

Effect of nickel loading on the performance of nano- and micro-sized ZSM-5 catalysts for methanol to hydrocarbon conversion

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Abstract: Methanol to hydrocarbon process is becoming increasingly important as methanol can be manufactured from flare gas, biomass, shale gas and coal. In this work, micro- and nano- sized ZSM-5 zeolites have been modified with low level nickel loading and tested for methanol to hydrocarbon process. It is shown that nano-sized ZSM-5 catalyst doped with nickel with or without H₂ reduction has higher yield of hydrocarbon than the micro-sized ZSM-5 catalyst. Pretreatment of the NiO/ZSM-5 catalyst with H₂ reduction does not decrease aromatics yield in the hydrocarbon products, but in contrast increases the yield of C₁-C₄ gaseous products, which may be due to the lower loading (1.0% in wt.) of nickel metal substitution. The introduction of NiO to ZSM-5 catalyst increases acid amount and also acid strength, which may be due to the nickel entering the framework, thus changing the coordination environment of Si and Al. The structure of nano-sized ZSM-5 catalyst is more affected by the loading of nickel, such as more AlO₅ units. In terms of catalytic performance, nano-sized ZSM-5 catalyst has high yield for hydrocarbon production, less gaseous yield, and less aromatics, which is probably due to the shorter distance for the diffusion and contact time of the dehydrated products over the acid sites.

Key words: methanol to hydrocarbon, nickel doping, nano-sized, ZSM-5

1. Introduction

Methanol has been a platform for reduction of fossil fuels consumption, recycling excess atmospheric CO₂, providing renewable fuels and feedstock for the chemical industry, because methanol can be produced from biomass, CO₂ hydrogenation natural gas or any gasifiable carbonaceous material, such as petroleum and coal.[1-3] The conversion of methanol to hydrocarbons (MTH) is a key technology in the methanol platform, which is generally denoted as the MTH reaction, where methanol is converted to gasoline over ZSM-5 derived catalysts, firstly discovered by Mobile [4, 5]

MTH process and products disdepends on acid strength, acid site density, catalyst topology, temperature, pressure, space velocity and other process conditions [[6-8]. Due to the formation of bigger molecules from methanol, which is relatively small, faster mass transfer is highly needed to decrease the diffusion. It has been reported that diffusion rate has a second-order inverse dependence on the size of catalyst crystal [7, 9, 10], smaller sizes of catalyst crystallites would be of help to promote the mass transfer. So far, there have been lots of studies on the synthesizing nano-sized zeolite for methanol to hydrocarbon process, and it is shown that the smaller crystallite does increase the yield of light olefins, adding high loading of transition metal can help the hydrogenation reaction and thus decreasing the aromatics content in the liquid yield. [10-14] However, few researches have been carried out in the effect of low loading nickel on the micro-sized and nano-sized ZSM-5 catalyst and their performance for methanol to hydrocarbon.

Modification of ZSM-5 catalyst with metal oxide has been widely studied, but these metal loading modifications focus on the micro-sized ZSM-5 catalysts, [15-19] and the metal loadings are often very high, which has much more complex distribution in the catalyst [6, 19]. Very few studies have been carried out on the effect of low metal loading on nano-sized ZSM-5 catalyst.

The aim of this work is to study the effect of the low nickel loading on the structure and acidity of the micro- and nano-sized ZSM-5, and their properties and

performance for methanol to hydrocarbon have been tested. It is found that loading 1wt% of NiO onto ZSM-5 catalyst significant changes the acidity of the catalyst, a high temperature hydrogen treatment of the supported nickel oxide catalyst leads to high acidity and also more aromatics. However, overall, the nano-ZSM-5 supported Ni catalyst gives more gasoline yield and less aromatics, which can be explained by the shorter diffusion distance, thus avoiding deep dehydration process.

2. Experimental

Preparation of Catalyst

In this research, the micro-sized and nano-sized ZSM-5 catalysts were supplied by catalyst plant of Nankai University. The 1.0wt% of NiO containing ZSM-5 catalyst samples were prepared using impregnation method. In the nickel loading, 1.5ml nickel nitrate solution (0.188M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Sigma Aldrich, A.R.) is impregnated with 2.0 g of the nano or micro-sized ZSM-5 powder (60-100 mesh), placed at ambient condition for 4 hours while stirring. They were then dried at 120 °C for 2 hours and calcined at 400 °C for 4 hours, and then cooled down to get the supported oxide. Then half of the samples were taken out and loaded into a quartz reactor and reduced in flowing H_2 (GHSV of H_2 at 6000h^{-1}) from room temperature to 500 °C and held at 500 °C for 4 hours, then cooled down to room temperature in flowing H_2 . The treatment with pure H_2 at high temperature is to reduce the 1.0wt% of NiO into metal Ni. The H_2 -reduced sample is marked as Ni/nano-sized ZSM-5 and Ni/micro-sized ZSM-5.

Catalyst testing

Catalyst performance tests were carried out in a fixed bed micro-reactor system (Beijing KLYT Co. Ltd, China). Methanol was injected using a HPLC pump and vaporized at 150 °C before entering the reactor. Flowing nitrogen (20ml/min) was used as carrier gas and internal standard for gas product quantification. The reaction took place in a tubular stainless steel reactor at 400 °C under the pressure of 1 atm; typically 1.0g of catalyst loaded in the reactor with a setting methanol Weight Hourly Space Velocity (WHSV) of 2h^{-1} . The gas products were analyzed using a GC system

(Shimadzu GC-2010SE) equipped with a thermal conductivity detector (TCD) for non-hydrocarbons and flame ionized detector (FID) for hydrocarbons every 30 minutes, after methanol injection started. The gas product separation in GC system employed a RESTEK MXT-1HT column.

