UDC 544.47

**V.A. Bandur, I.M. Petrushina, R. Refshauge, N.J. Bjerrum** *

# EXAMINATION OF THE CATALYTIC REDUCTION OF NO BY $CH_4$ IN A Pt—POLYBENZIMIDAZOLE MEMBRANE—Pt SYSTEM WITH AND WITHOUT POLARIZATION

The catalytic reduction of NO by methane was studied using a Pt—polybenzimidazole membrane—Pt system with and without polarization at 135 °C. It was concluded that a hydrogen counter electrode probably will be more useful in connection with electrochemical promotion of re-examined catalytic reactions.

Pollution from the burning of fossil fuels is a highly discussed issue these days. Burning of fossil fuels create numerous kinds of waste exhaust gases for example CO and $NO_x$. Previous studies have been concerned with the oxidation of CO and reduction of $NO_x$. This research has been performed by many different scientific groups, both in industry and at universities. Some of these investigations have focused on the development of catalysts; other investigations have been studying the reaction mechanism and activity of entire assembly systems, with different catalysts and with gas mixtures like $CH_4/NO_x$.

Promotion of a catalytic reaction can be done in many different ways; the most common known promotion method is pure chemical promotion. Pure chemical promotion is used in various industrial processes and the area is huge.

Recently it was found that it was possible to promote the catalytic reaction reversibly by electrochemical polarization of the catalyst. Discovered by Vayenas et al. [1, 2] the electrochemical promotion (EP) was performed using the solid oxide fuel cell membrane–electrode assembly (MEA), i.e. Pt|yttria stabilized $ZrO_2$|Pt.

A catalyst is often a system, which consists of an electronic (the catalyst) and an ionic conductor. That makes it possible to use EP for many catalytic reactions. The EP nature is based on the change of the Fermi level of electrons in a catalyst (i.e. potential of the catalyst) [3].

This effect is similar to pure chemical promotion of catalysts, where rate constant is altered by the change of the Fermi level of the catalyst by addition of promoters [2, 4]. The NEMCA effect has been demonstrated for more than 50 heterogeneous [5—19] and one homogeneous [20] catalytic reaction. Petrushina et al. [6] defined two types of electrochemical promotion depending on the value of the faradaic current (I) and the enhancement factor (A). The electrochemical promotion effect is made up of two parts:

1. The electrochemical promotion effect is the charge-induced change of the strength of chemisorptive bonds at the catalyst-support-reactant boundary in heterogeneous catalysis or electrode-catalyst interface in homogeneous catalysis (CI effect).

2. The effect induced by the electrochemical production of catalyst promoters (EPP effect).

Most published cases of electrochemical promotion [1, 4—14, 21] can be ascribed to the EPP effect or mixed CI and EPP effects, depending on the polarization resistance of the EPP reaction. The promotion of a homogeneous catalytic reaction [20] or alkenes isomerisation [17] are examples of the CI effect.

In most previous studies of electrochemical promotion of catalytic NO reduction with CO or propene, Na was pumped to the surface of the catalyst using electrochemical reduction of $Na^+$ ions from Na β"-alumina support [12—15]. This supply of Na greatly enhanced the reduction of NO on Pt, Pd, Rh, and several other catalytic materials with a reaction rate enhancement as high as 20. Simultaneously the selectivity of the production of $N_2$ against $N_2O$ increased.

Lambert et al. [12—15] showed that the effect of electrochemical promotion is equivalent to the effect seen from depositing Na chemically on the catalyst surface. It means that the EP effect had a pure EPP nature.

Although there is already an established industrial process of the reduction of $NO_x$ with $NH_3$, the use of hydrocarbons has attracted much attention, since the cost of hydrocarbons is much lower than that of ammonia. Particular methane as reducing agent has been investigated thoroughly in con-

---

* V.A. Bandur (В.А. Бандур) — канд. хим. наук (1991), работал с С.В. Волковым с 1977 по 1999 г., I.M. Petrushina (И.М. Петрушина) — канд. хим. наук (1989), работала в ИОНХ НАНУ с 1978 по 1993 г., N.J. Bjerrum — иностранный член НАН Украины (1992).

nection with $NO_x$ reduction. In the $NO_x$ reduction with $CH_4$ different catalyst efficiencies have been investigated [22—43]. Most of the experiments have been carried out at high temperatures in the range of 200—750 °C. A few groups have examined the process at low temperatures [24, 28]. Burch et al. [22, 23] compared silica and alumina supported Pt, Pd and Rh catalysts efficiency. It was found that Pt was 10 times more active than Pd and 50 times more active than Rh. Pt catalysts on silica support ($SiO_2$) were seen to be most active catalyst at low temperatures; this was ascribed to the morphology of the catalyst.

