Nickel impregnated silicalite-1 as an electro-catalyst for methanol oxidation

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Abstract

Nickel impregnated zeolite-modified electrodes were prepared by mixing Ni–silicalite-1 with conducting carbon black in different rations. Using the cyclic voltammetric technique the electrochemical oxidation of methanol at such electrodes was investigated. Experiments on silicalite-1 (S-1) and nickel–silicalite-1 (Ni–S-1) show that they are not electrochemically active towards methanol oxidation in KOH solution. The presence of nickel ions in the zeolite matrix, by soaking the electrode in an aqueous NiSO₄ solution, markedly enhances the electro-catalytic activity which was found to depend on the nickel content. On the other hand, the presence of zeolite and/or Ni metals in the catalyst is essential, however, the electro-catalytic activity depends on the Ni–S-1:carbon black ratio. Electrodes with Ni–S-1:carbon black ratio of 1:3, show the maximum electro-catalytic activity. The importance of impregnated Ni metal in the zeolite matrix is discussed on the basis of the experimental results. A weak dependence on bulk methanol concentration was observed. SEM analysis was used to characterize the Ni–S-1 catalyst. Dependence of methanol electro-oxidation on methanol concentration was discussed.
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1. Introduction

During the last 10 years, the characterization of chemically modified zeolites by electrochemistry has been widely described in the literature. They have many applications in the fields of electro-catalysis, molecular recognition-including size and chiral selectivity, amperometric determinations (electro-analysis), uses in photo-catalytic processes and electrochemical synthesis and assembly of intrazeolite conductive polymers [1,2]. Transition metal-containing zeolites exhibit high activity and selectivity in the catalytic reduction of NO with propane [3]. Ti–zeolite was used in the catalytic generation of hydrogen peroxide [4]. Ni, Co, Pt, and Pd supported on zeolites [5–7] are also known to be effective catalysts.

Zeolites are crystalline microporous solids that provide molecular-sized cages and passageways for excellent steric control of reaction paths. The pore windows and cages or channel structures of zeolites result in physical exclusion or inclusion of molecules or ions according their sizes relative to that of the pores. In addition, the presence of an array of channels allows relatively high gas permeability [8,9]. The primary building blocks of zeolites are SiO₄ and AlO₄ tetrahedra. These can link in several ways, resulting in arrays producing three-dimensional anionic net works. The presence of aluminum in the framework introduces a negative charge that is balanced by extra framework cation as a redox active guest. The framework Si to Al ratio can be controlled in the zeolite synthesis [10,11].

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Zeolites are best known as heterogeneous catalysts. They catalyze processes such as hydrocarbon cracking, methanol to gasoline conversion and disproportionation and alkylation of aromatics. On the other hand, several examples of electro-catalysis at zeolite-modified electrodes have appeared in the literature [12,13]. Rolison [1] had listed most of the methods used for the fabrication of zeolite-modified electrodes. In general, they are produced by forming a film containing the modifier on the electrode surface [14–18]. Variations involve the inclusion of the zeolite in a conductive composite with the use of conductive polymers as binders [18–24]. Some electrochemical examples were involved concerning the electro-catalytic use of porphyrins anchored to the external surfaces of zeolites [25] and the use of zeolite containing Pt(0) microstructures in water electrolysis [26]. The results showed improvements indicating the impact of a strong metal support on the electrochemistry.

The electrochemical oxidation of methanol is a main topic of research where noble metal catalysts particularly containing Pt are found to be the most effective and extensively investigated. The dispersion of the metallic catalyst in a conducting support greatly improves the oxidation process. This has explained the good results obtained for zeolite Y in copper based electro-catalyst [27]. In the present study the preparation of the Ni-modified zeolite electrode and its use as an electro-catalyst for the anodic oxidation of methanol in alkaline media was described.

