



Zeolite-templated NiO Nanostructure for Methanol Oxidation Reaction

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ABSTRACT

Nickel oxide nano with particle size of 10.0 to 15.0 nm using zeolite as a template were successfully prepared and loaded (NiO 10 wt.%) on functionalized carbon nanofibers (CNFs). The as-prepared material NiO-CNFs was characterized and tested as an electrocatalyst and a catalyst for the methanol conversion. Electrocatalytic results showed high stability which was evinced by repetitive cycles as a result of catalyst surface activation. Gas phase catalytic tests were carried out at 290°C over NiO-CNFs catalyst in fresh, reduced, and oxidized forms. The results showed that dimethyl ether (DME) and CO₂ were obtained as main products. Formaldehyde (FA), Methyl formate (MF) and Dimethoxymethane (DMM) were obtained as traces. The conversion of methanol in the absence of H₂ or O₂ over inactivated NiO-CNFs catalyst suggested that DME reacts with the formed H₂O to produce CO₂. In both cases, reactivation of the catalyst by H₂ (reduction) or by Air (oxidation), the conversion was increased indicating a regeneration of the catalyst.

Keywords: Zeolite, Electrocatalyst, NiO nanoparticles, Microporous, Template, Methanol oxidation, Fuel cell.

INTRODUCTION

Porous solids are categorized in three classes: Microporous materials with a pore diameter (< 2 nm), mesoporous materials are materials with a pore diameter of 2-50 nm and macroporous materials with a pore diameter (> 50 nm)^{1,2}. Mesoporous materials have attracted high interest due to their unique properties such as large surface area, uniform pore size and pore size distribution which makes them suitable for many applications such as energy conversion³, Sensors⁴, Catalysis⁵ and bio-related applications⁶. They are also used

as templates for making molecular sieves, sensors and synthesis of controlled size nanoparticles². On the other hand, microporous materials such as zeolite are known for many applications such as catalysis, and sorption due to their high stability and selectivity⁷. It has been reported that zeolite can be used as a starting materials to produce mesoporous structures through desiccation process by alkaline treatment of zeolite^{7,8}. Here we report the syntheses of Nickel oxide nanoparticles using zeolite ZSM-5 to produce mesoporous structure and then the removal of the zeolite by the alkali treatment. Prepared NiO Nanoparticles has been supported on carbon fibers



to be used as electrocatalyst and a catalyst towards methanol conversion.

MATERIALS AND METHODS

Zeolite Preparation and loading

In a typical hydrothermal synthesis procedure⁹, an exact amount of 3.4M NaOH solution was added to Pyramid sodium silicate (29.25% wt SiO₂, 8.85% wt Na₂O, 61.9% wt H₂O) (Crossfield Chemicals) under stirring at room temperature, then a mixture solutions of sodium Aluminate NaAlO₂ (52.3% wt Al₂O₃, 47.7% wt Na₂O) (BDH Chemicals) and Tetra Propyl Ammonium Hydroxide TPAOH (20% aqueous solution) (Aldrich Chemicals Co) were added individually with vigorous stirring. The reaction kept under stirring for at least 2 h and then transferred into a 250 ml Teflon-lined steel autoclave. Reaction kept at 170°C under pressure for 24 hours. The product was filtered, rinsed with deionized water, dried, and calcined at 540°C for 8 h to remove the template 10. A certain amount of the prepared ZSM-5 zeolites was then kept under vacuum at 150°C overnight, then added to a solution of Ni(NO₃)₂ and sonication for 4 h followed by vacuum drying. Zeolite sample loaded with Nickel salt was then calcined at 350°C for 2 hours. Zeolite template was removed using 1M NaOH solution for 5 h at 80°C with stirring.