Also metal-exchanged zeolites (Metal-ZSM-5) have been investigated as catalysts in the $NO_x$ reduction with $CH_4$ [26, 27, 29—36]. Okumura et al. [27] and Shimokawabe et al. [26] studied the reaction mechanism of $NO_x$ reduction with $CH_4$, on a Cu-zeolite catalyst, with temperature programmed desorption (TPD) and temperature programmed reaction (TPR) spectroscopy. Decomposition of NO, $NO_3$, $NO_2$ species adsorbed on catalysts together with O species was found at relative low temperatures (523 K), and evolution of $N_2$, $N_2O$ and $NO_2$ was seen. $NO_3$-adsorbed species was found to be well reduced by $CH_4$ at slightly higher temperatures (570—600 K), while $NO_2$-adsorbed species was seen to be less active also with $CH_4$ as reducing agent.

Gutierrez et al. [29] investigated the effect of the selective catalytic reduction (SCR) of $NO_x$ with $CH_4$ on a bimetallic-zeolite catalyst (Co/Pt) system and found that the multifunctional catalysts were very promising.

Later Heinisch et al. [33] worked further with bimetallic-zeolite (Pd/In) catalysts and found that there was a better $CH_4$ conversion in the bimetallic catalysts as compared with single-metallic (In) catalysts. However it was also discovered that the reduction of NO was lower in the bimetallic catalyst.

Li et al. [44] used Fourier transform infrared spectroscopy (FTIR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in situ: to clarify the reaction mechanism of $NO_x$ reduction with $CH_4$ and $O_2$, on a Co-ferrite catalyst. It was proposed that as a first step $NO_2$ was adsorbed on $Co^{2+}$ sites and then the activation of $CH_4$ would follow, resulting in a $CH_3^{\cdot}$ radical, creating a chain reaction involving NO and forming $N_2$, $H_2O$ and $CO_2$. There is a general agreement in nearly all previous studies that the rate-limiting step in the process of $NO_x$ reduction with $CH_4$ and $O_2$ is the breaking of the first C–H bond. This is due to the difficulty in the activation of the methane molecule since it is a very stable molecule, the most stable molecule amongst hydrocarbons [24]. However recent investigations [24—28] suggest that there might be more than one rate-limiting step in the reaction depending on many different factors such as catalyst, temperature, flow rate and composition.

Recently new catalysts have been investigated in connection with the discovery of the EPP effect, and the need for ion conducting material for electrolytes has arisen.

The solid electrolyte, for instance yttria-stabilized zirconium (YSZ), is a commonly used oxide conductor, recently however new conductors have been discovered. Perfluorosulfonic-acid polymer membrane also known as Nafion is a single-charged cation (usually $Na^+$ or $H^+$) conductive material.

Nafion has been used in the industry, in chloralkali cells to separate NaCl solutions and thereby produce $Cl_2$, and for $H_2O$ electrolysis. The properties of the Nafion electrolyte give however some problems [45]. The presence of water in the electrolyte limits the operational temperature at atmospheric pressure to below 100 °C. This operational temperature can result in a poisoning/contamination of the electrodes by impurities such as CO in the reaction gas, especially Pt containing electrodes have this problem. Due to this problem only very pure reaction gases can be used for Nafion systems.

Since catalytic activity is also very temperature dependent and generally increases at higher temperatures, it would be desirable to use a membrane that operates at higher temperatures.

Recently polybenzimidazole (PBI) membranes doped with phosphoric acid have been used as fuel cell electrolyte [5, 6, 45, 46]. PBI is proton conductive and has an operational temperature up to 200 °C, which makes it better than Nafion for catalytic use. PBI has no water management and CO contamination is lower due to the higher operational temperature.

It was found [5] that $NO_x$ can be reduced with $H_2$ in a [NO, $H_2$, Pt/PBI–$H_3P0_4$/Pt, $H_2$] assembly system with the same fuel cell set up at two different gas flow rates.