The calculation of the conversion and product selectivity are carried out according to the following equations:

$$\text{Methanol conversion} = \frac{\text{Methanol in} - \text{Methanol out}}{\text{Methanol in}}$$

$$\text{Gas product yield} = \frac{\text{Gas output in TOS} \times \text{number of C atom in each molecule}}{\text{Methanol injection in TOS}}$$

$$\text{Liquid product selectivity} = \frac{\text{The amount of specific product} \times \text{number of C atom in each molecule}}{\text{Total methanol converted}}$$

The liquid products were collected after the reaction, separated into water phase (water was generated in the reaction) and oil phase (hydrocarbon products) via still standing, both of which were then analyzed with an offline GC-MS system using FID detector (Shimadzu GCMS-QP2010 Ultra High-end). Separation of different liquid components proceeded in a SHIM-5MS column..

The methanol conversion was defined by amount of methanol consumed compared to the total methanol fed. The amount of methanol remaining in the liquid product (both oil phase and water phase) is analyzed with offline GC-MS. The gas product time-on-stream (TOS) yield (mol %) was calculated by comparing the instantaneous gas product methanol consumption (mol/min) with methanol injection rate (mol/min). The corresponding benzene, toluene, and xylenes (BTX) selectivity (taken after 5 hours) was calculated from the methanol consumption of selected products (mol.) and total methanol converted (mol.).

Characterization methods

The crystalline phase changes of the supported metal and zeolites were analysed with a PANalytical X'Pert PRO Diffractometer using Cu K α 1 radiation, the scan diffraction angle operated from 5° to 90° (2 θ angular range) and a scan rate of 0.8°/min in 2 θ X-Ray Powder diffraction (XRD),

The acidity of the catalyst is measured using a NH_3 -TPD method (TP-5078 Auto TPD system, Xianquan Co. Ltd, China). The catalyst samples were loaded into the reactor pre-treated in N_2 at 300 °C for 2 h to remove the adsorbed moisture. NH_3 was introduced at $\text{NH}_3:\text{N}_2=1:3$ on to the pre-treated catalysts at 120 °C for 30 min, and the system was then cooled down to room temperature for 1 h in pure N_2 . The samples were then heated at 8 °C /min from room temperature to 600 °C, the desorbed NH_3 was recorded with a Thermal Conductivity Detector (TCD).

The BET analysis proceeded with a Micromeritics Gemini VI BET surface area analyzer. The total surface area was calculated from adsorption data at $p/p_0=0.05$ and the total volume of all the tested samples was measured at $p/p_0=0.995$.

The SEM images were obtained with a JEOL scanning microscope 840F (JSM840F). The sample powder was deposited onto a dust-free scanning platform and trapped on the surface before analysis. The resolution was carefully adjusted to make sure the sharp and clear edge of the zeolite crystalline grains could be observed with as many as optical details of the external surface. TEM measurements were undertaken using a JEM-2100UHR microscope (200kV).

^{27}Al , ^{29}Si , ^{13}C and ^1H NMR experiments carried out with a Varian VNMRS spectrometer at ambient temperature with a resonance frequency of 104.198, 79.438 and 100.562 MHz, respectively. Cross Polarization (CP) for ^{13}C NMR and Direct Excitation (DE) for ^{27}Al and ^{29}Si were employed in the experiment. The ^{27}Al NMR measurements were performed on a 4mm probe, with an acquisition time of 20.0 ms, a recycle time of 5.0 second, and a sample spinning rate of 12.118 KHz. The ^{29}Si

NMR spectra were recorded with a 6mm probe at sample spinning rate of 6 KHz, in an acquisition time of 20.0 ms, with recycle delay of 5.0 second. The ^{13}C CP NMR used a 6 mm probe, with data acquisition in 30.0ms, recycle delay of 2.0 second and sample spinning rate at 6 KHz.

3. Results and discussion

3.1 Structural properties of the ZSM-5 samples

The XRD measurement results of the synthesized micro- and nano-sized ZSM-5 zeolites with the same Si/Al ratio (38.1) are shown in Fig. 1. The two samples exhibited typical ZSM-5 zeolite structure without the appearance of any peaks rather than the ZSM-5, although the diffraction intensity of nano-sized ZSM-5 is much weaker. This suggests that the crystalline phases of the synthesized samples have quite high purity of the ZSM-5 zeolite, the lower diffraction peaks of the nano-sized ZSM-5 zeolite sample suggests that the crystallite size of the sample is small, which has shorter ordered length. The strong diffraction peaks in the micron-HZSM-5 suggest it has the highest crystallinity, assuming it has the relative 100 % crystallinity. The relative crystallinity of nano-sized ZSM-5 is 40 % compared to the diffraction peak intensity of the micro-sized ZSM-5.