Preparation of NiO/Carbon fiber nanocatalyst

Carbon fibers support was prepared according to the method reported by Al-Enizi *et al.*,¹¹. In a typical synthesis, polyacrylonitril electrospun fibers were produced using electrospinning technique. Produced fibers were collected, dried then transferred to carbon fibers using pyrolysis process under Nitrogen atmosphere at 1100°C for 6 hours. The obtained NiO material was dried at 70°C overnight. To achieve 10 wt.% loading of NiO on the Carbon fibers (CNFs), an appropriate amount of NiO and CNFs was mixed and sonicated in deionized water for 30 minutes.

Materials characterization

The C, H, and N contents of prepared NiO/Carbon fiber nanocatalyst were determined using PerkinElmer 2400 Series II CHNS/O elemental analyzer and for the characterization of crystal structure, Bruker D8 Advance x-ray diffractometer

has been used. The TEM characterization of NiO nanoparticles was preform on Jeol high resolution transition electron microscope (HRTEM 2100) operated at 200kV.

Catalytic measurements

Conversion of methanol was used to test the acid and redox properties of the catalyst. Oxidation tests were carried out at atmospheric pressure using a fixed-bed continuous-flow reactor. The catalyst (250 mg), packed in a stainless steel reactor, was preconditioned at 330°C under air flow for 2 h at a rate of 80 ml/min. After the pre-treatment, the reagent mixture, which consisted of a mixture of methanol and air with volume ratio air/CH₃OH = 2/0.5, was admitted in the reactor (admission of methanol was carried out automatically and continuously by micro-injection through a syringe). The reaction was conducted at 250°C. AS for reduction tests, the loaded catalyst sample was preconditioned at 330°C under H₂ flow for 2 h at a rate of 80 ml/min. After the pre-treatment, the reagent mixture, methanol and H₂ (H₂/CH₃OH = 2/0.5), was admitted in the reactor. The reaction products were analyzed with a gas phase chromatograph (Agilent 6890N) equipped with a flame ionization detector and a capillary column (HP-PLOT Q length 30m ID 0.53 mm).

Electrocatalytic measurements

Working electrodes were fabricated by dispersing 0.2 mg of the prepared materials in a solution of 0.5 ml isopropyl alcohol and 0.1 ml Nafion (10 wt.%) and sonicating the solution for 1 h Next, 10 µl of the dispersion was cast onto a glassy carbon (GC) disk electrode (GAMRY Instrument Company, A = 0.071 cm²) and left to dry overnight. Before inserting the electrode into the electrolytic cell, its surface was flushed with the same electrolyte that was used in the measurements in order to confirm the surface wettability¹¹.

RESULTS AND DISCUSSION

The result of X-ray powder diffraction analysis of the calcined ZSM-5 zeolite is shown in Fig. 1. The sample exhibited the characteristic diffraction lines of the ZSM-5 framework characterized by the reflections in the 2 theta range of 7–9° and

23–25°, which matched well with the standard pattern of ZSM-5 zeolite¹². The obtained XRD spectrum confirmed successful preparation of a highly crystalline ZSM-5, as indicated by the well resolved XRD peaks and the weak background noise in the XRD patterns.

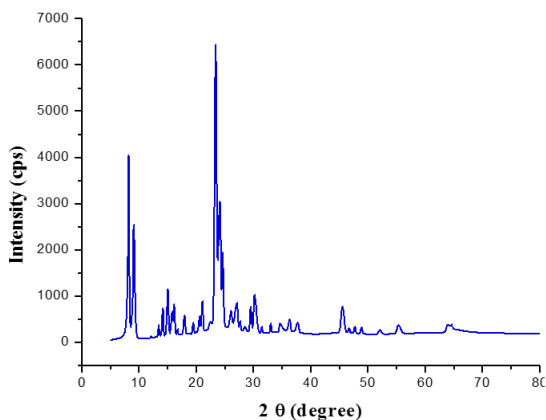


Fig. 1. XRD patterns of the ZSM-5 calcined at 540 °C for 8 hours

TEM image after alkali treatment of zeolite template (Fig. 2), indicate the formations of uniform NiO particles of thickness about 3-6 nm.