It was also found that products were $H_2O$ and $N_2$. At open circuit potential (OCP) a catalytic effect was observed and by electrochemical polarization the reaction proved to be of "volcano-type" promotion behavior for the reduction of NO. At high gas flow rate, the maximum value of the enhancement factor, Λ, was high which induced an EPP nature, it was suggested that the electrochemically produced hydrogen species at the three-phase boundary promoted the catalytic reaction.

At low flow rate it was observed that faradaic currents were absent in the potential range of promotion. This would lead to a CI nature of promotion, which is a charge-induced change in the strength of chemisorptive bonds.

The maximum electrochemical promoted $CH_4$ oxidation, and the maximum electrochemical promoted NO reduction, were both found at the approximately same applied potential. It would be interesting to examine the electrochemical promoted reduction of NO with $CH_4$ in the same assembly system.

In the current work the [$CH_4$, NO/Pt/PBI–$H_3P0_4$/Pt, $O_2$] assembly system will be examined to investigate the efficiency of the Pt–H sites produced from the MEA system (MEAS). The reason $O_2$ was used on the counter electrode was to be closer to real conditions. By not having $H_2$ on the counter side electrode there is a risk that the PBI membrane will be exhausted with protons, this however depends on the reaction mechanism at the Pt–H sites at the three-phase boundary.

The aim of this investigation is to examine if the Pt/PBI/Pt assembly system with the presented conditions for NO reduction by $CH_4$ will work, even without polarization and to see if the PBI membrane needs a continuous source of protons. Either way the results will prove important information in future investigations with this assembly system.

The set up for study of electrochemical promotion of the catalytic NO reduction is shown in fig. 1. In this investigation a carbon-supported catalyst with approx. Pt load of 0.5 mg/cm$^2$ was used.

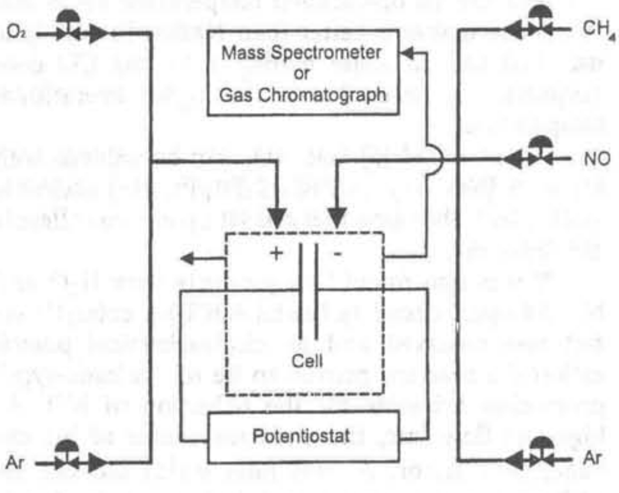

Fig. 1. Setup for study of electrochemical promotion of catalytic NO reduction.

The electrolyte was a polybenzimidazole (PBI) membrane doped with phosphoric acid. Li et al. [21] have developed a technique of preparing the membrane electrode assembly system (MEAS).

Graphite plates with gas channels were used as holders and current collectors. Two aluminium end plates with attached heaters were used to clamp the graphite plates. The temperature was controlled with a homemade temperature controller.

Commercial gases NO (≥ 99.9 %) from Hede Nielsen, $CH_4$ (≥ 99.5) from Strandmollen, $O_2$ (≥ 99.6) from Strandmollen and Ar (<40 ppm $O_2 + H_2O$) from Strandmollen were used. Mass flow meters (5850 S Brooks smart) and 0154 Brooks Instrument controllers were used to control the inlet gas composition on both the working electrode and counter electrode side.

The flow on both the working and counter electrode side was kept constant at 174 mL/min. The mixture at working electrode was 17 mL/min $CH_4$, 17 mL/min NO and 140 mL/min Ar while the mixture on counter side was 37 mL/min $O_2$ and 137 mL/min Ar. The temperature was kept at 135 °C by placing the fuel cell in an isolated box and controlling the heated end plates with a homemade thermostat.

The outlet gas composition was measured by an on-line quadrupole mass spectrometer system (QMG 421, Pfeiffer) with a Faraday detector with an electrometer preamplifier (EP112, Pfeiffer) and a cross-beam ion source with a wolfram filament. The ionization voltage was 70 V. Data from QMG was obtained by Quadstar (QMS 421) software. The outlet gases were admitted to the mass spectrometer from the fuel cell through a 0.8mm stainless steel capillary , which was cleaned on a regular basis. A bypass pump with a precision valve (Micro Hoke MTE) controlled the suction through the capillary, which made sure that during the experiments there was no suction of atmospheric air to the spectrometer.