2. Experimental technique

Silicalite is a crystalline material with a special structure and it contains 100% SiO_2. The silicalite-1 (1 SiO_2:0.437 TPAOH:26 H_2O), used as substrate, is of a MFI-type zeolite structure [28,29], it has been synthesized in Institut fur Technische Chemie, Technische Universtat Dresden, Dresden, Germany. It has a surface area (N_2-adsorption) of 466 m^2/g and the volume of the micropores is 0.182 cm^3/g. The nickel–silicalite-1 catalyst was prepared by the impregnation technique through the suspension of 8 g of silicalite-1 in 150 ml aqueous solution of 0.404 g $Ni(NO_3)_2 \cdot 6H_2O$, followed by the transfer with glass spherules in a rotary evaporator under mild vacuum at 70 °C to dry the substance. This method results in the preparation of 1% Ni in the substrate; therefore it was repeated to finally prepare 2% Ni catalyst. The catalyst was then dried at 110 °C for 2 h, followed by the calcinations step at 450 °C in air (to decompose the nitrate) for 2 h.

The 2% Ni–S-1 electrode was then mixed with the activated carbon black (high surface area acetylene black as P1042, Stickstoffwerk Piesteritz, Germany) 1:1 ratio in a water bath at around 80 °C with constant stirring for 3 h. This step was particularly necessary to ensure that the zeolite component of the catalyst becomes fully conducting prior to the electrochemical tests. Subsequently and using a micropipette, 10 wt.% suspension of PTFE (used as suspension, Dyneon

TF5032) was slowly added to it with constant stirring over a period of 30 min. An appropriate amount of isopropyl alcohol was added and the slurry was allowed to wet for 2 h. The resulting paste was spread over a gold plated stainless steel mesh of 1 cm^2 apparent surface area and pressed under 4 t cm^{-2} pressure for a period of 5 min. The electrode discs obtained were then dried in air oven at 110 °C for 1 h and subsequently heated in an air oven at 300 °C for 15 min. Electrodes prepared by the above procedure were already successfully used earlier as catalysts [30]. Two other modified electrodes of Ni–silicalite-1:carbon black ratios of 1:3 and 1:5, respectively, were prepared following the same procedure above.

The electrochemical measurements were performed using an Amel 5000 system (supplied by Amel instrument, Italy) driven by a PC for data processing. The PC was interfaced with the instrument through a serial RS-232C card. Amel Easyscan software was used in connection with the PC to control the Amel 5000 system. A conventional three-electrode glass cell with a Pt sheet as a counter electrode and Hg/HgO/1.0 M KOH (MMO) as a reference electrode was used. Chemicals were obtained from BDH ($NiSO_4$ analytical reagent and AR methanol). They were used without further purification and solutions were prepared using triply distilled water. All experiments were carried out at room temperature of 30 ± 2 °C.

3. Results and discussion

Scanning electron microscopy (SEM) was performed in order to analyze the surface structure of the samples. Fig. 1 shows the micrographs recorded for the silicalite-1 (Fig. 1a) and the Ni–silicalite-1–carbon black catalyst (Fig. 1b). In Fig. 1a, the sample of the silicalite-1 consisted of homogeneous crystals with a size within the range 4–7 μm. On the other hand, Fig. 1b shows the Ni–S-1 crystals at the electrode surface within the conducting carbon black. The prepared catalyst with Ni–S-1:carbon ratio of 1:1 was examined as it is in the electro-oxidation of methanol in KOH solution, but it was inactive. Fig. 2a shows the cyclic voltammetric behaviour of that electrode in 0.8 M KOH solution in presence of methanol at a scan rate of 10 mV s^{-1}. It is noted that the voltammetric behaviour of the electrode in KOH solution is silent electrochemically towards methanol oxidation. This inactivity towards methanol electro-oxidation may arise from one or more of the following reasons:

1. The catalyst is selectively "electrochemically" inactive towards these types of reactions.
2. The conductivity of the electrode composite is relatively low.
3. The relative distribution of nickel (as the proper catalyst for methanol electro-oxidation in the present system) in the zeolite matrix is not catalytically suitable to catalyze the reaction.
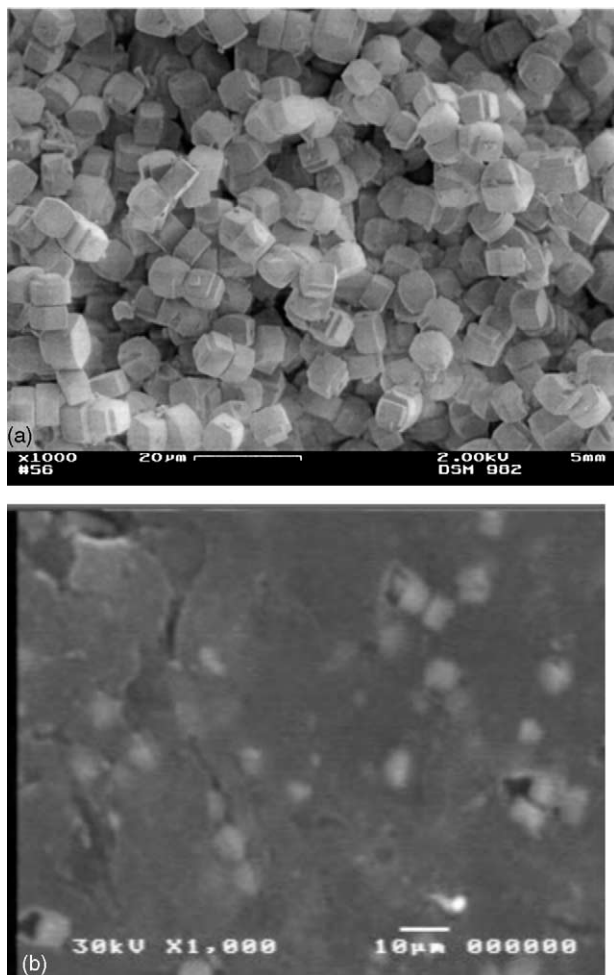
Fig. 1. (a) Scanning electron micrograph of the silicalite-1 sample. The scale bar indicates 20 nm. (b) Scanning electron micrograph of the Ni–zeolite catalyst prepared with Ni–S-1:carbon black ratios of 1:3. The scale bar indicates 10 nm.

4. The amount of nickel is not enough in the zeolite matrix.

For the second reason, the relative amount of carbon in the electrode was increased by mixing Ni–zeolite with carbon black in the ratio of, respectively, 1:3 and in another electrode to 1:5. The experimental results of methanol electro-oxidation in KOH solution at these electrodes also showed that they are inactive. In another trial, the electrodes were soaked in a nickel sulphate solution for some time. Fig. 2b represents the voltammetric behaviour of the three different electrodes (Ni–zeolite:carbon black ratios of 1:1, 1:3 and 1:5, respectively) in the KOH solution in presence of 0.25 M MeOH at 10 mV s^{-1}. An anodic peak for methanol oxidation was observed in case of the three electrodes. Good experimental reproducibility was inherent with these electrodes indicating a good mechanical stability. Electrode of a Ni–zeolite:carbon black ratio of 1:3 shows the best electrochemical behaviour as inferred from the peak height and peak potential. Accordingly, electrodes of this ratio (1:3) were used
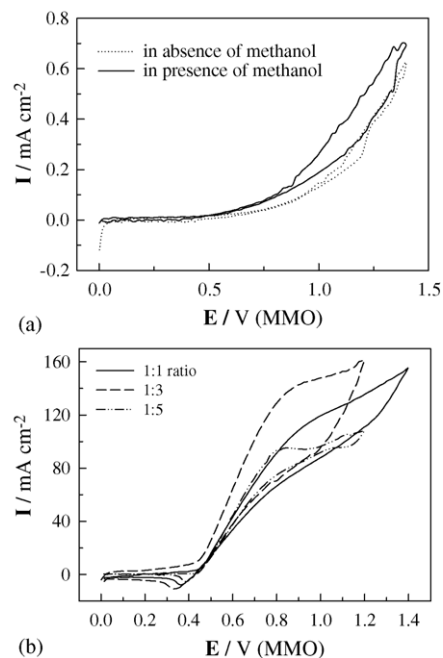