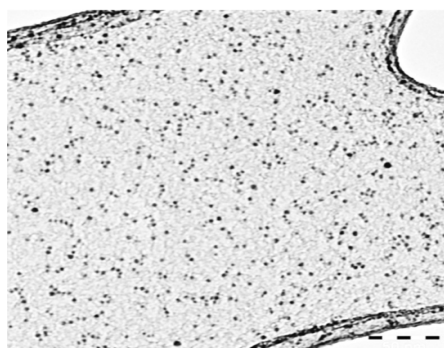


Fig. 2. TEM images of NiO nanoparticles

The XRD pattern of the prepared NiO/CNFs electrocatalyst shows diffraction peaks at 2θ 37.3°, 43.3°, indexed to the (111) and (200) of cubic NiO phases respectively (Fig. 3)¹³ and a diffraction peak at about 26° which can be assigned to plane (002) of the hexagonal structure of the carbon nanofibers CNFs 10. The other smaller XRD peaks at about 2θ 52° and 77° are assigned to (004) and (110) planes of the hexagonal structure of Graphite C 2H (ICDD 00-041-1487) respectively.

The prepared electrocatalyst with composition of 10% NiO/CNFs has been tested for the methanol oxidation reaction. The electrocatalytic

activity has been recorded in Fig. 4, indicating the presence of methanol oxidation peak in the potential range between + 1.1 to + 1.3 V. On the other hand, Fig. 5 shows the effect of the scan rate on the peak current, indicating the increase of the peak current with increasing the scan rate. Stability proof of the Prepared electrocatalyst, can be assured by repetitive cycling between + 0.5 V and + 1.5 V in 0.5 M KOH + 1 M MeOH solution at temperature of 25°C and a scan rate of 50 mV s⁻¹, results were depicted in Fig. 6. Fig. 6 shows that, the peak current density increased from 0.95 mA cm⁻² in the 1st cycle to 1.2 mA cm⁻² in the 20th cycle as a result of catalyst surface activation by repetitive cycling. However, after NaOH treatment of the zeolite, the formation of nickel silicate cannot be excluded. This can be in partial, the reason for the high stability of the catalyst. Additional studies of both the intermediate NiO material and the final NiO-CNFs catalyst are needed.

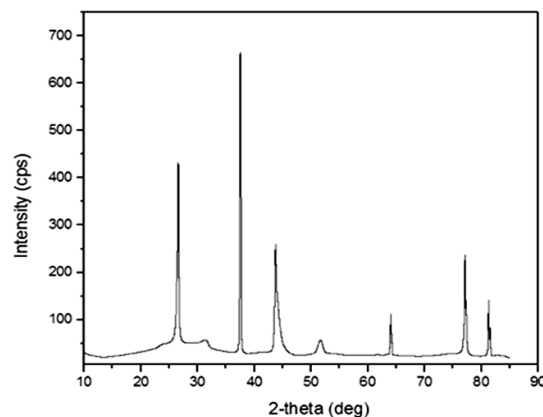


Fig. 3. XRD patterns of CNFs loaded with 10%NiO

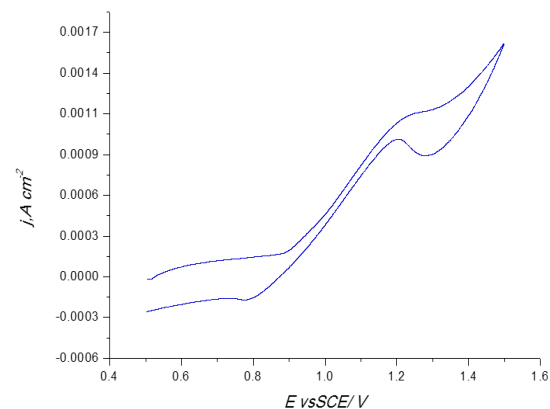


Fig. 4. CV 10%NiO/CNF in a solution of 0.5 M KOH/1M MeOH at a scan rate of 50 mV s⁻¹

