Mesopor. Mater. 96
(2006) 413-418.

[22] Z. Zhou, J. Feng, H. Cheng, C. Zhang, Q. Gao, J. Wang, Progress in study on the removal of templates during the syntheses of ordered mesoporous materials, Mater. Rev. 19 (2005) 36-39.

[23] F. Kleitz, S.H. Choi, R. Ryoo, Cubic Ia3d large mesoporous silica: synthesis and replication to platinum nanowires, carbon nanorods and carbon nanotubes, Chem. Commun. (2003) 2136-2137.

[24] S.G. de Avila, L.C.C. Silva, J.R. Matos, Optimisation of SBA-15 properties using Soxhlet solvent extraction for template removal, Micropor. Mesopor. Mater. 234 (2016) 277-286.

[25] Z.L. Hua, J.L. Shi, L. Wang, W.H. Zhang, Preparation of mesoporous silica films on a glass slide: surfactant template removal by solvent extraction, J. Non-Cryst. Solids 292 (2001) 177-183.

[26] J. He, X.B. Yang, D.G. Evans, X. Duan, New methods to remove organic templates from porous materials, Mater. Chem. Phys. 77 (2003) 270-275.

[27] L.P. Xiao, J.Y. Li, H.X. Jin, R.R. Xu, Removal of organic templates from mesoporous SBA-15 at room temperature using UV/dilute H₂O₂, Micropor. Mesopor. Mat. 96 (2006) 413-418.

[28] A.N. Parikh, A. Navrotsky, Q.H. Li, C.K. Yee, M.L. Amweg, A. Corma, Non-thermal calcination by ultraviolet irradiation in the synthesis of microporous materials, Micropor. Mesopor. Mat. 76 (2004) 17-22. [29] G. Buchel, R. Denoyel, P.L. Llewellyn, J. Rouquerol, In situ surfactant removal from MCM-type mesostructures by ozone treatment, J. Mater. Chem. 11 (2001) 589-593.

[30] R. van Grieken, G. Calleja, G.D. Stucky, J.A. Melero, R.A. Garcia, J. Iglesias, Supercritical fluid extraction of a nonionic surfactant template from SBA-15 materials and consequences on the porous structure, Langmuir 19 (2003) 3966-3973.

[31] B.Z. Tian, X.Y. Liu, C.Z. Yu, F. Gao, Q. Luo, S.H. Xie, B. Tu, D.Y. Zhao, Microwave assisted template removal of siliceous porous materials, Chem. Commun. (2002) 1186-1187.

[32] X. Feng, L.F. Ma, L.Y. Wang, J.S. Zhao, A unique tetranuclear nickel(II) complex containing pyridine-2-carboxaldehyde derivative bearing an intramolecular acetato: Synthesis, crystal structure and magnetic property, Inorg. Chem. Commun. 14 (2011) 584-589.

[33] B. Jiang, T. Zhu, H. Song, F. Li, Hydrodeoxygenation and hydrodesulfurization over Fe promoted Ni₂P/SBA-15 catalyst, J. Alloy Compd. 806 (2019) 254-262.

[34] J. Pang, J. Sun, M. Zheng, H. Li, Y. Wang, T. Zhang, Transition metal carbide catalysts for biomass conversion: A review, Appl. Catal. B-environ. 254 (2019) 510-522.

[35] X. Li, J. Zhang, B. Liu, J. Liu, C. Wang, G. Chen, Hydrodeoxygenation of lignin-derived phenols to produce hydrocarbons over Ni/Al-SBA-15 prepared with different impregnants, Fuel 243 (2019) 314-321.

[36] G.M. Kumaran, S. Garg, K. Soni, M. Kumar, J.K. Gupta, L.D. Sharma, K.S.R. Rao, G.M. Dhar, Synthesis and characterization of acidic properties of Al-SBA-15 materials with varying Si/Al ratios, Micropor. Mesopor. Mater. 114 (2008) 103-109.

[37] A.A. Dwiatmoko, J. Seo, J.W. Choi, D.J. Suh, J. Jae, J.M. Ha, Improved activity of a CaCO3-supported Ru catalyst for the hydrodeoxygenation of eugenol as a model lignin-derived phenolic compound, Catal. Commun. 127 (2019) 45-50.

[38] S. Lin, L. Shi, H. Zhang, N. Zhang, X. Yi, A. Zheng, X. Li, Tuning the pore structure of plug-containing Al-SBA-15 by post-treatment and its selectivity for C-16 olefin in ethylene oligomerization, Micropor. Mesopor. Mater. 184 (2014) 151-161.

[39] J. Socci, A. Osatiashtiani, G. Kyriakou, T. Bridgwater, The catalytic cracking of sterically challenging plastic feedstocks over high acid density Al-SBA-15 catalysts, Appl. Catal. A-Gen. 570 (2019) 218-227.