Fig. 2. (a) Cyclic voltammogram of Ni–S-1 (1:1) electrode in 0.8 M KOH solution in absence and in presence of 0.25 M MeOH at a scan rate of 10 mV s^{-1}. (b) Effect of the zeolite:carbon ratio on the oxidation of 0.25 M MeOH at the Ni-modified zeolite electrodes in 0.8 M KOH solution at a scan rate of 10 mV s^{-1} (the electrodes were pre-soaked in 1.0 M NiSO$_4$ solution for 90 s).

in all the forgoing studies. These results confirm that the percentage of nickel in the catalyst needs to be increased. Based on this result, one may conclude that the existence of anodic peak for methanol oxidation in the voltammogram of the three electrodes could be due to the presence of conducting carbon black in the catalyst and no role for zeolite or even nickel in this process. For this reason, an electrode composed only of carbon black was prepared and examined for the electrochemical oxidation of methanol without and with soaking in NiSO$_4$ solution. The results are represented in Fig. 3a at a scan rate of 10 mV s^{-1}. It is clearly shown in this figure that this electrode is electrochemically inactive towards methanol oxidation even after soaking in NiSO$_4$ solution. In addition, the presence of zeolite in the catalyst is essential as it can provide a high surface area and contains many channels or pores which permit the diffusion of electrolyte inside the electrode. The charge transport mechanism postulated by Shaw et al. [18] implies that electron transfer to a zeolite-bound (or entrained) electro-active species can occur at/on/in the zeolite environs as long as a cation from the electrolyte solution can enter the zeolite system to balance the extra negative charge brought in by the electron.

On the other hand, the presence of nickel in the zeolite matrix seems to be essential for the catalyst in presence of nickel ions. An electrode was prepared by mixing silicalite-1 (free from impregnated Ni) with carbon black in a ratio of 1:3, respectively, and was examined for the electrochemical oxidation of methanol in KOH solution. Fig. 3b
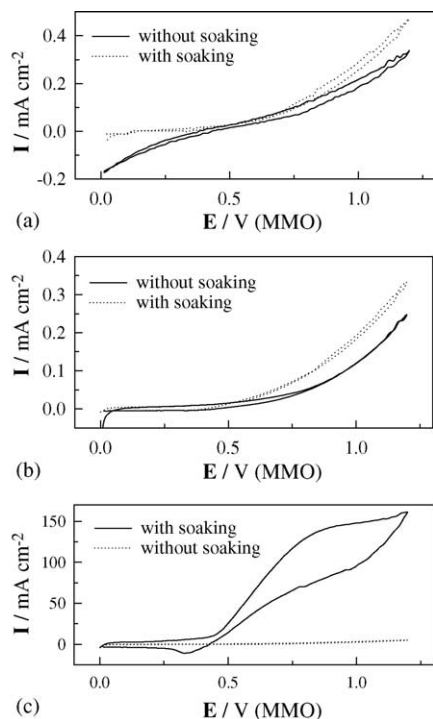
Fig. 3. (a) Cyclic voltammetric behaviour of the carbon electrode (without and with pre-soaking for 90 s in 1.0 M $NiSO_4$ solution) in 0.8 M KOH solution in presence of 0.25 M methanol. (b) Cyclic voltammetric behaviour of the silicalite-1 electrode (without and with pre-soaking for 90 s in 1.0 M $NiSO_4$ solution) in 0.8 M KOH solution in presence of 0.25 M methanol. (c) Cyclic voltammetric behaviour of the Ni–silicalite-1 electrode (without and with pre-soaking for 90 s in 1.0 M $NiSO_4$ solution) in 0.8 M KOH solution in presence of 0.25 M methanol (scan rate is 10 mV s^{-1}).

shows the cyclic voltammograms of this electrode, without and with soaking for 90 s in Ni ions, in 0.8 M KOH containing 0.25 M MeOH. A relatively very small current in the micro-range was observed for the electrode even with soaking the electrode in Ni ion solution. This confirms that the silicalite-1 without nickel cannot catalyze the methanol oxidation reaction. Fig. 3c shows the same experiments carried out using 2% Ni–S-1 electrode. This result proves that the presence of nickel in the zeolite matrix is essential for the electrode to be a good catalyst in presence of soaked nickel ions.

