

Study of catalytic hydrodeoxygenation performances of mesoporous Ni/KIT-6 catalyst—Effect of reduction temperature

Xianming Zhang^{1*#}, Shuang Chen^{1#}, Fengjiao Wang², Lidan Deng², Jianmin Ren²,
Zhaojie Jiao¹, Guilin Zhou^{1,2*}

*1. Engineering Research Center for Waste Oil Recovery Technology and Equipment,
Ministry of Education, Chongqing Technology and Business University, Chongqing
400067, China*

*2. Department of Materials Science and Engineering, Chongqing Technology and
Business University, Chongqing 400067, China*

These authors contributed equally to this work and should be considered co-first authors

* Corresponding author: Tel: +86–23–62769785

E-mail address: xm215@126.com (Xianming Zhang) or

dicpglzhou@ctbu.edu.cn(Guilin Zhou)

Abstract

A series of Ni/KIT6 catalyst precursors with 25wt.%Ni loading amount were reduced in H₂ at 400, 450, 500, and 550°C, respectively. The studied catalysts were investigated by XRD, Quasi*in-situ* XPS, BET, TEM, and H₂-TPD analysis methods. It was found that reduction temperature is an important factor affecting the hydrodeoxygenation (HDO) performance of the studied catalysts. The reduction temperature influences mainly the content of active components, crystal size, and the ability for adsorbing and activating H₂. The developed pore structure and large specific surface area of the KIT-6 support favored the Ni dispersion. The RT450 catalyst, which was prepared in H₂ atmosphere at 450 °C, has the best HDO performance. Ethyl acetate can be completely transformed, and maintain 96.8% ethane selectivity and 3.2% methane selectivity at 300 °C. The calculated apparent activation energies of the prepared catalysts increased in the following order: RT550 > RT400 > RT500 > RT450.

Keywords: Mesoporous Ni/KIT-6 catalyst; Active Ni species; Catalytic hydrodeoxygenation; Biodiesel

Introduction

With the process of economic globalization, the energy demand is increasing in the human society¹. The developments of non renewable energy have not fully met the needs of the industry and society developments^{2,3}. Therefore, finding a reliable alternative energy product is imminent. In order to cope with the above energy crisis, the new green energy concept and energy conversion technology have been put forward. The use of fed oil to prepare biodiesel is one of the most effective ways to reduce the supply pressure of petrochemical diesel⁴. The fed oil mainly includes vegetable oil, animal oil and gutter oil, which are mainly composed of fatty acid or ester with long chain. Fatty acid or ester usually contains rich carbon resources with C₁₂-C₂₄ bonds^{5,6}. Then, the successful transformation of fed oil to biodiesel may effectively mitigate the current tense energy situation. At present, the first-generation biodiesel cannot completely deoxygenate due to technical limitations. The products contain high oxygen content, resulting in low calorific value and poor adaptability⁷⁻⁹. In contrast, the second-generation biodiesel can completely deoxygenate because of technical advantage, and the prepared product has excellent performance. The second-generation biodiesel produced by HDO technology is more close to the petrochemical diesel on the physical and chemical properties than the first-generation biodiesel. Therefore, HDO technology has attracted wide attention because of the important applicable value. Of course, it also will play a dominant role in promoting chemical industry in the future.

The research and development of high performance catalytic materials is the core of the HDO technology. At present, the most widely used catalytic materials are the supported noble metal catalysts, such as Pt¹⁰, Pd¹¹, Ru¹², and so on. Pd/C catalyst has high yield of alkane products, which used in the stearic acid HDO reaction. The yield of *n*-C₁₇ alkane is over 60%, olefins and polymers are also produced in the

products¹³. Yang et al.¹⁴ prepare Pt/ZIF-67/zeolite 5A catalyst for oleic acid HDO, and found that the oleic acid is completely transformed at 320 °C/2.0 MPa when Pt loading is only 0.5% due to the special structure of the studied catalyst. 2%Ru/TiO₂ is good at stearic acid HDO reaction. The results show that the product is composed of C₁₇ and octadecanol with the selectivity is 18.1 and 78.2%, respectively, which indicates the product is the hydrolyzate product, and the hydrolysis rate is greater than the HDO rate¹⁵. Chen et al.¹⁶ reports that the Ru/zeolite catalyst is used in the HDO study of fatty acid methyl ester. It is found that the fed oil mainly go through decarbonylation pathway. At 300°C/3.0MPa, the fed oil conversion reaches 90.8%, and the selectivity of C₁₇ reaches 64.3%. As well known, the main advantage of the noble metal catalyst is the high catalytic activity, that is, the HDO reaction can be achieved at a relatively low reaction temperature. Nevertheless, noble metal catalysts are expensive. Therefore, transition metal catalyst has attracted much attention in the research and application in the HDO field. HDO and hydrodesulfurization have many similar characteristics, therefore, HDO catalysts are originally developed primarily as hydrodesulfurization catalysts. Kubicka et al.¹⁷ use the CoMoS/MCM-41 to catalyze the HDO reaction of rapeseed oil in a fluidized bed, mainly obtaining the diesel components such as C₁₇ and C₁₈, under the condition of 300~320°C, 2.0-11.0 MPa, and 1.0-4.0 h⁻¹. The introduction of S element is conducive to preventing catalyst from being poisoned, and even reducing some negative factors such as carbon deposition¹⁸. However, the S element may also be introduced into the product to reduce the environmental protection of the corresponding product¹⁹. Therefore, sulfur-free catalysts are getting more and more attentions. Imane Hachem et al.²⁰ use the sulfur-free Ni/γ-Al₂O₃ catalyst for the fatty acids HDO. Under 300°C/3.0 MPa, 6.0 h is running stably. The selectivity of C₁₇ reaches 96.2%, while the conversion of fatty acid reaches 100%. Mesoporous silicon-based materials

have developed mesoporous structure and large specific surface area, which facilitates the active component in high dispersion on the support surface²¹⁻²³. Therefore, replacing traditional support with mesoporous silicon-based material is a good method to solve the above problems we have met at the moment. At the same time, the use of ethyl acetate as a model compound can even effectively eliminate the influence of long chain alkyl structures over the studied catalytic HDO performance, thus obtaining more accurate information on HDO of oxygen containing functional groups^{24,25}. As we all know, the reduction temperature can affect the valence state of the variable valence transition metal species, then influence the activation ability of the corresponding catalysts for oxygen containing functional groups in the ester molecules and H₂ molecules in the reaction system. Zs. Ferenczet al.²⁶ study the reduction of Co/Al₂O₃ catalyst at different reduction temperatures. It is found that the composition of the corresponding catalyst is obviously affected by the reduction temperature. The higher the reduction temperature is, the more the Co content is. Furthermore, the temperature higher is, the particle size distribution narrower is. Therefore, the reduction temperature of the studied catalyst is a very important factor in the hydrogen reaction. However, the impact of the reduction temperature of Ni/KIT-6 catalyst on its HDO properties has rarely reported.

In this paper, a series of 25wt.%Ni/KIT-6 catalysts at different reduction temperatures. Ethyl acetate was used as model compound to investigate the catalytic HDO performance of the studied catalysts. The morphology structure, chemical composition, and physicochemical properties of the prepared catalysts were studied by means of XRD, Quasi *in-situ* XPS, BET, TEM, and H₂-TPD.

Results and discussion

XRD characterization

The XRD spectra of the catalysts, which were produced by H₂ reduction at different temperatures, are shown in Fig.2. RT400, RT450, RT500, and RT550 catalysts form a series of XRD diffraction peaks at $2\theta=44.51$, 51.81 , and 76.41° , which corresponds to the face-centered cubic phase of metallic Ni (JCPDS NO. 04-0850) with {111}, {200}, and {220} planes, respectively²⁹. In addition, the intensity of the metallic Ni diffraction peak is related to the reduction temperature. There is no other characteristic diffraction peak in the prepared catalysts expect for RT400 obtained by H₂ reduction at 400°C for 2.0h. In addition to the diffraction peak of the metallic Ni, the RT400 catalyst forms NiO peaks corresponding to the {111} and {220} planes at $2\theta=37.28$ and 62.62° , using standard data (JCPDS No. 44-1159)³⁰. The diffraction peaks of NiO phase have not been observed in RT450, RT500, and RT550 catalysts.