In between experiments the primary high vacuum valve (Nupro, 44094, $10^{-8}$ bar) shut off the flow to the mass spectrometer, making sure that the mass spectrometer was kept evacuated at all times.

An EG&G Instrument (Princeton Applied Research) 283 potentiostat/galvanostat, controlled by 352 SoftCorr™ III Software, was used for electrode polarization and steady-state volumetric measurements. The initial open circuit potential (OCP) catalytic activity was measured after the yield of gas products had stabilized, *i.e.*, under steady-state conditions. For each value of polarization, the measurements were performed after stabilization of the yield of gas products (1—1.5 h). A calibration curve was made before the experiments started.

The fuel cell was made of two current collectors, which are also contact elements, two heating plates and the MEA. The electrode was cut into size 4x4 cm$^2$. Two electrodes of the wanted size were hot pressed with a PBI membrane to complete the MEA [47]. The mass spectrometer was evacuated for 48 h and the wolfram filament was stabilized before experiments.

After stabilization of the QMA, a calibration curve was made. All measurements were made after stabilization of the system for approx 1 h.

The calibration curve was made by supplying the same relative flow of Ar as in the experiments to the QMS and by supplying the same relative flow of $CH_4$ as the experiment to the QMS. After calibration, the fuel cell was heated and the desired gas composition led through the cell and to the QMS.

After stabilization of the system, the OCP was measured and the data was recorded with Quadstar and SoftCorr software. The potentials were chosen starting in positive polarization, and by moving further in the positive direction, the data was recorded by Quadstar and SoftCorr software after stabilization at each polarization.

After positive polarization a new calibration curve was made to ensure stability of the system with time. Finally the same process was performed in negative direction.

The studied assembly system was found to have a catalytic effect on the NO reduction with $CH_4$ even without polarization. The result of the present investigation is given in fig. 2.

It can be seen that the maximum catalytic effect was achieved at OCP with a $CH_4$ oxidation of 9.63 %. Furthermore, it can be seen that the activity of the catalyst decreases with polarization both in negative and positive direction. The data was obtained by first polarizing the catalyst negatively to –100 mV, then further negatively to –200 mV and after the last polarization 50 mV (positive) was applied to the catalyst. After this the catalyst was polarized positively from 50 to 200 mV.

The OCP was found to be approximately –0.1 V vs. reversible oxygen electrode (ROE).

The products of the reaction were found to be $N_2$, CO and $H_2O$. Therefore the assumed catalytic reaction was:

$$CH_4 + 3NO \rightarrow CO + 2H_2O + 1\frac{1}{2}N_2. \quad (1)$$

By using the stoichiometric ratio from (1) it is found that at OCP the $CH_4$ oxidation equals an NO reduction of 28.98 %. Since the maximum catalytic effect was found at OCP, obviously there is no positive electrochemical promotion of the catalyst under this condition.

Earlier investigations of the catalytic NO reduction by $CH_4$ have all been carried out at much higher temperature, as a matter of fact it was found that the catalytic effect increased proportionally with increasing temperature [22—43].

Investigations with the present assembly system have shown [6] that the assembly system works well with $H_2$ on the counter side and that it markedly improves the catalytic effect. But it was never investigated if the proton supply on the counter side was essential for the promotion.

It was always an assumption that the PBI membrane would be exhausted for protons during the performance of the experiment. Due to this the order in which the measurements were performed was taken into account.

A graph of $CH_4$ reduction vs. ordering in which the measurements were performed is shown in fig. 3. This figure shows that the catalytic effect decreases with time, this means that the catalyst is

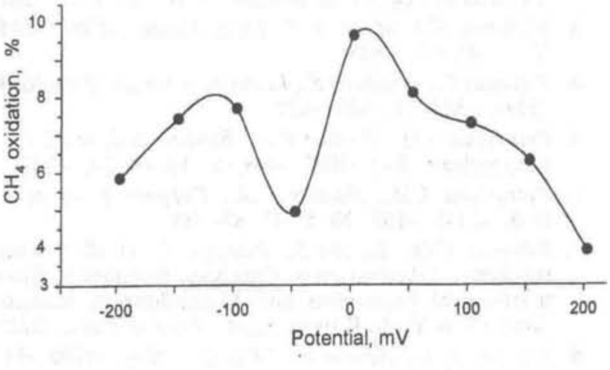

Fig. 2. The oxidation of $CH_4$ at different applied potentials.