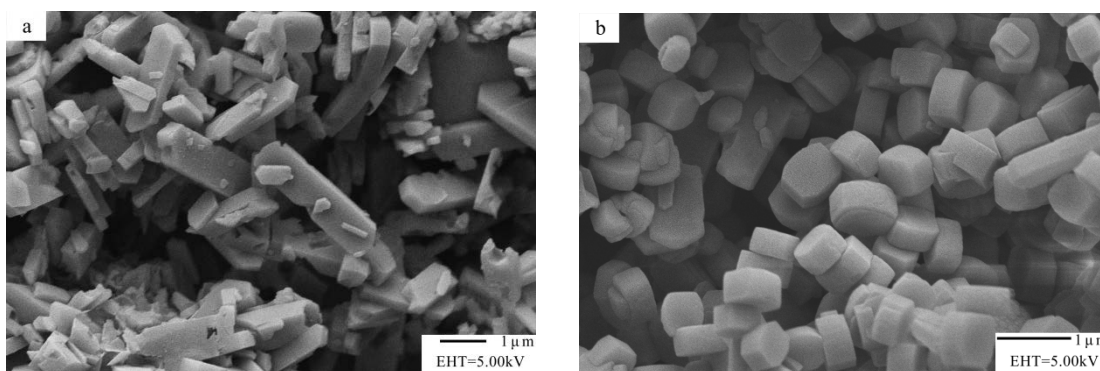
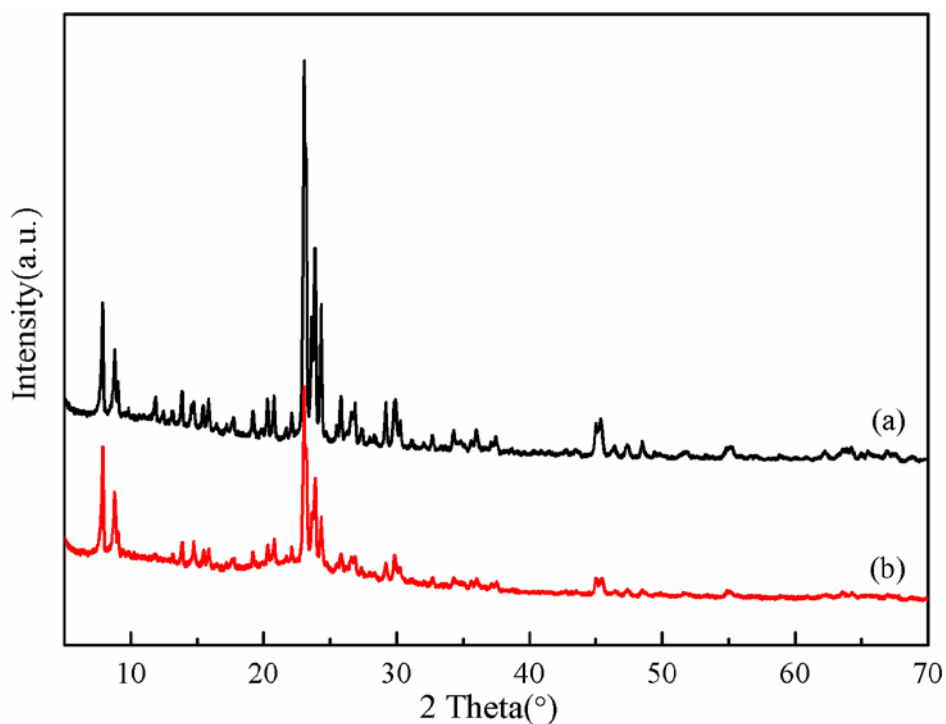


Fig.1 XRD patterns and SEM images of ZSM-5, (a) micro-sized ZSM-5, (b) nano-sized ZSM-5

The scanning electron microscopes (SEM) images of the synthesized micro-sized and nano-sized ZSM-5 catalysts are shown in Fig 1 too. As expected, the crystallite size of the micro ZSM-5 sample is about 2 μm long and 0.4 μm wide, composing of rod like particles. The morphologies of the nano-ZSM-5 are pellet like, with diameter of 0.3 μm , and 0.2 μm thickness. There are also a few rod-like crystallites, however with very low content. The SEM results are in agreement with the XRD

measurement, and show that the synthesis method is useful to control the sizes of the ZSM-5 catalyst morphologies.

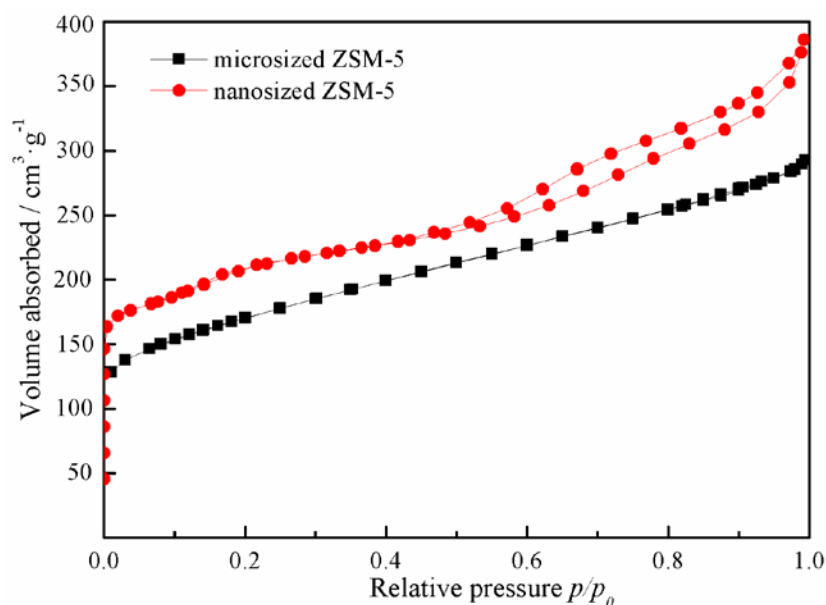


Fig.2 N₂ adsorption-desorption isotherms of micro-sized and nano-sized ZSM-5

The BET N₂ adsorption curves of the nano- and micro-sized ZSM-5 zeolites are shown in Fig 2. It is seen that the micro-sized ZSM-5 zeolite shows a typical type II curves, where the adsorption-desorption are in good overlap, which suggest that the ZSM-5 powders with diameters exceeding micro-pores in it. This is indeed in agreement with the SEM and XRD results. For the nano-sized ZSM-5 catalyst, it shows a typical V adsorption-desorption curves, suggesting it has porous adsorbtion with pores in the range of 1.5–100 nm.