After reducing precursors at different temperatures, NiO species in precursors can be effectively reduced by H₂ to form metallic Ni species. The reduction temperature directly affects the reduction degree of NiO species, crystallinity, and dispersion of the metallic Ni species. Non reductive NiO species in the RT400 catalyst may belong to the NiO species that exist in the KIT-6 support pore structure. Meanwhile, the intensity of XRD diffraction peak of metallic Ni increases with increasing reduction temperature. The high reduction temperature can promote the migration and aggregation of metallic Ni to form stable Ni particles with large crystal size. Calculated by the Scherrer equation, the metallic Ni crystal sizes of the RT400, RT450, RT500, and RT550 catalysts are 5.9, 7.4, 9.1, and 10.0nm, respectively (see Table 1). Under the heat dissipation action of H₂ flow, the migration and accumulation rate of metallic Ni during the reduction process of NiO/KIT-6 precursor can be decreased, thus, the high dispersion of metallic Ni crystal is maintained when the complete reduction is achieved. The lower reduction temperature is, the slower reduction rate of NiO species is. This

can also be beneficial to the refinement of the metallic Ni crystal size. By contrary, at high reduction temperature, the effect of H₂ flow is not enough to prevent the high temperature sintering of metallic Ni, which reduces the dispersion and increases the crystal size. The reduction rate of NiO species is accelerated when the reduction temperature is too high, so that the formed metallic Ni particles with high surface energy can overcome the limitation of the support structure and migrate to the surface of the support²⁴. At this time, the metallic Ni exists on the support surface with supersaturated state, unfortunately, the crystal size increases gradually³². Therefore, too high reduction temperature will lead to the aggregation of metallic Ni, which may cause excessive crystallization of metallic Ni active components and even decrease the number of exposed active sites to affect the catalytic performance. At the high reduction temperature, the metallic Ni component may even produce a crystal surface that is not conducive to the HDO reaction. The XRD results are also confirmed that the NiO species can be effectively reduced by H₂ at 450°C for 2.0 h to form metallic Ni. This result is consistent with the previous H₂-TPR results and previous reports^{24,31}. However, there may still be some amorphous NiO or/and NiSiO₃ species which formed at high-temperature calcination. What's more, it is also possible that the amount of NiO or/and NiSiO₃ is lower than the detection limit of XRD. This is probably the reason why NiO or/and NiSiO₃ has not been observed in RT450, RT500, and RT550 catalysts in XRD spectra.

Quasi *in-situ* XPS studies

Quasi *in-situ* XPS technology is mainly used to analyze surface elements and the state of the surface elements of the studied RTx catalysts. The XPS spectra of Ni 2p for RTx catalysts are shown in Fig. 3. The peaks of Ni 2p at 856.5 and 852.7 eV are attributed to Ni²⁺ and Ni⁰ species, respectively^{32,33}. From the results of *in-situ* XPS, it is

found that the RTx catalysts have rich metallic Ni species, which indicates that Ni^{2+} in the catalyst precursors can be effectively reduced to metallic Ni active species. The results are similar to that of the XRD studies. Ni^{2+} species may originate from the amorphous NiO species in the pore structure or the NiSiO_3 species formed at high-temperatures calcination or/and reduction. However, the peak area and intensity corresponding to Ni^0 are different in the RTx catalysts, which can be attributed that the interactions between the active component and the KIT-6 support have significant difference at the function of the different reduction temperature.

H₂-TPD studies

The H₂-TPD spectra of the studied RT400, RT450, RT500, and RT550 catalysts, which were reduced at different temperatures, are shown in Fig. 4. It is known from Fig. 4 that the prepared Ni based catalysts have good hydrogen desorption capacities and mainly form two hydrogen desorption regions, which are recorded as α and β , respectively. There are significant differences in the peak area and strength on the H₂-TPD patterns of the studied Ni/KIT-6 catalysts prepared at different reduction temperatures. The area of α peak increases with the increase of the reduction temperature and then decreases, and RT450 catalyst has the largest area of α peak among that of RTx catalysts. Conversely, the area and desorption temperature of β peak increase with the increase of the reduction temperature. The RT400 catalyst has a significant γ peak, mainly for the desorption of the bulk hydrogen species which can store and supply the reactive hydrogen species for the reaction.

H₂-TPD can be used to effectively study the adsorption of H₂ molecules by corresponding catalyst and the ability to provide reactive hydrogen species for the HDO reaction³⁴. Hydrogen species exist on the surface and in the bulk of the prepared Ni-

based catalyst after reduction, and the physically adsorbed hydrogen species on the catalyst surface have been removed by Ar purge. In contrast, the chemisorbed hydrogen species are difficult to be removed at room temperature by Ar purge because of the formation of chemical bond between chemisorbed hydrogen species and metallic Ni active center. Therefore, the α and β hydrogen desorption regions formed by the catalysts can be attributed to the desorption of surface chemisorbed hydrogen species and metal hydride^{24,32}. As well known, the chemisorbed hydrogen species can also be effectively desorbed to form the reactive hydrogen species which required for the reaction by increasing the system temperature. Moreover, the bond energy of the chemisorbed hydrogen species is relatively weak, so it can be desorbed at low temperature (<400°C). Unfortunately, compared with the chemisorbed hydrogen species, metal hydrides need to be decomposed at a higher temperature and release the hydrogen species. KIT-6 support has developed mesoporous structure, so Ni active components can penetrate into the inner surface, which helps to form active centers with different strength. H₂ molecules can also be adsorbed on the inner surface of the studied Ni/KIT-6 catalyst which is concluded as weakly and strongly adsorbed hydrogen. According to the XRD and quasi *in-situ* XPS results, a small amount of non reductive NiO species exist in the RT400 catalyst, which is not conducive to the formation of the active center in the catalyst. As a result, the adsorption capacity of H₂ decreases on the RT400 catalyst, resulting in showing a poor low temperature desorption ability of H₂. After elevating the reduction temperature, α region of the RT450 catalyst has the maximum peak area among that of the studied RTx catalysts. These findings suggest that the RT450 catalyst has the best hydrogen adsorption storage capacity, which can provide more reactive hydrogen species for the HDO reaction. With continuing to increase the reduction temperature of the prepared catalyst, the area of the α hydrogen desorption region

gradually decreases, which is attributed to the gradual weakening of the hydrogen adsorption and storage capacity of the corresponding catalysts. The XRD results also confirm that the crystal size of Ni increases with the increase of the reduction temperature. However, the large crystal size leads to reducing the exposed active crystal surface. Moreover, the large crystal size is not conducive to the formation or fracture of the “Ni-H” species, thus weakening the adsorption and activation ability of the catalyst for the H₂ molecules. The area of the β region increases with the increase of the reduction temperature, the desorption peak temperature increases gradually. This finding may suggest that the formed hydrogen species in the high temperature region are mainly due to the decomposition of the metal hydride, the stable metal hydride is more easily to be formed at higher reduction temperature.