During the study of the electrochemical oxidation of methanol at the Ni–S-1 electrode in KOH solution, the electrode after soaking in 1.0 M $NiSO_4$ for 90 s was first examined in pure KOH solutin. In this solution, the soaked Ni ions at the electrode surface will be converted into $Ni(OH)_2$ species according to the following reaction:

$$Ni^{2+} + 2OH^- \Leftrightarrow Ni(OH)_2 \tag{1}$$

A cyclic voltammogram was recorded in blank 0.8 M KOH solution at 10 mV s^{-1} (Fig. 4). Two peaks appear in the voltammogram, one in the anodic direction at 0.60 V and the other in the cathodic direction at 0.2 V. These peaks represent, respectively, the oxidation of the hydroxide [$Ni(OH)_2$] to the
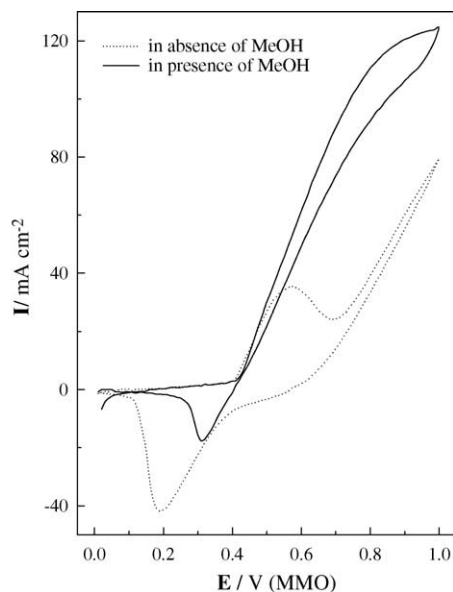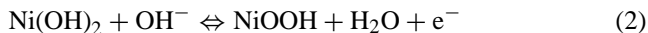

Fig. 4. Cyclic voltammogram of Ni–S-1 electrode in 0.8 M KOH in absence and in presence of 0.25 M MeOH at a scan rate of 10 mV s^{-1}.

oxy-hydroxide [NiOOH] in the anodic run and the reduction of the produced oxy-hydroxide in the cathodic half cycle, in accordance with the following equation [31–33]:

$$Ni(OH)_2 + OH^- \Leftrightarrow NiOOH + H_2O + e^- \tag{2}$$

This reaction commences at about 0.4 V reaching its maximum rate at the peak potential, at 0.6 V. The electrode was then introduced into another cell containing 0.25 M methanol solution in the KOH solution, and a cyclic voltammogram was recorded at 10 mV s^{-1}. The resulting CV is shown in Fig. 4. In comparison with the voltammogram of the electrode in blank KOH, considerable anodic current density for the methanol oxidation was observed. A cathodic peak is also observed here, however, its current density value is much smaller than the anodic one as a result of the oxy-hydroxide reduction. The relative decrease of the cathodic peak height in presence of methanol is attributed to the partial consumption of nickel oxy-hydroxide species for the oxidation of methanol with the formation of nickel hydroxide in accordance with the following reaction:

$$NiOOH + methanol \Leftrightarrow Ni(OH)_2 + products \tag{3}$$

Values of the charge under the cathodic peaks in both cases are calculated. From the calculated values, it is noted that in presence of methanol the cathodic peak reduces to about 30% of its value in absence of methanol. Therefore, about 70% of the NiOOH species produced during the anodic oxidation of $Ni(OH)_2$ (Eq. (2)) in the anodic half cycle are consumed in the oxidation of methanol (Eq. (3)).