¹H MAS NMR analysis

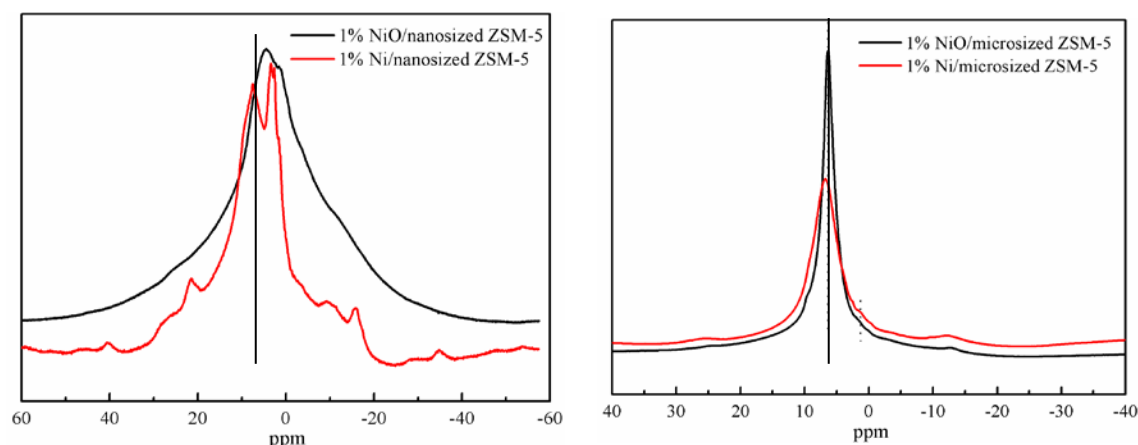


Fig.3 ^1H MAS NMR spectra of 1% NiO and Ni supported over (a) nano-sized ZSM-5 and (b) micro-sized ZSM-5

The ^1H NMR spectra of the nickel containing nano and micro-sized zeolites are shown in Figs 3-a and b. For the nano-sized ZSM-5 supported NiO, a broad NMR spectrum is seen with the main band at 4.5 ppm, which is a typical for bridging OH groups ($\text{Si}(\text{OH})\text{Al}$) in the a-cages of ZSM-5, with a second peak at about zeolite A weak signals at 0.5 ppm mainly caused by silanol groups located at framework defects [20,21] After flowing H_2 treatment, the ^1H NMR peaks changes significantly, and the peak is becoming narrow with clear two peaks at 1.3 ppm, which is ascribed to the surface Al-OH or Ni-OH group, or the terminal silanol group. A low field shifted peak is seen at 7.8 ppm, which is attentively assigned to the disturbed bridging OH group in ZSM-5. The narrowing width of the peak may be due to the heat treatment which can remove the absorbed moisture of water.

In the micro-sized ZSM-5 sample ^1H NMR spectra have obvious difference with the nano-sized ZSM-5. A main sharp peak is seen at 7.2 ppm, which is assigned to the disturbed bridging OH group in $\text{Si}(\text{OAl})_2\text{OHAl}$ [20]. It shifted slightly to the low field with a broader peak, which does not have substantial changes. These results show that the micro-sized ZSM-5 is more stable than the nano-sized ZSM-5, and H_2 treatment has more influence on the nano-ZSM-5 catalyst.

^{27}Al MAS NMR analysis

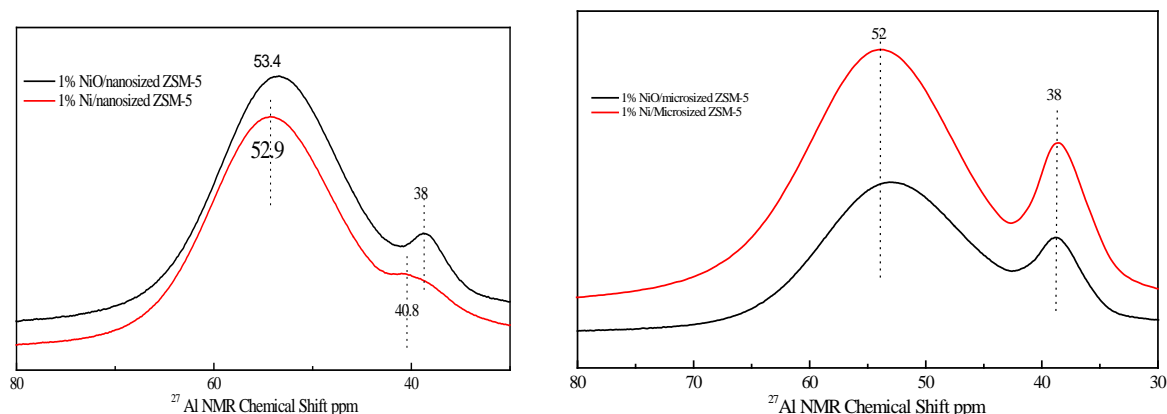


Fig.4 ^{27}Al MAS NMR spectra of 1% NiO and Ni supported (a) nano-sized ZSM-5 and (b) micro-sized ZSM-5

The ^{27}Al Mas NMR spectra of the ZSM-5 supported nickel catalysts with different nickel treatment are given in Fig.4. The nano-ZSM-5 zeolite without Ni loading without nickel shows one NMR peak centering at 53.5 ppm, which is assigned to tetrahedral coordinated AlO_4 in the framework of the zeolite. When NiO is loaded over the nano-ZSM-5 zeolite, besides the main NMR peak at 53.4 ppm, which is the framework tetrahedrally coordinated Al, a small should peak is seen at 38.0 ppm, which can be assigned to the non-framework tetrahedrally coordinated Al atom [21], or because of the nano-sized zeolite, or the unwell crystallized very small ZSM-5 zeolite. [22] When the nano-sized NiO/ZSM-5 is treated with flowing H_2 to high temperature it is interesting to see that the peak at 38.0ppm tends to disappear while the peak at about 53.0 ppm is almost unchanged This results show that the thermal treatment with H_2 to high temperature may help the non-framework tetradedrally coordinated to enter the framework, which may leads to more stronger acidic sites.