BET characteristics

The porosities of the prepared RT400, RT450, RT500, and RT550 catalysts and KIT-6 support were studied by BET, as shown in Fig. 5. The pore size distributions of the corresponding catalysts and KIT-6 support, which calculated from the adsorption isotherm, were showed in the inset Fig. 5. Because all prepared RTx catalysts have a type IV isotherms with clear H1-type hysteresis loop, which indicates the corresponding catalysts have mesoporous structure. The specific surface area, pore volume and pore diameter of the prepared catalysts are showed in Table 1. The prepared catalysts have inherited the developed pore structure of the KIT-6 support. Unfortunately, compared with the KIT-6 support, the specific surface area, pore volume and pore diameter of the corresponding catalysts obviously decreases. These findings can be attributed that the loading of metallic Ni species enter into the pore structure of KIT-6, resulting in the blockage of the pore structure. At the same time, the loading of Ni species also reduces the support content in the unit volume or unit mass catalyst,

which leads to decreasing the specific surface area of the corresponding catalyst. The results of Table 1 show that the RTx catalysts obtained at different reduction temperatures have maintained a specific surface area of about 340 m²/g, the pore size also around 6 nm. It can be known that the change of the reduction temperature does not have a significant effect on the structure of the prepared catalysts. Because the high temperature accelerates the agglomeration of crystal and the increase of crystal size, the specific surface area has a slightly decrease with elevating the reduction temperature. However, the average pore diameter and total pore volume have not been affected by elevating the reduction temperature, that is to say, in the studied temperature region, the average pore diameter and total pore volume have no obvious rule to be observed with increasing reduction temperature. The pore diameter range is 6.03-6.35 nm, which is close to the pore diameter of KIT-6 support as showing in the Table 1. Based on the BET results, the developed pore structure and large specific surface area of KIT-6 contribute to support metallic Ni on its inner and outer surface, which leads to the metallic Ni in a high dispersion state and may even reach monolayer dispersion. With the filling and attachment of the metallic Ni on the KIT-6 inner surface, the micropore may be blocked, while the macropore structure can be filled to form mesopore structure. The reduction temperature can only change the chemical state and crystal size of Nispecies, fortunately, it cannot change the structure of KIT-6 support. Therefore, the pore structure can be maintained the pore size distribution and pore volume because of the confinement and attachment effects of pore structure²⁴. The slightly changes of average pore diameter and total pore volume are mainly due to the growth of metal Ni crystal in the pore structure.

TEM characteristics

The prepared Ni/KIT-6 catalysts were studied by TEM, as shown in Fig. 6. The

prepared catalysts have obvious mesoporous structure, which is similar to that of the BET results. The metal Ni mainly presents two states. Some of the metal Ni successfully enters the pore of the support KIT-6, and some of the metal Ni mainly disperses on the KIT-6 surface. As the reduction temperature increases, the Ni particles size gradually increases, which is similar to that of XRD study. This phenomenon is mainly due to the high temperature accelerated the accumulation and migration of metal Ni particles, leading the metal Ni particles gradually increased at high temperature. The particle size of the metal Ni is shown in Table 1.

Catalytic activity test

The prepared RT400, RT450, RT500, and RT550 catalysts exhibit good catalytic HDO performance, and the ethyl acetate (EA) catalytic HDO activity and products selectivity, as shown in Fig. 7a to d. The catalytic HDO performances of the studied catalysts are obviously influenced by the reduction temperature, which are mainly reflected in the complete conversion temperature (T_{100}) of reactant and selectivity of the product (S). The reduction temperature has a significant effect on the catalytic performance. The T_{100} is 300°C on the RT450 catalyst, the T_{100} of RT400 and RT500 catalysts rise to 320°C, while the T_{100} of RT550 catalyst is further increased to 340°C. When the reaction temperature is 220°C, the RT450 catalyst has the highest S_{ethane} , which is 86.9%, among the RTx catalysts at this point, a small amount of ethanol is detected, S_{ethanol} is 6.7%. However, the intermediate product ethanol can be completely transformed at 240 °C. S_{ethane} can reach 96.8% but S_{methane} is only 3.2% at 300°C over the RT450 catalyst which shows the best catalytic performance. For RT400 catalyst, at the initial reaction temperature, S_{ethanol} reaches 37 %, and the complete conversion temperature of the ethanol is higher by 40°C than that of the RT450 catalyst. Finally, S_{ethane} is 97.3%, while S_{methane} is just only 2.7% at 320°C. For RT500 catalyst, S_{ethanol} is

more than 13% at the initial temperature of 220°C, and the complete conversion temperature of the ethanol is the same as that of the RT400 catalyst. At 320°C, S_{ethane} and S_{methane} are 97.1 and 2.9 %, respectively. However, the activity of RT550 catalyst is poorest. When ethyl acetate completely transforms, the reaction system also has a few ethanol and methane, which are up to 1.5 and 1.3%, respectively. At the beginning of the reaction, in the RT550 catalyst, S_{ethanol} is 30.5 percent points higher than that of RT450 catalyst, conversely, S_{ethane} is 24.1 percent points lower than that of RT450 catalyst at 220°C.

In chemical reaction system, the molecules of the reactant can be effectively activated to promote the chemical reaction³⁵. Following the general catalytic reaction law, increasing the reaction temperature helps to elevate the energy of the reaction system to accelerate the chemical reaction³⁶. Therefore, H_2 molecules are difficult to be effectively activated at low reaction temperature, which is not conducive to the formation of reactive H species. When the reaction system energy is low, the activation ability of the corresponding catalyst for the reactants and intermediates is limited. At this time, the intermediate product ethanol is difficult to achieve further HDO, so the reaction maintains high S_{ethanol} at relative low reaction temperature. The energy of the reaction system increases with enhancing reaction temperature, which accelerates the shift rate of the reactant molecules and the effective collision frequency between activated reactant molecules. Therefore, the HDO reaction of ethyl acetate and intermediate product ethanol can be promoted, and the conversion of ethyl acetate and S_{ethane} can also be significantly improved. Under the studied conditions, ethyl acetate may hydrolyze to produce two intermediate products: acetic acid and ethanol, which can be further deoxygenated to produce ethane³⁶. Acetic acid can also react with metallic Ni to produce nickel acetate, and nickel acetate can be further hydrogenated to

produce ethane and methane, as shown in Fig. S1. At the same time, the ethane molecules can be cracked to methane at a high reaction temperature²⁵. In the ester HDO reaction, decarboxylation or decarboxylation can also happen to generate CO₂/CO. The generated CO₂/CO can react with H₂ over the metallic Ni catalyst to produce methane, which is also called methanation reaction³⁷. Therefore, the corresponding catalysts show high S_{methane} at studied reaction temperatures.

Based on the results of XRD, NiO species in RT400 catalyst cannot be completely reduced to form metallic Ni species, the result is similar to that of the quasi *in-situ* XPS studies. The content of active centers in the prepared Ni/KIT-6 catalyst is relatively low, which may weaken the ability of the corresponding catalyst to activate H₂ molecules, H₂-TPD can also well confirm the results. In addition, water formed during the HDO reaction could be competing for the active sites together with ethyl acetate as the conversion increases. Also, these effects could be enhanced if the Ni particles are not completely reduced during reaction as water can bind strongly on oxidized metal surfaces. Then, the performance of the RT400 catalyst is weakened. RT450 catalyst, which was obtained by H₂ reduction at 450 °C, shows good HDO performances, and its catalytic performance is obviously higher than that of RT400 catalyst. Compared with RT400, this interesting result can be attributed to the effective reduction of NiO in the precursor of RT450 catalyst. At the same time, quasi *in-situ* XPS confirmed the formation of active metallic Ni in the RT450 catalyst. The crystallinity of the metallic Ni active component is relatively low and the crystal size is relatively small in RT450 catalyst, which is more conducive to the formation of the catalytic active center. Meanwhile, the smaller crystal size of metallic Ni can also promote the exposure of more active planes to a certain extent, which are conducive to the activation of H₂ molecules, and also promote the HDO of reactants and intermediates. Therefore, the

RT450 catalyst shows wonderful reactant conversion and S_{ethane} . The catalytic activities of RT500 and RT550 catalysts are significantly poorer than that of RT450 catalyst, and the conversions of ethyl acetate and S_{ethane} continue to decline at low temperature (220-260°C) with increasing the reduction temperature. This can be attributed that the high reduction temperature may result in a change in the chemical composition of the catalyst. The samples may even generate new inert crystal planes under high temperature, resulting in a decrease in the ratio of the active crystal planes, which weakens the ability of the corresponding catalyst to activate the reactants. The crystallinities and crystal sizes of metallic Ni in RT500 and RT550 catalysts obviously increase, and the crystal sizes of two catalysts reach 9.1 and 10 nm, respectively. The high crystallinity and large crystal size limit the formation and exposure of the active crystal plane, at the first, this weakens the adsorption and activation ability of the active crystal to H_2 molecules, in addition, this hinders the formation or fracture of the “Ni-H” bond, what’s more, this weakens the activation capacity of the corresponding catalyst for the “C=O” bond and the “C-O” bond. Therefore, the HDO performance is influenced. According to the results of BET and TEM, the prepared catalysts have large specific surface areas and developed mesoporous structures, which effectively promote the migration and diffusion of gaseous reactant molecules in the pore structure. Therefore, the studied catalysts have perfect catalytic HDO performances.