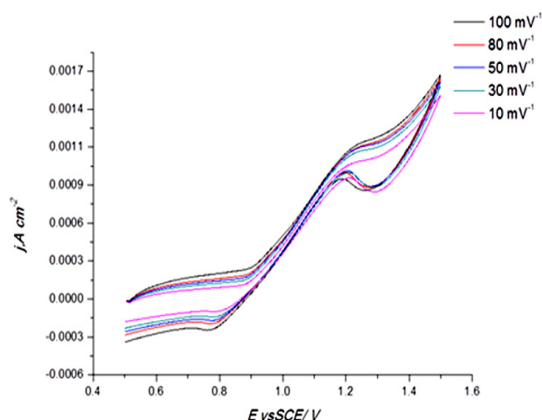


Fig. 5. CV for the 10%NiO/CNF in a solution of 0.5 M KOH/1M MeOH at different scan rate

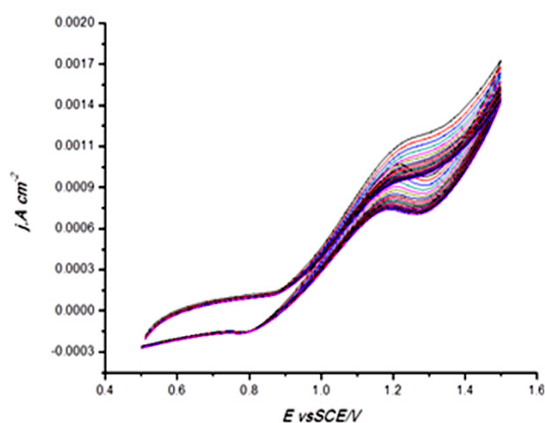
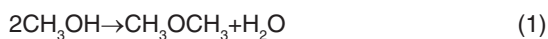


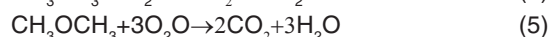
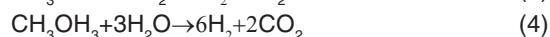
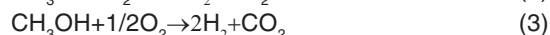
Fig. 6. Repetitive CVs for 10%NiO/CNFs in a solution of 0.5M M KOH + 1 M MeOH at 25°C at a scan rate of 50 mV s⁻¹

The reaction of methanol conversion is considered to be sensitive to the structure¹⁴, the dispersion¹⁵ and the interaction force between the active phase and the support¹⁶. For this reason it was selected as a reaction test to characterize the as-prepared catalyst. The reactions of conversion of methanol were carried out at 290°C and 250°C over the as-prepared catalyst. The results show that the reaction led to dimethyl ether (DME) and CO₂ as main products while formaldehyde (FA), methyl formate (MF) and dimethoxymethane (DMM) were observed as traces.

DME can be produced by methanol dehydration:



CO₂ can be produced by methanol or by DME total oxidation



The acid character of the catalyst is indicated by the amount of dimethyl ether (DME) formed, while the redox character is indicated by the formation of CO₂. Besides CO₂, the other reaction products such as FA, (FM) and DMM, which are formed by condensation of methanol and FA in consecutive reactions, also indicate the redox character of the catalyst.

The catalyst was tested initially, for the conversion of methanol at a reaction temperature of 290°C without being activated. The results Fig. 7 showed that the conversion increased as the reaction time increased from 0.5 to 2 hours. Beyond 2 h it decreased, indicating the deactivation of the catalyst. As for the variation of the selectivities with time on stream, it has been found that when the reaction time increases from 0,5 to 2 h the selectivity of the DME decreased in favor of CO₂. The formation of the DME is due to the acidic sites (OH) created during the functionalization (treatment with H₂SO₄) of the CNFs support. In fact, the treatment with H₂SO₄ leads to the creation of oxygenated groups (Acid sites and redox) such as COOH, C=O and OH. Then, the DME form is oxidized by the redox sites of the support and NiO leading to the formation of CO₂. These results are in agreement with those reported in the literature¹⁷ where it was mentioned that methanol leads to DME which reacts with H₂O to produce CO₂ (CH₃OCH₃ + 3H₂O → 6H₂ + 2CO₂)¹⁸. CO₂ is also formed by reactions of methanol with H₂O¹⁹.