Based on the above results, a schematic representation of the catalytic oxidation of methanol at the Ni–silicalite-1 electrode pre-soaked in Ni ions is suggested and represented in Fig. 5. It is proposed that the catalytic oxidation reac-
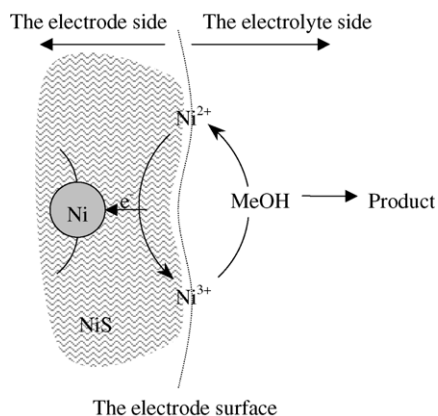
Fig. 5. A schematic representation of the catalytic oxidation of methanol at the Ni–silicalite-1 electrode pre-soaked in NiSO$_4$ solution.

tion of methanol takes place once the oxy-hydroxide species [NiOOH] starts to be electrochemically formed by the anodic oxidation of nickel hydroxide [Ni(OH$_2$)] at the electrode surface, at about 0.4 V (see Fig. 4). The Ni(OH)$_2$/NiOOH transformation preferably occurred at the Ni sites in the zeolite matrix's surface, i.e., bonded Ni species act as an electron relay to the Ni^{2+}/Ni^{3+} redox system. This might explain the catalytic inactivity of silicalite-1, that free from impregnated Ni, towards methanol oxidation. Fig. 6 represents the scanning electron micrographs recorded for the Ni–silicalite-1 after soaking in 1.0 M NiSO$_4$ solution (Fig. 6a) and another micrograph for an electrode pre-soaked in NiSO$_4$ solution and after methanol oxidation (Fig. 6b). Comparing the two micrographs, one can notice that parts of the electrode surface wetted with Ni ions were converted into Ni(OH)$_2$ precipitates
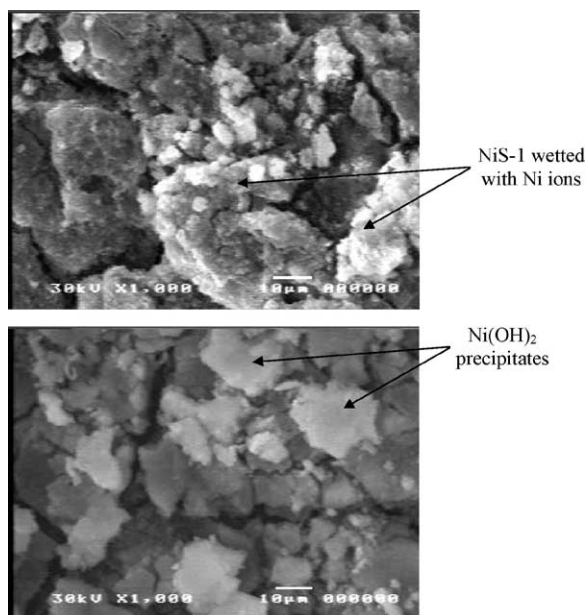

Fig. 6. Scanning electron micrographs for the Ni–zeolite electrode after soaking in NiSO$_4$ solution (a) and for another electrode, pre-soaked in Ni ions, after methanol oxidation (b). The scale bar indicates 10 nm.
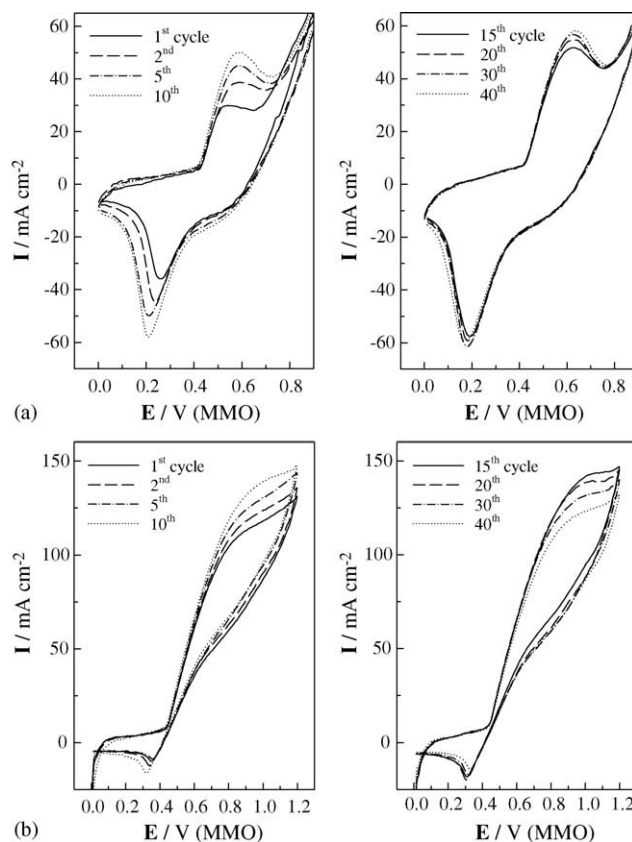