Activation energy studies

Under the condition of atmospheric pressure and $12,000 \text{ mL/h} \cdot \text{g}_{\text{cat}}$ space velocity, the influence of internal and external diffusion is eliminated, and using the fixed bed reactor to study the mechanism of the prepared RTx catalysts for HDO performance by activation energy experiments. According to the Arrhenius equation: $k = k_0 \cdot \exp(-E_a/RT)$, this equation can be obtained: $\ln k = \ln k_0 - E_a/RT$ (where k_0 is the pre-

exponential factor, E_a is the activation energy, R is the gas constant, and T is the thermodynamic temperature). Map the $-\ln k$ to T^{-1} over RTx catalysts with different reduction temperature, as shown in Fig. 8. From Fig. 8, the activation energies of ethyl acetate HDO on RT400, RT450, RT500 and RT550 catalysts are 81.0, 67.7, 79.5, and 90.9 kJ/mol, respectively, according to the slope of the obtained straight line, as shown in Table 2.

There are significant differences in the activation energies of the HDO reaction on the studied RTx catalysts, indicating that the changes of the reduction temperatures can further alter the energy barriers over the corresponding catalysts for HDO reaction. In the gas–solid heterogeneous catalytic hydrogenation reaction, the purposes of the adsorption and activation of the reactant molecules on the catalyst surface are to reduce the reaction activation energy. Therefore, the activation energy represents the energy required by the reactant molecules from the normal state to the active state in the chemical reaction under the function of the corresponding catalyst. In other words, under the function of the catalyst, the activation energy, which reflects the difficulty of the catalytic reaction, is the minimum energy needed for the chemical reaction. Meanwhile, chemical reaction rate is closely related to the activation energy. The lower the activation energy is, the faster the reaction rate is, thus reducing activation energy will effectively promote the reaction rate. Moreover, the reaction system with lower activation energy can ensure that more reactant molecules are activated to form activated molecules, which increases the amount of activated molecules and further to increase the effective collision probability between the activated molecules, thus accelerating the corresponding chemical reaction rate. According to the XRD and *quasi in-situ* XPS results, the RT400 catalyst obtained by lower temperature reduction has lesser active component, which cannot effectively activate the reactant molecules,

thereby elevating the activation energy and the difficulty of corresponding reaction. With the increase of the reduction temperature, even though the content of the active metallic Ni increases, the crystal size of the metallic Ni gradually increases. The large crystal size reduces the number of the exposed active planes on the metallic Ni, then, this action weakens the interaction between catalytic active centers and reactant molecules, which is not conducive to further decreasing the activation energy of ethyl acetate HDO reaction. The increase of crystal size may also lead to the formation of inert crystal plane, which reduces the number of active centers of the corresponding catalyst and affects the activation ability of the studied catalyst to the reactant molecules. Therefore, these adverse factors result in the amount of activated molecules in the reaction system lower, and the activation energy of the corresponding reaction is higher. The activation energy of ethyl acetate HDO reaction under the function of RT450 catalyst is lowest among that of the RTx catalysts, and the energy required for effective collision is lowest. This find shows that the effective activation among the reactant molecules can be realized in the relative lower energy system, thus forming more activated molecules, which is beneficial to the catalytic hydrogenation reaction. At the same time, the lower reaction activation energy leads that the formation of active molecules more likely to have effective collisions in the lower energy system, which is beneficial to improve the HDO reaction performance. Hence, decreasing the reaction activation energy can provide an easy way for the ethyl acetate HDO reaction, thus accelerating the reaction to thermodynamic equilibrium. H₂-TPD results also strongly confirm that under the same conditions, RT450 catalyst reaction system has the best adsorption and activation ability for reactant H₂ molecules, thus forming large amount of reactivated hydrogen species. Effective collisions among activated molecules will help reduce reaction activation energy. This is mainly attributed to the

sufficient metallic Ni content, large specific surface area, and suitable crystal size for the RT450 catalyst. The activation energies of the RT500 and RT550 catalysts obtained by enhancing the reduction temperature significantly increase, indicating that the higher the reduction temperature is, the larger the activation energy is. Simultaneously, the BET and TEM results show that the specific surface area of the studied catalyst slightly decreased with the increase of the reduction temperature. High reduction temperature may accelerate the shrinkage or even collapse of mesoporous structure, which weakens the adsorption and activation ability of reactant molecules in the mesoporous structure of corresponding catalyst, as well as further to affect the migration and effective collision of activated molecules in mesoporous structure. The effective collision frequency between activated molecules is reduced, which leads that the difficult of ethyl acetate HDO reaction increase, as well as the increase of activation energy. H₂-TPD also confirms that a series of changes in the chemical composition of the studied catalysts have a significant effect on the adsorption and activation ability for the H₂ molecules. The results show that the chemical composition and particle structure of the studied catalyst have a conspicuous influence on the ethyl acetate HDO reaction. In our previous study, it is also found that ethyl acetate HDO reaction is a structural sensitive reaction³⁰. To sum up, the amount of active metallic Ni and its crystal size, as well as other chemical compositions may be important reasons for the change of activation energy of RTx series reaction system. The activation energy of the Ni/KIT-6 catalysts prepared at different reduction temperatures for ethyl acetate HDO reaction has the lowest value. The activation energies of the prepared catalysts obey the following order: RT550 > RT400 > RT500 > RT450.

Conclusions

A series of Ni/KIT-6 catalysts with a metallic Ni loading of 25wt.% were prepared at different reduction temperatures. They show good catalytic HDO performance to the model compound ethyl acetate. Ethyl acetate is completely converted, while high S_{ethane} , all greater than 95%, can be maintained. The catalytic performance of RT450 catalyst is the best among the prepared Ni/KIT-6 catalysts. The complete conversion of ethyl acetate can be achieved at 300°C, S_{ethane} is up to 96.8%, S_{methane} is only 3.2%, and the intermediate product ethanol is completely converted at 240°C. This is mainly attributed to the abundant metallic Ni content in the RT450 catalyst, the small crystal size, only 7.4nm. KIT-6 support promotes the highly dispersed Ni components and also promotes the migration and activation of reactant molecules in the pore structure. In the range of studied reduction temperature, the mesoporous structure does not change significantly, but the reduction temperature affects the HDO performances of the corresponding catalyst. The adsorption and desorption properties of the prepared catalysts for H_2 molecules are in the following order: RT450 > RT500 > RT550 > RT400, and the order of HDO activities of the prepared catalysts is consistent with that of H_2 desorption. By calculation, the activation energy of the prepared catalysts obeys the following order: RT550 > RT400 > RT500 > RT450.

Method

Catalyst preparation

The Ni/KIT-6 catalyst was prepared by impregnation method. KIT-6, which is prepared following the procedure described by our subject group^{27,28}, was used as the support for the Ni/KIT-6 catalysts. 0.62g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water with HNO_3 . 0.38g KIT-6 was added. The sample continued to dry overnight in an oven and then calcined at 550 °C for 4.0 h in air. Finally, the obtained catalyst precursor was subjected to hydrogen reduction 2.0 h to produce the Ni/KIT-6 catalyst at 400, 450,

500, and 550 °C, which were labeled as RT400, RT450, RT500, and RT550, respectively.