For the micro-sized ZSM-5 zeolite, the loading of 1.0 wt% NiO, an even stronger non-framework tetrahedrally coordinated AlO_4 peak is seen compared to the main framework AlO_4 unit. However, similar to the nano-sized ZSM-5 zeolite, the high temperature flowing H_2 treatment of the NiO/ZSM-5 also reduces the signal intensity of the non-framework AlO_4 . This suggests that the loading of low content NiO onto ZSM-5 zeolite both to nano and micro-sized lead to some framework tetrahedrally coordinated AlO_4 unit dis-located outside of the framework, maybe due to the partially substitution of Al by Ni in the framework

^{29}Si MAS NMR analysis

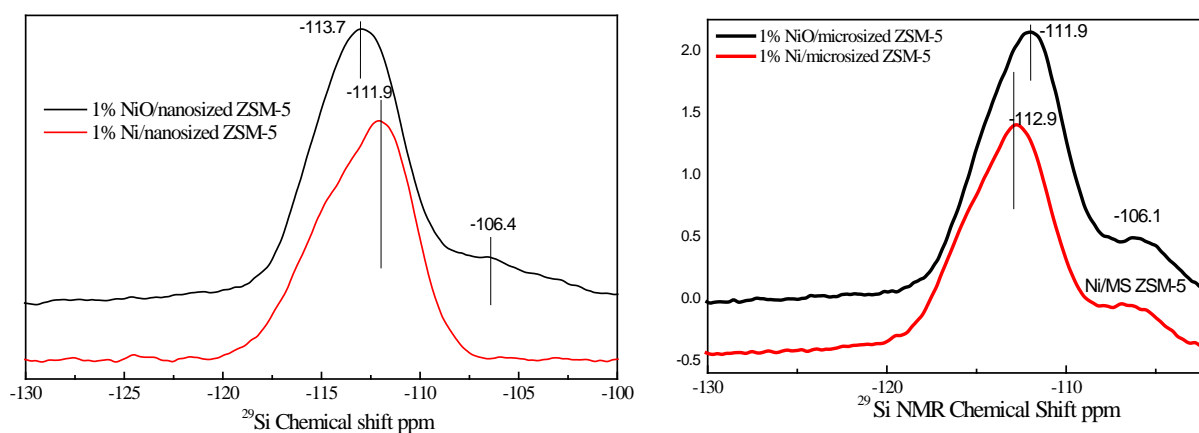


Fig.5 ^{29}Si MAS NMR spectra of 1% NiO and Ni supported (a) nano-sized ZSM-5 and micro-sized ZSM-5

The ^{29}Si MAS NMR spectra of the micro-sized and nano-sized ZSM-5 supported nickel samples catalysts shown in Fig 5. The NiO/Nano-ZSM-5 sample shows one main NMR peaks at 113.7 ppm, which is assigned to the tetrahedral SiO_4 linked with 4 Si atoms, e.g., Q4(0Al), There is a very small peak at about 106.4pp, which is due to the tetrahedral SiO_4 in the framework lined with 3 Si and 1 Al, e.g., Q3(1Al). This suggest that there exist very little Al in the framework of NiO/nano-ZSM-5. However, after flowing H_2 treatment at 600 $^\circ\text{C}$, the small peak at 106.0 ppm almost disappeared, while the main Q4(0Al) NMR peak shifted slightly to higher field, centering at 111.9 ppm, which may have some effect of long range aluminum atoms from the framework. The treatment of the NiO/nano-ZSM-5 does cause the re-location of aluminum in the framework. In the micro-sized ZSM-5 supported NiO sample, the ^{29}Si MAS NMR spectra is shown in Fig 5-b. in the oxide sample the main peak is seen at 111.9 ppm, with a small peak at 106.1 ppm, which are assigned to Q4(0Al) and Q4(1Al).. The relatively stronger peak at 106.1 ppm implying that more framework Al is present in the micro-sized ZSM-5 supported NiO sample. After thermal treatment in flowing H_2 , the main peak of ^{29}Si NMR shifted slightly lower field to 112.9 ppm, and the peak at 106.0 ppm is still present, suggesting that the hydrogen treatment causes some changes in the framework

silinal, but less than the nano-sized ZSM-5 supported NiO sample

In combining the ^{27}Al MAS NMR results of the micro and nano-sized ZSM-5 samples, we can see that the hydrogen treatment at higher temperature of the NiO/ZSM-5 sample has opposite effect on the micro and nano-sized ZSM-5 samples. For the nano-sized ZSM-5 sample, the hydrogen treatment leads to less non-framework AlO_4 unit, which may enter the framework, but for micro-sized ZSM-5, the hydrogen treatment leads to more framework AlO_4 unit out of the framework. The reasons for these are not clear yet, but there are differences between the structure changes of the nano and micro-sized ZSM-5 supported NiO.

The acidities of the nano-sized and micro-sized ZSM-5 zeolites samples and their supported nickel catalysts were measured using NH_3 -TPD, and the results are shown in Fig 6-a and b. It is seen that the nano-sized ZSM-5 zeolite sample has NH_3 desorption peaks 100-200 $^\circ\text{C}$, which are assigned to the weak and medium acid site over the ZSM-5 catalyst, and caused by the terminal $\text{Si}(\text{OH})$, the peak is broad, suggesting that the acidic sites have a wide distribution range. A second desorption peak is seen at 360 $^\circ\text{C}$, which is ascribed to the strong acid site, arising from the non-framework AlO_4 or the Q_4Al site. When 1.0 wt% nickel is loaded over nano-sized ZSM-5 and calcined, maybe due to the NiO replacement of Al, giving rise to more verities of OH groups, as shown in Fig. 3, the NH_3 desorption peak at lower temperature shifts to slightly higher temperature with the weak acid peak centering at 150 $^\circ\text{C}$, and the NH_3 desorption peak at higher temperature becomes weaker, maybe due to the less non-framework AlO_4 unit after NiO substitution. However, it is interesting to note that after H_2 reduction of the oxide to 400 $^\circ\text{C}$, the NH_3 desorption peak at lower temperature further shifted to a higher temperature centering at 185 $^\circ\text{C}$, although the intensity decreased to some extent. However the NH_3 desorption peak at higher temperature becomes more intense and also shifted even to higher temperature. This suggests that the H_2 treatment of the NiO/nano-ZSM-5 changed the catalyst acidity, which may arise from the NiO entering the framework, and generates more OH groups.