Fig. 7. Effect of the potential cyclization on the behaviour of Ni–zeolite electrode in 0.8 M KOH solution (a) and in 0.8 M KOH solution containing 0.25 M MeOH (b) at a scan rate of 10 mV s^{-1}.

after methanol oxidation and were distributed along the electrode surface in the form of separated islands.

In order to study the stability and the efficiency of the catalyst, the effect of potential cyclization on the voltammetric behaviour of Ni–S-1 electrodes was investigated in KOH solution in absence and in presence of methanol. Fig. 7 shows these results which reflect the following observations:

In absence of methanol, an increase of the anodic and cathodic peak heights was observed with repeated cyclization up to 40 cycles in a potential window between 0.0 and 1.2 V versus MMO (Fig. 7a). The increase of peak heights with potential cyclization is expected as a result of the increase of the Ni(OH)$_2$/NiOOH transformation in presence of OH$^-$ ions in solution under the influence of the applied potential.

In presence of methanol in the electrolyte, the peak height of methanol oxidation increased with the increase of potential cyclization up to the 15th cycle after which it decreased (Fig. 7b). The increase in peak height in the first 15 cycles could be due to the increase of the amount of NiOOH formed with potential cyclization as inferred from the results of Fig. 7a. This NiOOH species acts as the start material for oxidation of methanol. However, on the other hand, as a result of prolonged polarization time it is expected to have an accumulation of methanol oxidation products at the active centers on the electrode surface. The accumulation of these
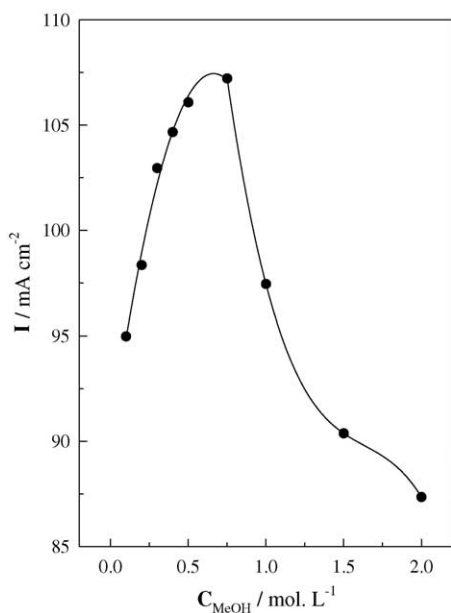
Fig. 8. Dependence of the methanol oxidation peak current density, at the Ni–S-1 electrode in 0.8 M KOH solutions, on the methanol bulk concentration.

products in high concentrations could possibly alter the oxidation process of methanol which leads to a decrease in the anodic peak height of methanol oxidation. Although the reaction is relatively retarded by potential cyclization, the results showed that an efficiency of about 86% was obtained for the catalytic oxidation of methanol.