Catalyst characterization

XRD characterization

X-ray diffraction (XRD) patterns were recorded on a Shimadzu-6100 diffractometer with a rotating anode using Ni filtered Cu K α radiation at 40 kV of a tube voltage and 30 mA of a tube current. The data of 2θ from 20 to 80° range were collected with the step size of 0.02 at the rate of 3 °/min, according to our previous work²⁴.

Quasi *in-situ* XPS studies

The prepared RT x catalyst samples ($x=400, 450, 500, \text{ and } 550$) were *in-situ* reduced in a pretreatment chamber in high purity hydrogen at 400 °C for 60 min to obtain RT x catalysts and then obtained RT x catalysts were cooled down to room temperature. Then the RT x catalysts were directly moved to analysis chamber without being exposed to the environment to analyze the Ni 2p message. The chemical states of the RT x ($x=400, 450, 500, \text{ and } 550$) samples were determined using *in-situ* X-ray photoelectron spectra (*in-situ* XPS). The XPS signals were collected using an ESCALAB 250Xi analyzer.

BET characterization

The Brunauer–Emmett–Teller (BET) analysis of the catalysts was determined by N₂ adsorption–desorption using an ASAP 3020 (Micro USA) instrument. The catalysts were outgassed at 300 °C for 3.0 h before being subjected to N₂ adsorption, according to our previous work²⁴.

H₂-TPD studies

Temperature-programmed desorption of H₂ (H₂-TPD) was conducted as follows: 50 mg of catalyst precursor was placed in a quartz U-tube reactor. The catalyst precursors were reduced with a 5% H₂/Ar mixture (25 mL/min) at 400, 450, 500, and 550 °C for 2.0 h, respectively. Afterward, the catalyst is flushed with Ar flow (25

mL/min) to remove all physically adsorbed molecules. The studied catalysts were then heated at 10 °C/min to 700°C with pure Ar at a flow rate of 25 mL/min. The hydrogen desorption signals were monitored using a thermal conductivity detector (TCD), according to our preview work²⁴.

TEM characterization

The transmission electron microscopy (TEM) was performed using a FEI Tecnai G² F30 microscope operating at an acceleration voltage of 300 KV.

Catalytic activity measurement

Catalytic tests of all the studied catalysts were carried out in a tubular, continuous-flow, fixed-bed reactor under atmospheric pressure. The quartz tube reactor containing 50mg of the supported nickel oxide precursors were placed inside the tubular furnace. High-purity hydrogen was flowed downward through the reactor containing the catalyst bed, while an electronic mass flow controller was used to control the hydrogen gas flow rate. The precursors were reduced at 400, 450, 500, and 550 °C at hydrogen flow for 2 h, followed by cooling under a H₂ flow to the studied temperature. Catalytic activity tests were performed at temperature range of 220 to 340°C. The actual reduction and reaction temperatures were measured using a thermocouple which was directly inserted into the catalyst bed and were monitored by a temperature programmable controller at a heating rate of 10°C/min. The fed gas was obtained by bubbling hydrogen through a saturator, which contains the studied model bio-oil compound ethyl acetate in liquid phase, kept at constant temperature to achieve the fed gas mixture consisting of gaseous acetate ester (3.3%) and H₂ (96.7%), the fed gas was led over the catalyst at a flow rate of 10 mL·min⁻¹, which is equivalent to a gas mass space velocity of 12,000 mL/g·h. The gas products were monitored using an on-line gas chromatograph (SC-3000B), equipped with a FID, according to our preview work²⁴.

The conversion of reactant and the selectivity of products were calculated according to our previous study²⁴.

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Author Contributions

Xianming Zhang, Shuang Chen and Guilin Zhou conceived and designed the experiments. Xianming Zhang and Guilin Zhou supervised the study. Shuang Chen, Fengjiao Wang, Lidan Deng and Zhaojie Jiao carried out materials syntheses. Fengjiao Wang, Lidan Deng and Jianmin Ren performed all kinetic degradation tests and related measurements and interpretation of results. All authors discussed the results, co-wrote and edited the manuscript. All authors reviewed and approved the manuscript.

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Table and Figures Caption

Table 1 Physicochemical properties of RTx catalysts.

Table 2 Activation energy studies of RTx catalysts. (x=400, 450, 500, and 550)

Fig.2 XRD patterns of RTx catalysts. (x=400, 450, 500, and 550)

Fig. 3 Quasi *in-situ* XPS spectra of the RTx catalysts. (x=400, 450, 500, and 550)

Fig. 4 H₂-TPD patterns of RTx catalysts. (x=400, 450, 500, and 550)

Fig. 5 N₂ adsorption-desorption isotherms and pore diameter distributions of the prepared RTx catalysts. (x=400, 450, 500, and 550)

Fig. 6 TEM patterns of the studied catalysts: a.) 400, b.) 450, c.) 500, and d.) 550.

Fig. 7 Influence of reduction temperature on the ethyl acetate hydrodeoxygenation conversion and products selectivity over the RTx catalysts. a.) RT400, b.) RT450, c.) RT500, and d.) RT550.

Fig. 8 The relationship of lnK and T⁻¹.

Table 1 Physicochemical properties of RTx catalysts.

Catalyst	Crystal size from XRD (nm) ^a	H ₂ -TPD (α region) Quantity ($\mu\text{mol/g}$)	Surface area(m^2/g) ^b	Average pore diameter (nm) ^c	Total pore volume (cm^3/g) ^d	Particle size from TEM (nm) ^e
RT400	5.9	27.6	349.2	6.08	0.55	6.3
RT450	7.4	65.8	348.9	6.35	0.56	7.7
RT500	9.1	52.4	347.7	6.17	0.54	9.7
RT550	10	49.9	343.4	6.03	0.56	10.3
KIT-6	—	—	562.5	6.56	1.22	—

^aAverage Ni crystal diameter calculated from Ni(111) plane using Scherrer equation from XRD.

^bCalculated by the BET equation.

^cBJH adsorption average pore diameter.

^dBJH adsorption pore volume.

^eAverage Ni particle size observed from TEM images.

Table 2 Activation energy studies of RTx catalyts (x=400, 450, 500, and 550)

Catalysts	Equation	Activation energy (kJ/mol)
RT400	$Y=9.208X-12.44$	81.0
RT450	$Y=8.066X-23.17$	67.7
RT500	$Y=9.264X-16.14$	79.5
RT550	$Y=11.33X-9.65$	90.9