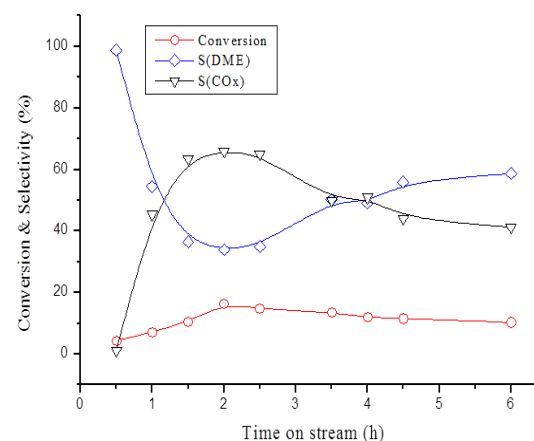


Fig. 7. Dependence of the conversion and product selectivities on time on stream reaction over NiO/CNFs, at 290°C

The sample that was tested for the reaction of methanol alone at 290°C was activated by H₂ and tested for the CH₃OH/H₂ reaction, then after it was activated by air, it was tested for the CH₃OH/Air reaction at the same reaction temperature. The change of the conversion and the selectivities with time on stream are shown in Fig. 8 and 9 respectively. It can be seen that in both cases the conversion increased with temperature and reached a value higher than that obtained for the reaction of methanol alone. As for the selectivities, it can be seen that H₂ increased the selectivity of DME to the detriment of that of CO₂, whereas air (O₂) decreased DME selectivity in favor of that of CO₂. These results can be explained by the fact that H₂ shifts the equilibrium of the conversion of DME to the left (equation 4) and thus decreased the conversion of DME into CO₂. On the other hand, O₂ increased the conversion of methanol and DME to CO₂.

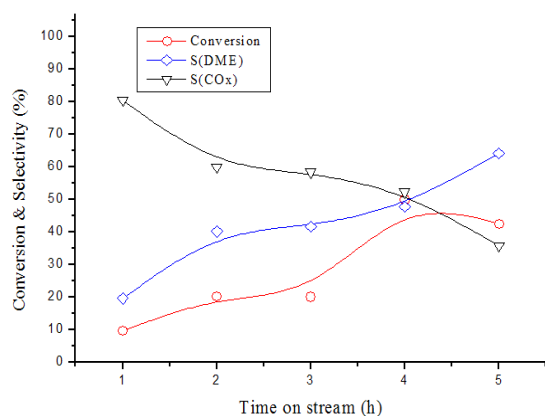


Fig. 8. Dependence of the conversion and product selectivities on time on stream reaction over NiO/CNFs. Reaction conditions: reaction temperature 290°C; activation temperature 330°C for 2 h under H₂; volume ratio H₂/CH₃OH = 2/0.5

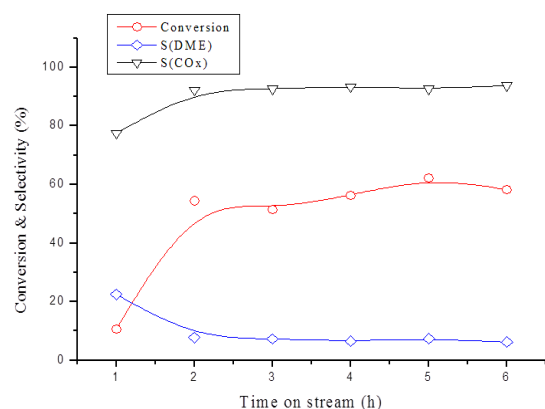


Fig. 9. Dependence of the conversion and product selectivities on time on stream reaction over NiO/CNFs. Reaction conditions: reaction temperature 290°C; activation temperature 330°C under Air for 2 h; volume ratio Air/CH₃OH = 2/0.5