[40] F. Song, X. Zhao, N. Liu, Q. Chen, Y. Li, Different Methods for Removal of Mesoporous Silica Organic Template Agent, Bulletin of the Chinese Ceramic Society, 37 (2018) 332-336,341.

[41] P. Van Der Voort, P.I. Ravikovitch, K.P. De Jong, M. Benjelloun, E. Van Bavel, A.H. Janssen, A.V. Neimark, B.M. Weckhuysen, E.F. Vansant, A new templated ordered structure with combined micro- and mesopores and internal silica nanocapsules, J. Phys. Chem. B 106 (2002) 5873-5877.

[42] L. Shi, Y. Xu, N. Zhang, S. Lin, X. Li, P. Guo, X. Li, Direct synthesis of Al-SBA-15 containing aluminosilicate species plugs in an acid-free medium and structural adjustment by hydrothermal post-treatment, J. Solid State Chem. 203 (2013) 281-290.

[43] K.B. Baharudin, Y.H. Taufiq-Yap, J. Hunns, M. Isaacs, K. Wilson, D. Derawi, Mesoporous NiO/Al-SBA-15 catalysts for solvent-free deoxygenation of palm fatty acid distillate, Micropor. Mesopor. Mater. 276 (2019) 13-22.

[44] Y. Zhao, B. Liu, R. Amin, CO₂ reforming of CH4 over MgO-Doped Ni/MAS-24 with microporous ZSM-5 structure, Ind. Eng. Chem. Res. 55 (2016) 6931-6942.

[45] W. Gac, W. Zawadzki, G. Slowik, A. Sienkiewicz, A. Kierys, Nickel catalysts supported on silica microspheres for CO₂ methanation, Micropor. Mesopor. Mater. 272 (2018) 79-91.

[46] L. Liu, Y. Liu, J. Song, S. Ahmad, J. Liang, Y. Sun, Plasma-enhanced steam reforming of different model tar compounds over Ni-based fusion catalysts, J. hazard. Mater. 377 (2019) 24-33.

[47] S. Wang, Y. Wang, C. Hu, The effect of NH₃ center dot H₂O addition in Ni/SBA-15 catalyst preparation on its performance for carbon dioxide reforming of methane to produce H-2, Int. J. Hydrogen Energ. 43 (2018) 13921-13930.

[48] X. Liu, Z. Jiang, S. Feng, H. Zhang, J. Li, C. Hu, Catalytic depolymerization of organosolv lignin to phenolic monomers and low molecular weight oligomers, Fuel, 244 (2019) 247-257.

[49] S. Xing, P. Lv, J. Fu, J. Wang, P. Fan, L. Yang, Z. Yuan, Direct synthesis and characterization of pore-broadened Al-SBA-15, Micropor. Mesopor. Mater. 239 (2017) 316-327.

[50] X. Zheng, B. Dong, C. Yuan, K. Zhang, X. Wang, Direct synthesis, characterization and catalytic performance of Al-SBA-15 mesoporous catalysts with varying Si/Al molar ratios, J. Porous Mater. 20 (2013) 539-546.

[51] D.A. Cabrera Munguia, E. Tututi-Ríos, A. Gutiérrez-Alejandre, J. Luis Rico, H.
González, Reaction study for the esterification of oleic acid over M-SBA-15-SO₃H
(M=Al, Ti) catalysts, Energ. Procedia 142 (2017) 590-596.

[52] W. Hu, Q. Luo, Y. Su, L. Chen, Y. Yue, C. Ye, F. Deng, Acid sites in mesoporous Al-SBA-15 material as revealed by solid-state NMR spectroscopy, Micropor. Mesopor. Mater. 92 (2006) 22-30.

Highlights

- Physicochemical properties of Al-SBA-15 were notably impacted by template \geq removal approaches
- Template removal approaches can affect the catalytic activity of Ni/Al-SBA-15 \geq
- Eugenol hydrodeoxygenation over Ni/Al-SBA-15 was investigated \succ
- \succ Two-step calcination method for Al-SBA-15 template removal was more effective

.iplate

Xiangping Li and Jianguang Zhang designed the research and collected the experiment data; Xiangping Li and Han Yin wrote this paper; Xiangping Li and Jianguang Zhang revised the paper; Guanyi Chen and Juping Liu edited the manuscript and provided some suggestions for manuscript organization.

The named authors have no conflict of interest, financial or otherwise.

Journal Preproof

Physicochemical properties of Al-SBA-15 were notably impacted by template removal approaches and two-step calcination method for Al-SBA-15 template removal and eugenol hydrodeoxygenation was more effective.

Journal Prendrook