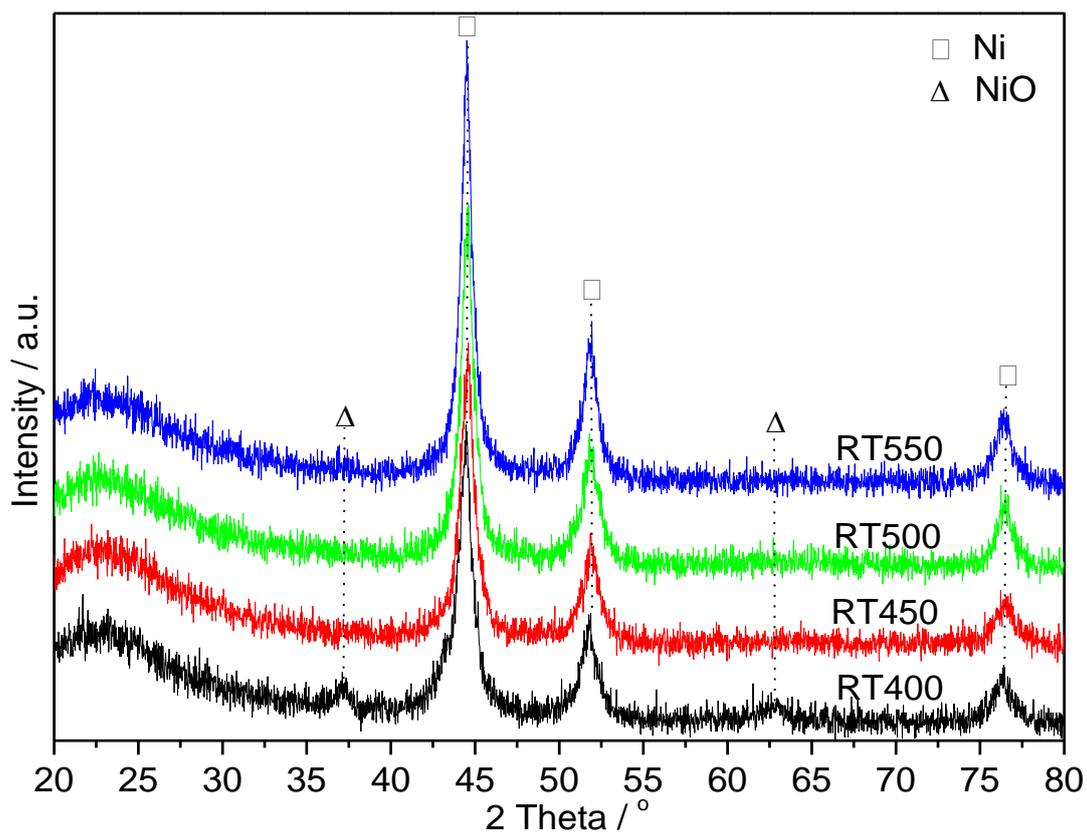


Fig.2 XRD patterns of RTx catalysts. (x=400, 450, 500, and 550)

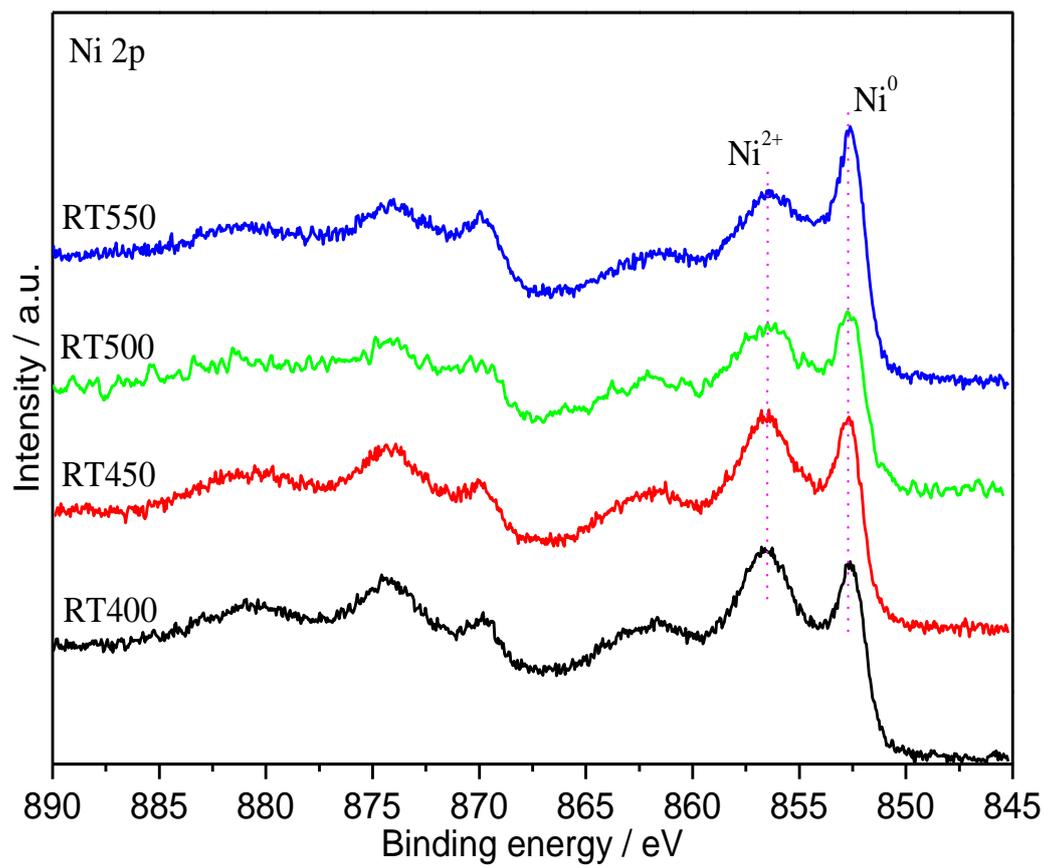


Fig. 3 Quasi *in-situ* XPS spectra of the RT_x catalysts. (x=400, 450, 500, and 550)

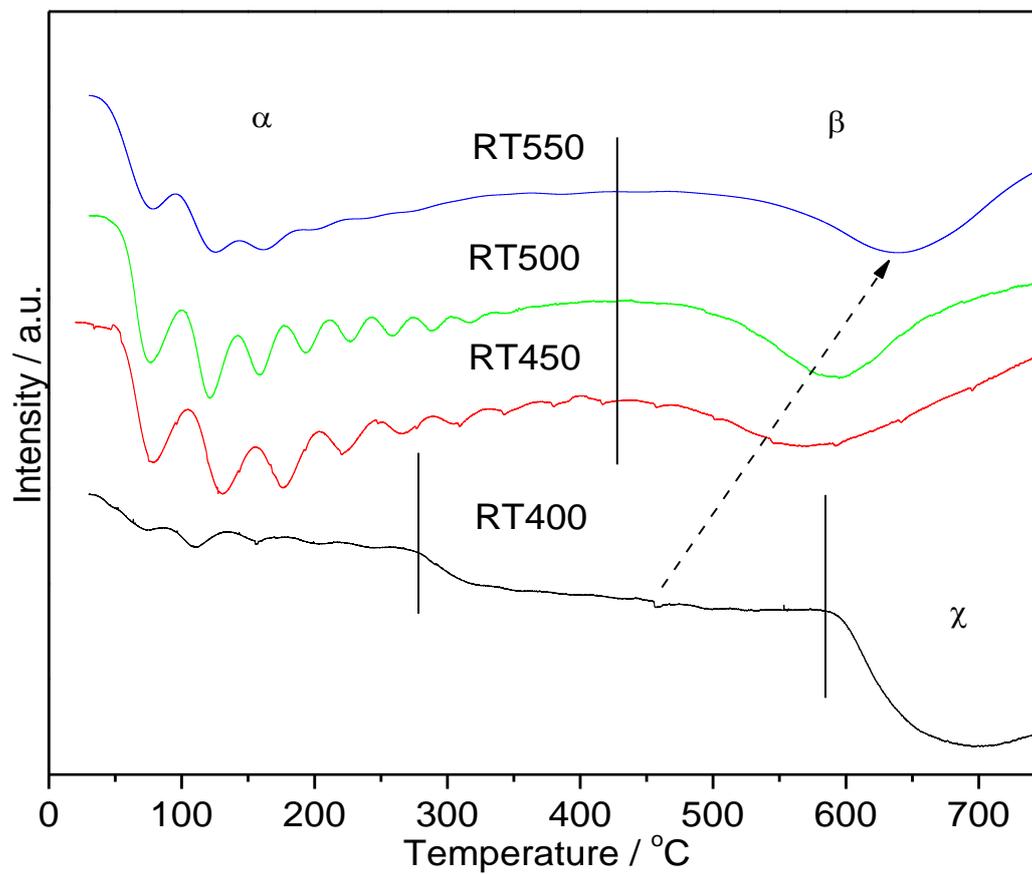


Fig. 4 H₂-TPD patterns of RT_x catalysts. (x=400, 450, 500, and 550)