In order to see the effect of temperature on the CH₃OH/O₂ reaction, the catalyst sample was activated at 330°C and then tested at 250°C. The results Fig. 10 show a slight decrease in the conversion, which indicates a slight deactivation of the catalyst. On the other hand, a slight decrease in the selectivity of the DME in favor of FM and DMM was observed while the selectivity of CO₂ remained almost unchanged. These results are in agreement with those reported in the literature^{20,21} where it has been reported that DMM and MF can be formed from DME. Compared to the results obtained at 290°C, it can be concluded that MF, DMM which are formed from CH₃OH or via DME, are converted to CO₂ by total oxidation. Taking into account the obtained results, the possible reaction routes of CO₂, DME, MF and DMM can be found in scheme 1.

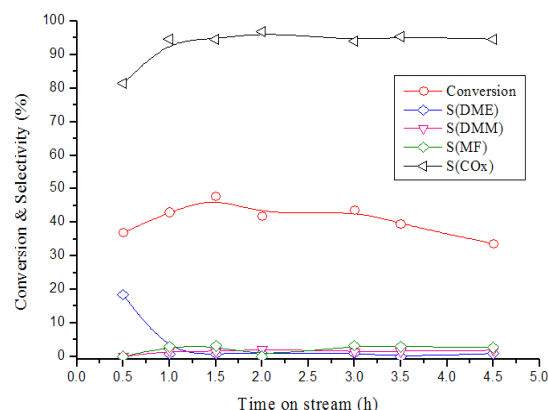
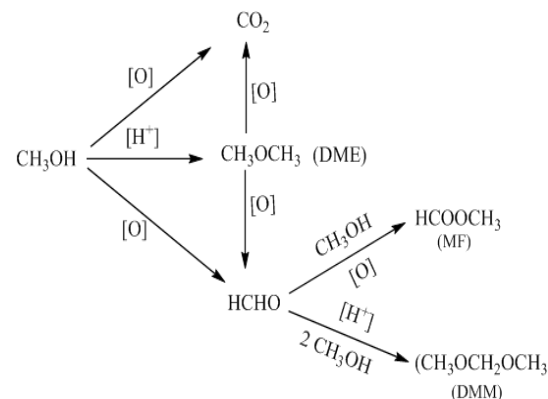


Fig. 10. Dependence of the conversion and product selectivities on time on stream reaction over NiO/CNFs. Reaction conditions: reaction temperature 250°C; activation temperature 330°C under Air for 2 h; volume ratio Air/CH₃OH = 2/0.5



Scheme 1. Proposed methanol reactions pathways on 10%NiO/CNF catalyst

CONCLUSION

NiO nano particles were successfully prepared and loaded on functionalized carbon nanofibers (CNFs). The as-prepared NiO-CNFs material was tested as electrocatalyst and catalyst for the conversion of methanol in gas phase. The results show that the NiO/CNFs catalyst has considerable activities for methanol oxidation. In fact it showed high stability which proofed by repetitive cycles as a result of catalyst surface activation. However, additional studies of both the intermediate NiO material and the final NiO-CNFs catalyst are recommended for future work. The conversion of methanol in gas phase at 290°C over NiO-CNFs catalyst in fresh, reduced, and oxidized forms, led to dimethyl ether (DME) and CO₂ as main products. Formaldehyde (FA), methyl formate (MF) and dimethoxymethane (DMM) were observed as traces.

The conversion of methanol alone at 290°C over fresh (neither reduced nor oxidized) NiO-CNFs catalyst showed a decrease of the

selectivity of DME in favor of that of CO₂ which suggest that DME reacts with the formed H₂O to produce CO₂.

Reactivation of the catalyst by H₂ (reduction) increased the selectivity of DME to the detriment of that of CO₂ (partial oxidation), whereas reactivation by air (oxidation) decreased DME selectivity in favor of that of CO₂ (total oxidation). Both cases of reactivation increased the conversion of methanol.

Results of methanol conversion at lower reaction temperature 250°C showed a decrease of DME selectivity in favor of that of FM and DMM which indicated that DMM and MF can be formed via DME at lower temperature.

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