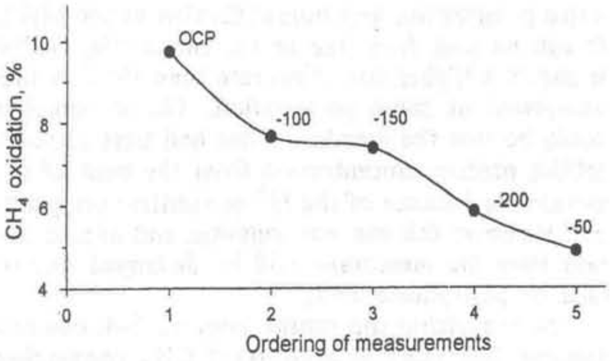

Fig. 3. The oxidation of $CH_4$ vs. the ordering of measurements in time.

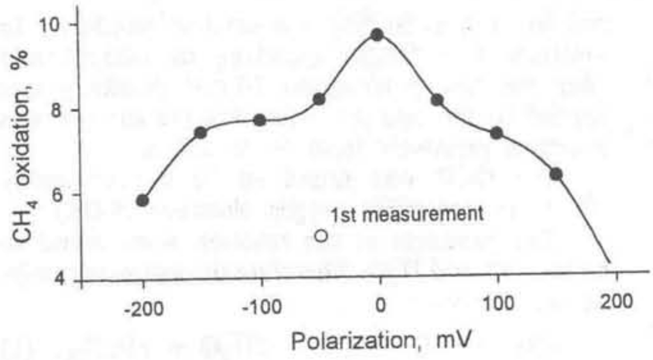

Fig. 4. CH$_4$ oxidation at different applied potentials with compared with 1st –50 mV measurement.

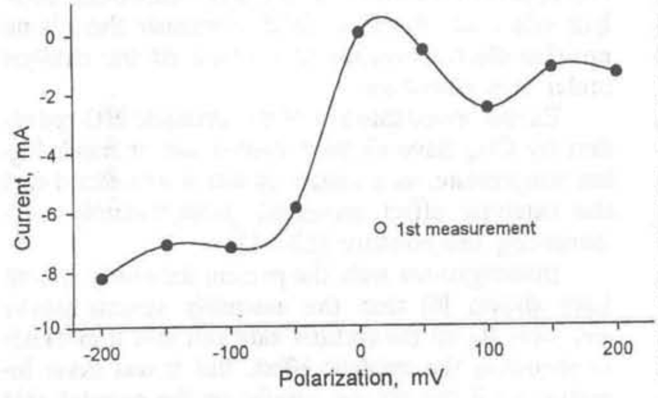

Fig. 5. Current vs. potential during the experiment.

getting worse when polarized.

As can be seen in fig. 2, the –50 mV measurement is lower than the rest of negative measurements; this can very well indicate that the membrane in fact was getting exhausted in H$^+$, since the –50 mV measurement was the last of the negative measurements. To clarify if this proton exhaustion had occurred, a new –50 mV measurement was made, see fig. 4.

The new measurement was performed after positive polarization and humidification of the MEA. It can be seen from the measurement (fig. 4) that it shows a higher oxidation rate than the first measurement at same polarization. The explanation could be that the membrane has had time to re-establish proton concentration from the bulk of the membrane because of the H$^+$ concentration gradient. However this can not continue, and after a certain time the membrane will be destroyed due to lack of phosphoric acid.

Summarizing the results from fig. 2–4, one can assume that there is a constant CH$_4$ conversion between –50 and –150 mV. One explanation is that at these potentials the drop in catalytic activity because of the proton concentration decrease at the Pt | PBI interface is compensated by the promoting effect of negative polarization.

This explanation was confirmed by a steady-state voltammogram obtained at Pt | PBI catalyst (see fig. 5). It can be seen that there is a cathodic voltammetric wave in the –50 — –150 mV potential region. On the basis of the results obtained in ref. [5, 6], we can assume that this is the electrochemical reduction of H$^+$ with the formation of adsorbed hydrogen atom. Pt–H sites, produced in this way, promote the catalytic CH$_4$ oxidation.