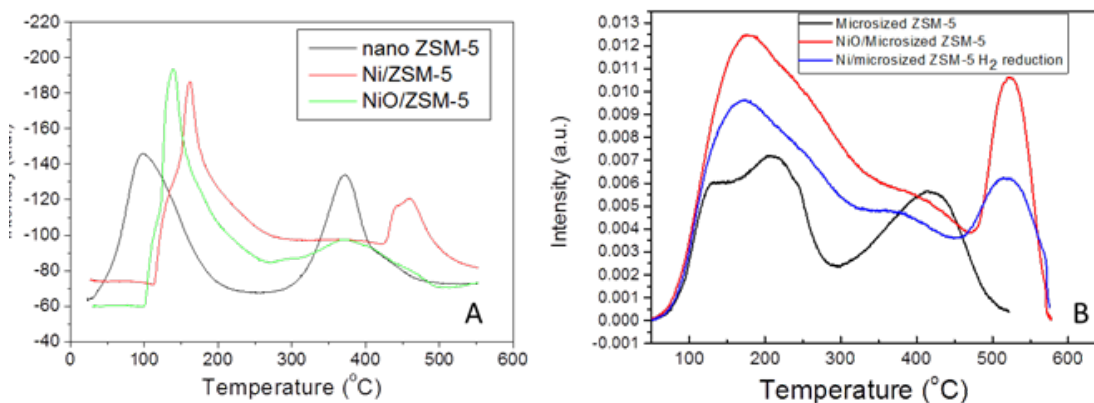


Fig. 6 NH₃-TPD profiles of the nano and micro-sized ZSM-5 zeolite and their supported NiO catalysts, a) nano-sized ZSM-5 supported catalyst, b) micro-sized ZSM-5 supported samples

For the micro-sized ZSM-5 zeolite, even with the same Si/Al ratio and same crystalline structure, the crystallite size also has influence on the acidity, as shown in Fig 6-b. The micro-sized ZSM-5 zeolite has a broad distribution both at lower temperature region (100-260 °C) and high temperature region (300-500 °C). This might be due to the broad distribution of Nickel in and outside of the zeolite pore, exerting more effect on the silanol groups in the catalyst. When 1.0 wt% NiO is loaded over the micro-sized ZSM-5, similar to the nano-sized, the NH₃ desorption peak intensity at lower temperature increases significantly, suggesting more acidic site generated by loading NiO over the micro-sized zeolite. In addition, the strong acidic site becomes stronger as the NH₃ desorption peak even shifted higher. The treatment of NiO/micro-sized ZSM-5 catalyst with H₂ decreases the acidic amount at both higher temperature and lower temperature regions, although the acidic strength of the weaker and strong acid site do not changes significantly.

The above results show that the nano-ZSM-5 and micro-sized ZSM catalyst have different acidic properties, The NiO loading does have significant effect on the ZSM-5 acidic amount and strength, and it increases the acidic amount at lower temperatures and higher temperatures. In the micro-sized ZSM-5, the NiO loading leading to the more acid amount and acid strength, and a broad acid site distribution. In general, it is seen that in both

micro-sized and nano-sized ZSM-5 zeolite, the loading of nickel increase the strong acidic sites, which is in agreement with the literature results.[23]