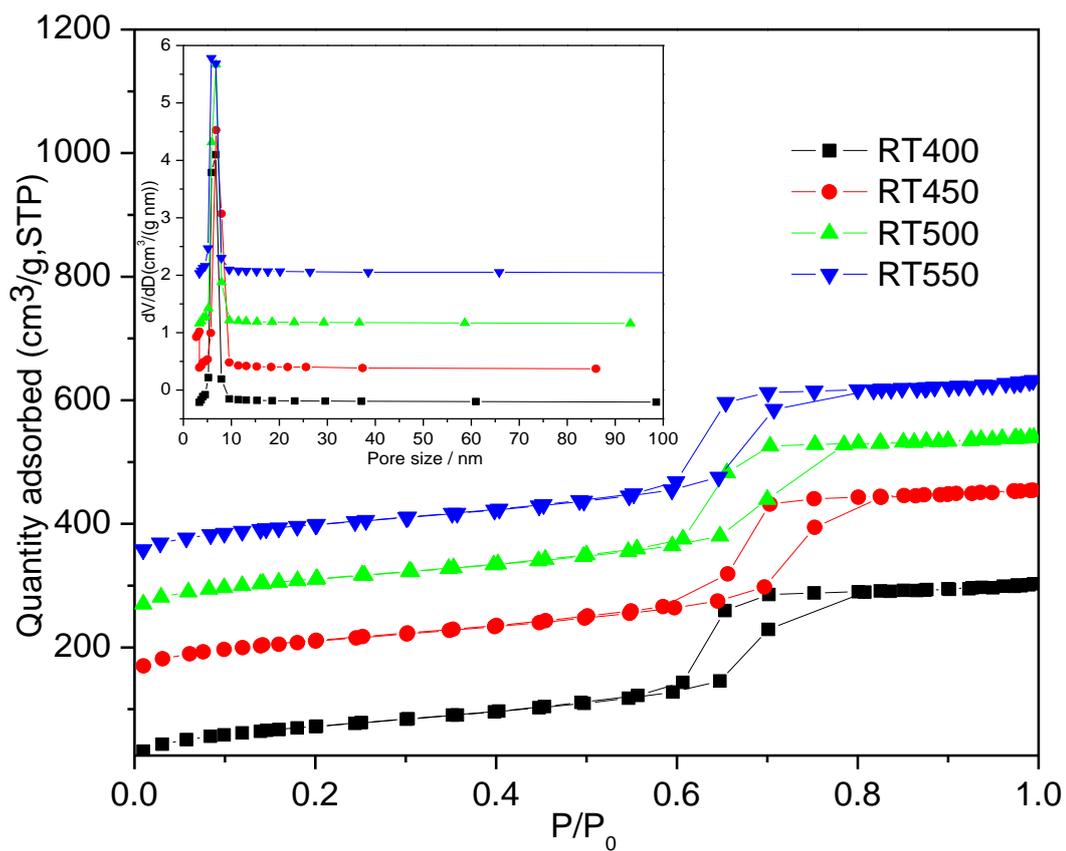


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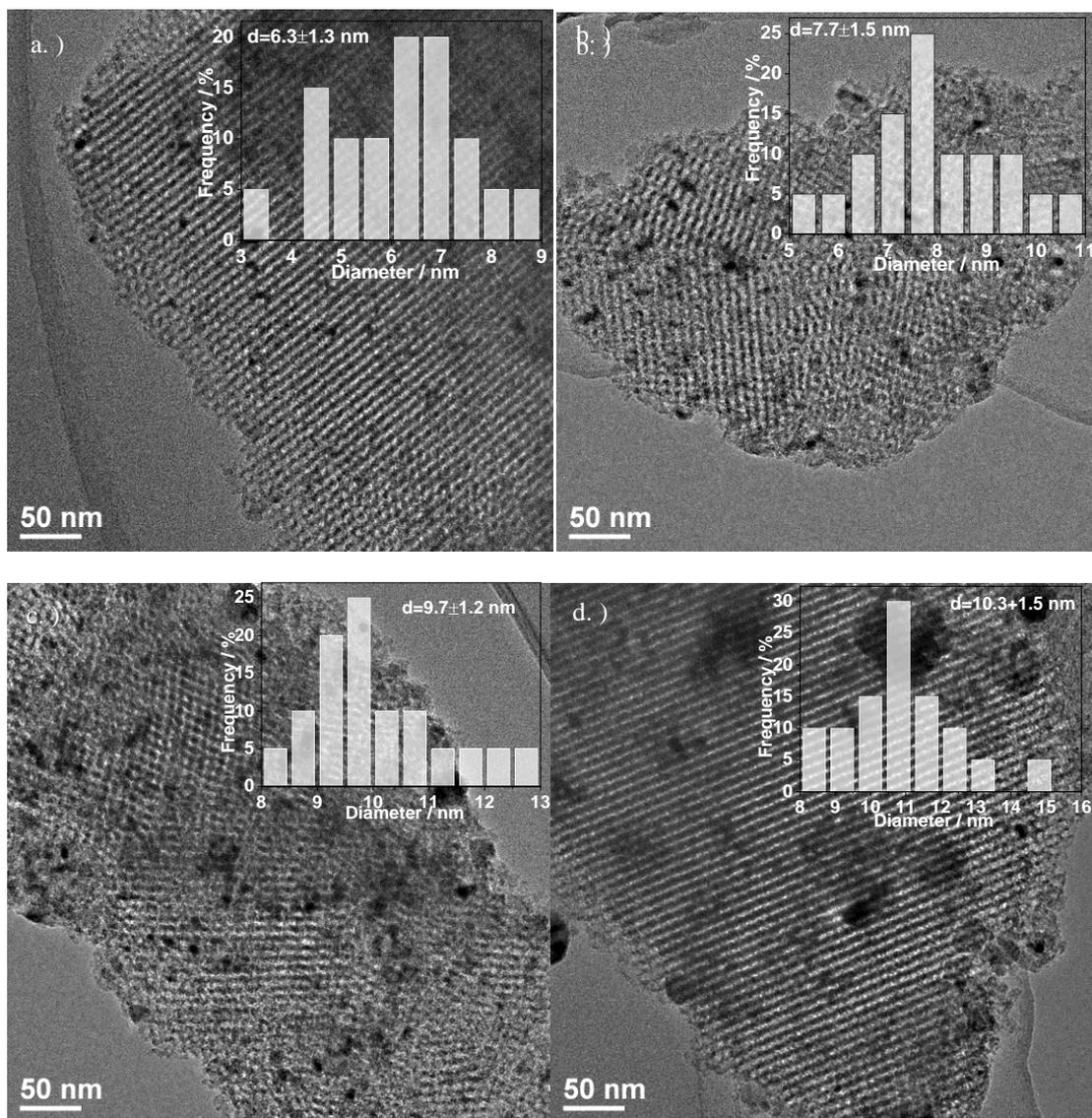
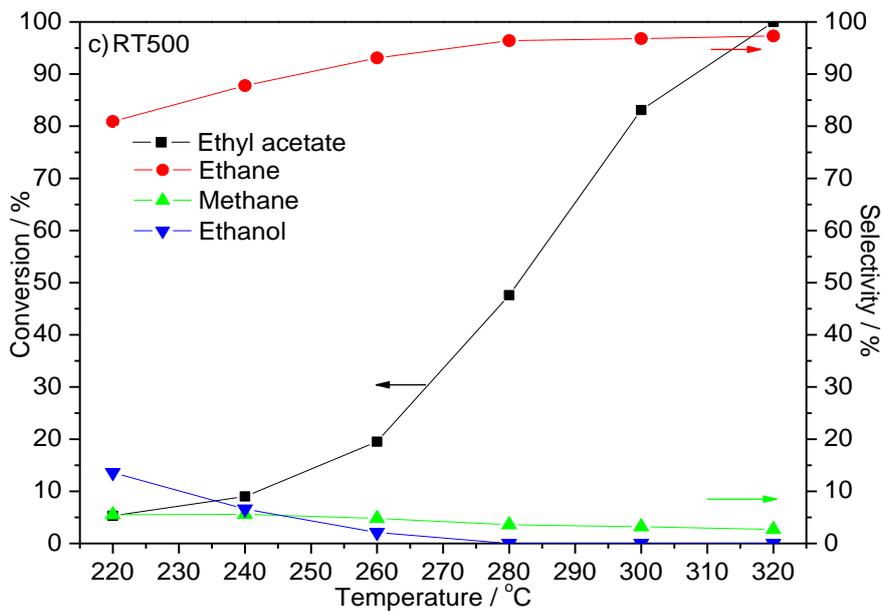
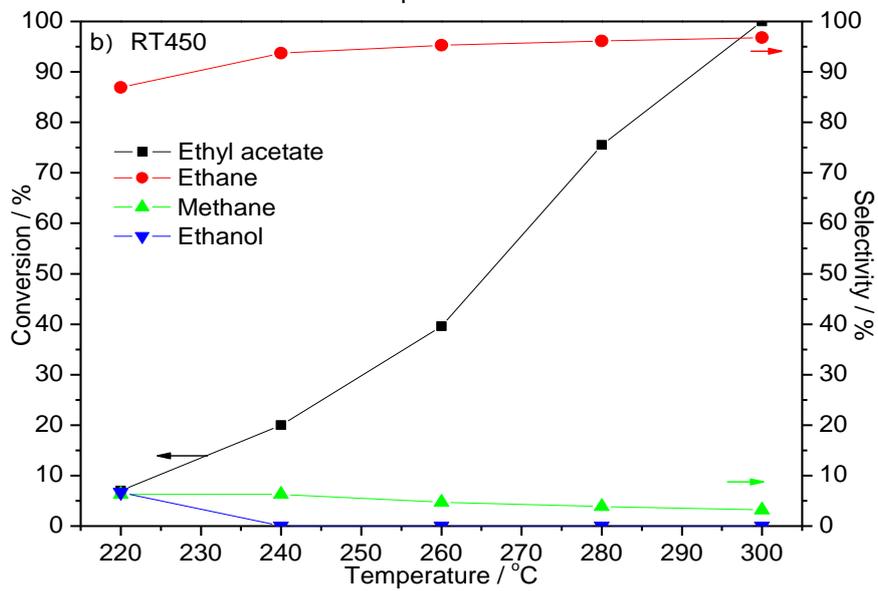
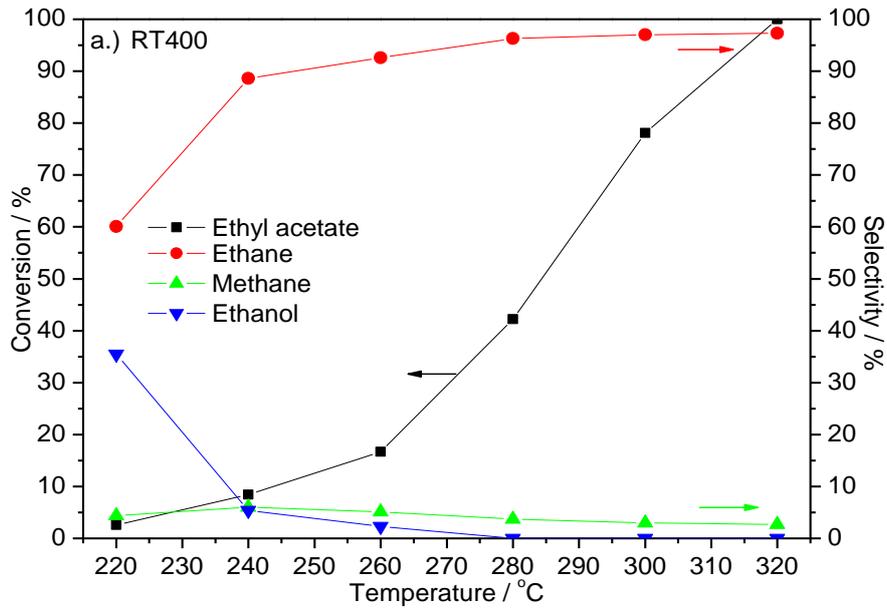