Quantitative estimation of the dependence of the methanol oxidation on methanol bulk concentration was investigated. For this purpose, a Ni–S-1 electrode (1:3 ratio) electrode pre-soaked in 1.0 M NiSO$_4$ solution for 90 s was used. Cyclic voltammetric curves at a scan rate of 10 mV s^{-1} were then recorded in 0.8 M KOH solution in presence of various concentrations of methanol. Various methanol concentrations ranging from 0.10 to 2.0 M were used in this study. Fig. 8a represents the dependence of the peak current density values of methanol oxidation on the bulk concentration of methanol. It was found from this figure that the methanol oxidation peak current density increased with the increase of methanol bulk concentration up to 0.75 M, after which a radical decrease was observed. This concentration value seems to represent a critical concentration after which the accumulation of adsorbed oxidation products at active cites on the electrode surface causes the hindrance of further oxidation. The relatively low increase in peak current density (about 12.5 mA cm^{-2} compared to 95 mA cm^{-2} the value of peak height at 0.1 M methanol) with the increase of methanol concentration from 0.10 to 0.75 M showed a weak dependence on the methanol concentration. This leads to the assumption that the process is not diffusion controlled by methanol.

Comparison between the performance of Ni–zeolite electrodes and both dispersed Ni and Pt on graphite is shown in Fig. 9. The Ni–zeolite electrode was pre-soaked in NiSO$_4$
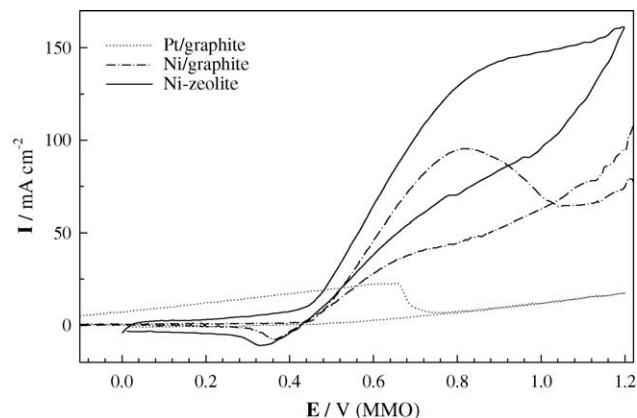

Fig. 9. Comparison between the electro-catalytic activities of Pt–graphite, Ni–graphite and Ni–zeolite electrodes towards methanol oxidation in KOH solution.

solution for 90 s, while the Ni–graphite electrode was prepared by the potentiostatic deposition of nickel from an acidic NiSO$_4$ solution for 15 min at −1000 mV (MMS). On the other hand, the Pt–graphite electrode was prepared by the potentiostatic deposition of Pt from an acidic solution of H$_2$PtCl$_6$ for 10 min at −1000 mV (MMS). It is clear from Fig. 9 that Ni–zeolite electrodes are superior electro-catalysts for methanol oxidation compared to the other electrodes. Much higher current densities are obtained on Ni–zeolite electrodes. They suffer less than Pt from the blocking of the active sites by repeated utilization.

4. Conclusion

Electrochemical measurements showed that the nickel impregnated silicalite-1 mixed with carbon black in various ratios is not electrochemically active for the oxidation of methanol in alkaline medium. Increasing the nickel content via soaking of the prepared catalyst paste in an aqueous nickel sulphate solution improves the electro-catalytic behaviour. There would be a certain maximum concentration of Ni in the zeolite matrix, beyond which the catalytic activity decreases. In view of the results represented in this paper, it appears that the presence of both Ni metals and silicalite-1 in the electrode is essential to be a good catalyst for the electrochemical oxidation of methanol in alkaline solution.

The experimental results led to the conclusion that the electrochemical oxidation of methanol occurred chemically at the electrolyte side of the zeolite/electrolyte interface by the reduction of Ni-oxy-hydroxide species to Ni-hydroxide. On the other hand, oxidation of Ni-hydroxide to Ni-oxy-hydroxide occurred electrochemically at the Ni–S-1 side at the Ni-centers within the zeolite matrix. A weak dependence of methanol peak current density on methanol concentration is observed.

Much higher current densities for methanol oxidation are obtained on Ni–zeolite electrodes compared to other

electrodes prepared by dispersing Ni and Pt metals on graphite.

Acknowledgments

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