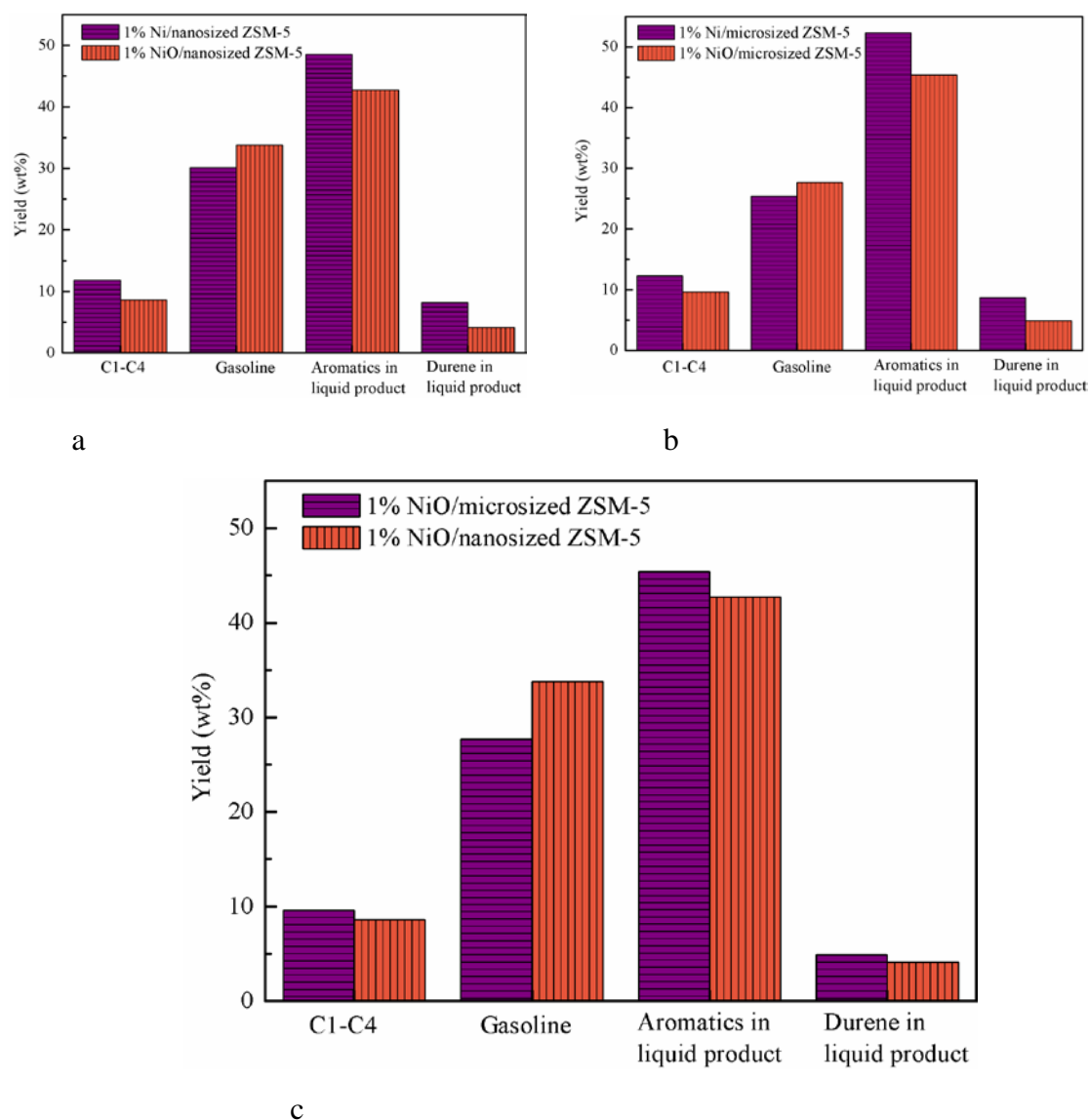


Fig.7 Performance comparison of Ni and NiO supported ZSM-5. (a) nano-sized ZSM-5, (b) micro-sized ZSM-5, and c) 1% NiO over nano-sized and micro-sized ZSM-5 in MTG reaction

Micro and nano-sized ZSM-5 supported Ni catalysts were tested for methanol to hydrocarbon, which is a very important process for future energy and chemical industry. The results are shown in Fig 7. For NiO/Nano-ZSM-5 sample. The gasoline yield is about 33%, and aromatics selectivity in the liquid is 42%, less than 10% of methanol is converted into

C1-C4 gases hydrocarbons. When the NiO/nano-ZSM-5 is treated with H₂ at high temperature, the liquid hydrocarbon yield dropped to about 30.5%, but aromatics do increase in the liquid products, suggesting that the H₂ treatment leads to stronger acidity, as the more aromatic is the results of the deep dehydrogenation of the -CH₂ groups over the acidic sites.

For the NiO/Micro-sized ZSM-5 sample, the performance for methanol to hydrocarbon process are shown in Fig. 7-b. The C1-C4 product selectivity over the supported NiO is slightly higher than the nano-ZSM-5, but the gasoline yield is about 28.9%, lower than the nano-zeolite sample. However, the selectivity to aromatics in the liquid product is about 45.2%, which is more than the nano-ZSM-5 supported NiO. The heavy aromatics content, e.g., durene in the liquid products is about 4.8 wt%, which is slightly higher than in the nano-zeolite. After H₂ treatment of the NiO/Micro-sized ZSM-5, the gasoline yield decrease to 25%, but the aromatics content does increase significantly compare to the Ni/nano-sized ZSM-5. The effect of H₂ treatment at high temperature may lead to more none-framework AlO₄ unit in the micro sized ZSM-5 catalyst, which are mostly Lewis acid sites, leading to deep dehydrogenation content, thus give more aromatics and durene.

In comparing the Fig 7-a and b as shown in Fig 7-c, the higher yield of gasoline over nano-sized ZSM-5 catalyst may result from the smaller crystallite size, which makes the products easy to migrate from the catalyst channels, and thus have less carbon deposition and higher liquid products yield. This has been validated by many researchers [11, 15, 24-27].

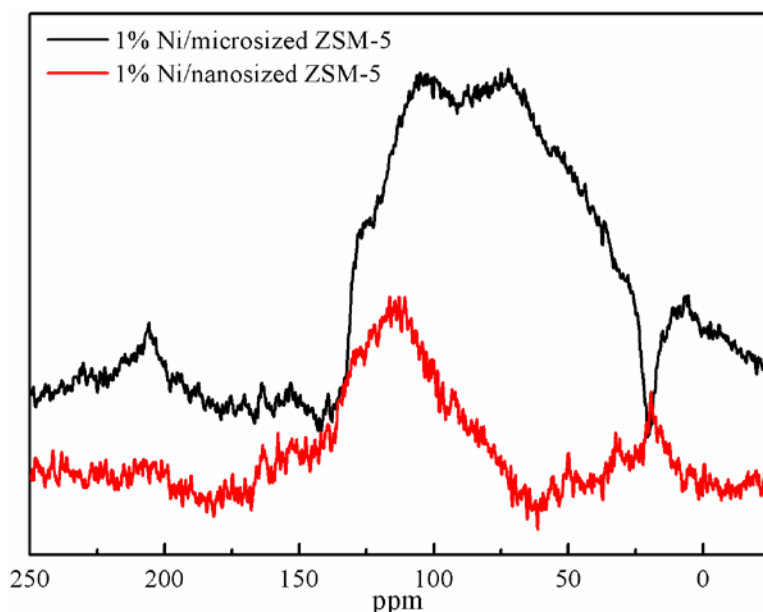


Fig.8 ^{13}C MAS NMR spectra of coked Ni/microsized and nanosized ZSM-5 after 10 h