Fig. 6 TEM patterns of the studied catalysts: a.)400, b.) 450, c.)500, and d.)550



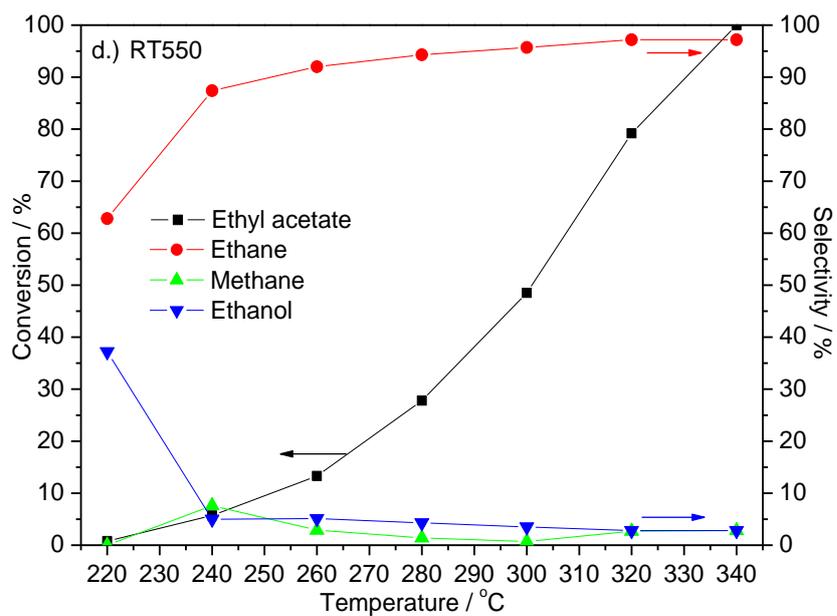


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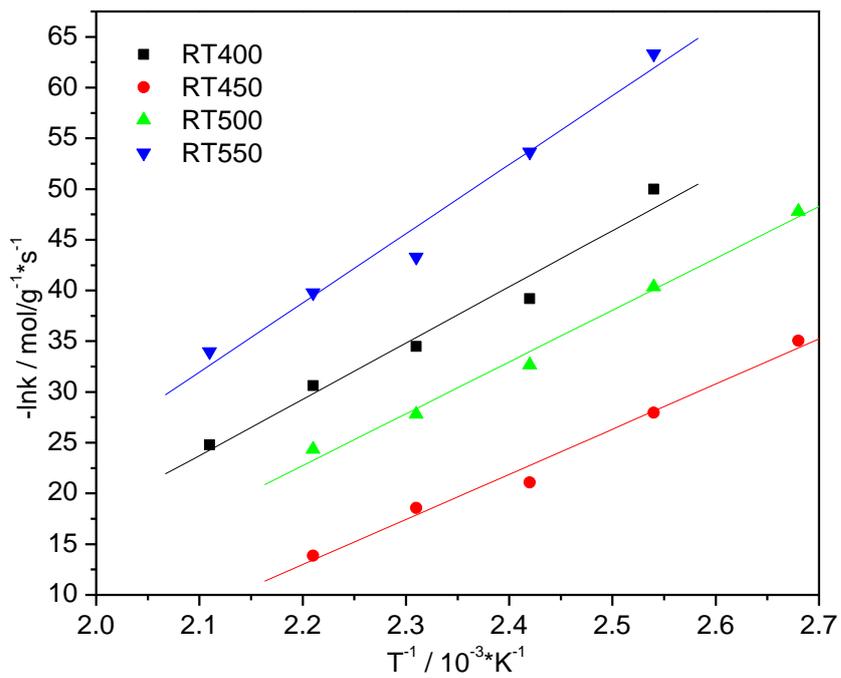


Fig. 8 The relationship of $\ln k$ and T^{-1}