The spectra of ^{13}C MAS NMR of the spent micro-sized and nano-sized ZSM-5 supported Ni catalysts are shown in Fig 8. It is clearly seen that the 1.0 wt% Ni/Nano-ZSM-5 catalyst has a weak NMR band at about 128 ppm, is assigned to aromatic carbons or polyene chains. The peaks below 50 ppm, especially these at around 30.0 ppm to $-\text{CH}_2$ groups in long paraffinic chain, and 23.0 ppm (CH_2 groups linked to terminal methyl group). As it indeed there are liquid hydrocarbon products still presenting in the catalyst. For the ^{13}C MAS NMR spectra of the micro-sized ZSM-5 supported Ni catalyst, the carbon peaks is much broader, ranging from 50 ppm to 135 ppm and the peaks intensity is much more stronger, suggesting that there have been much more aromatics and absorbed hydrocarbon in the micro-sized ZSM-5 supported Ni catalysts, this may be explained by the longer channel for the products diffusion, as micro-crystallite ZSM-5 catalyst has longer pore and channel, which makes it difficult for the products with big molecules to diffuse out, thus residing in the catalyst. This results is in agreement with the catalyst test performance, as the micro-sized ZSM-5, where the micro-sized ZSM-5 catalyst gives less yield of gasoline

The TG-DTA results of the spent nickel catalyst are given in Fig 9, and it is clearly seen that for the nano-sized ZSM-5 supported Ni catalyst more weightloss is seen at temperature below 100 $^{\circ}\text{C}$, which may be due to the physisorption compounds such as moisture or methanol reactant. There is 3.0% wt. of weight loss at temperature 400-800 $^{\circ}\text{C}$, which is

assigned to the burning of the heavy coking species like aromatics in the catalyst pore. However, for the micro-sized ZSM-5 supported Ni catalyst, there is much less weight loss seen at temperature below 100 °C, which show that the physi-sorbed components such as methanol or moisture is much less, but a much big weight loss is seen from 400-800 °C, which is due to the hard coking species, this also confirm the ^{13}C NMR results, There have been much more hard-coking species in the micro-sized ZSM-5 supported Ni catalyst, this is due to the increase of acidity in the Ni loaded catalyst, but mostly due to the bigger size of the micro-sized ZSM-5, leading them to a slow diffusion of the organic compounds products,

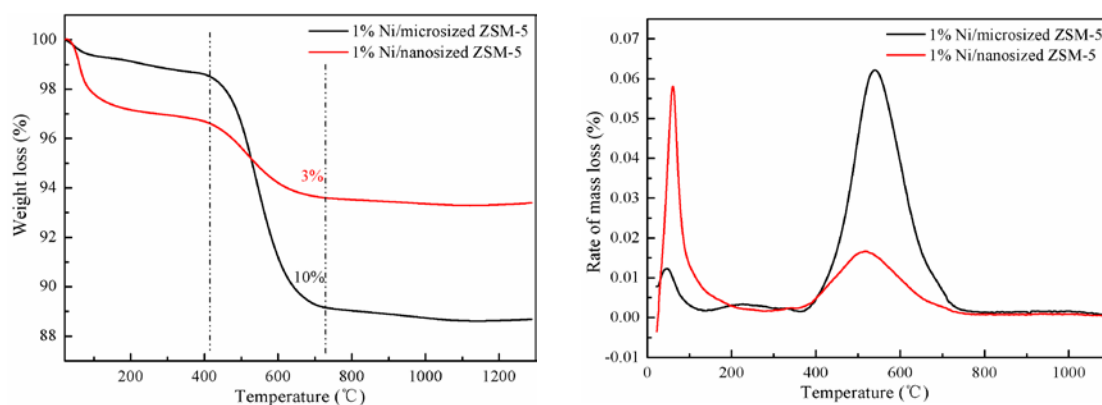


Fig.9 TG and DTA profiles of used Ni/microsized and nanosized ZSM-5 after 10 hs time on stream.

Conclusion:

Nano- and micro-sized ZSM-5 zeolite supported nickel oxide catalysts have been prepared and tested for methanol to hydrocarbon process. The loading of low amount of nickel has significant effect on the acidity and coordination environment of silicon and aluminum, and also the acidic sites. There are clear differences between the nano and micro-sized ZSM-5 supported Ni catalyst.

The hydrogen treatment of the nano-ZSM-5 supported NiO leads to some non-framework AlO_4 re-locate in the framework, while has little effect on the micro-sized ZSM-5 supported NiO, which has higher stability.

The nano-sized ZSM-5 supported NiO gives more liquid yield of hydrocarbon than

micro-sized ZSM-5 supported NiO. The high temperature hydrogen treatment leads to the lower yield of liquid hydrocarbon but higher selectivity to aromatics, although the micro-sized ZSM-5 always has lower yields of HCs and higher selectivity to aromatics, which shows that the crystallite size does have a dominant effect on the reaction, as micro-crystallite size has a longer channel for the products to diffuse than the nano-zeolite. As reflected in the test results. The micro-sized ZSM-5 supported NiO catalyst has much higher content of coking species, which has a very broad range of carbon species, while nano-sized ZSM—5 catalysts have less coking accumulated in the catalyst, which is mainly aromatics.

Compared to the ZSM-5 only catalyst for methanol to hydrocarbon, the loading of 1.0wt% NiO with or without H₂ treatment is not beneficial to the liquid product yield, but help to increase the aromatic selectivity. Therefore the low content nickel containing catalyst may be more suitable for methanol to aromatics process.

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