The reduction of NO with CH$_4$ was found to take place at the catalytic surface of the Pt supported carbon catalyst with PBI-phosphoric acid doped membrane. Maximum catalytic effect was found at OCP with a CH$_4$ oxidation of 9.6 %, which corresponds to 28.98 % NO reduction. However no positive electrochemical promotion effect was found; it was found that the membrane was exhausted for protons and the effectiveness decreased as the assembly system was used. It was presumed that the fuel cell reaction regarding consumption of CH$_4$ was rather effective especially at positive polarization, which gave rise to a negative current. It has been found that the PBI membrane needs a proton supply to electrochemically promote the catalytic surface.

РЕЗЮМЕ. Изучено каталитическое восстановление NO метаном в системе Pt—полибензимидазолиновая мембрана—Pt при и в отсутствие поляризации. Сделан вывод о целесообразности использования водородного электрода сравнения при электрохимическом промотировании для перепроверки каталитических реакций.

1. *Vayenas C.G., Brosda S., Pliangos C.* // J. Catal. -2001. **-203**, № 2. -P. 329—350.
2. *Vayenas C.G., Jaksic M.M., Bebelis S.I., Neophytides S.G.* // Mod. Asp. of Electrochem. -1996. **-29**. -P. 57—202.
3. *Williams F.J. et al.* // J. Phys. Chem. -2000. **-104**, № 3. -P. 615—621.
4. *Vayenas C.G., Bebelis S., Ladas S.* // Nature (London). -1990. **-343**. -P. 625—627.
5. *Petrushina I.M., Bandur V.A., Bjerrum N.J. et al.* // J. Electrochem. Soc. -2002. **-149**, № 10. -P. 143—147.
6. *Petrushina I.M., Bandur V.A., Cappeln F. et al.* // Ibid. -2003. **-150**, № 5. -P. 87—90.
7. *Vayenas C.G., Bebelis S., Pliangos C. et al.* // Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions. -New York: Kluwer Acad. / Plenum Publ., 2001.
8. *Vayenas C.G., Bebelis S.* // Catal. Today. -1999. **-51**, № 3–4. -P. 581—594.
9. *Bebelis S., Makri M., Buekenhoudt A. et al.* // *Solid*

*State Ionics*. -*2000*. -**129**, № 1–4. -P. 33—46.
10. *Pliangos C., Raptis C., Badas Th. et al.* // Electrochim. Acta. -2000. -**46**, № 2–3. -P. 331—339.
11. *Pliangos C., Raptis C., Badas Th. et al.* // Solid State Ionics. -2000. -**136–137**. -P. 767—773.
12. *Williams F.J., Palermo A., Tikhov M.S., Lambert R.M.* // Ibid. -2001. -**482–485** (Pt. 1). -P. 177—182.
13. *Yentekakis V., Konsolakis M., Lambert R.M. et al.* // Ibid. -2000. -**136–137**. -P. 783—790.
14. *Macleod N., Isaac J., Lambert R.M.* // J. Catal. -2001. -**198**, № 1. -P. 128—135.
15. *Williams F.J., Palermo A., Tikhov M.S., Lambert R.M.* // J. Phys. Chem. B. -2001. -**105**, № 7. -P. 1381—1388.
16. *Foti G., Lavanchy O., Comminelis C.* // J. Appl. Electrochem. -2000. -**30**, № 11. -P. 1223—1228.
17. *Ploense L., Salazar M., Gurau B., Smotkin E.S.* // Solid State Ionics. -2000. -**136–137**. -P. 713—720.
18. *Kim S., Haller G.L.* // Ibid. -2000. -**136–137**. -P. 693—697.
19. *Poppe J., Volkening S., Schaak A. et al.* // Phys. Chem. Chem. Phys. -1999. -**1**, № 22. -P. 5241—5249.
20. *Petrushina I.M., Bandur V.A., Cappeln F., Bjerrum N.J.* // J. Electrochem. Soc. -2000. -**147**, № 8. -P. 3010—3013.
21. *Li Q., Hjuler H.A., Bjerrum N.J.* // J. Appl. Electrochem. -2001. -**31**, № 7. -P. 773—779.
22. *Burch R, Ramli A.* // Appl. Catal. -1998. -**15**, № 1–2. -P. 49—62.
23. *Burch R., Ramli A.* // Ibid. -1998. -**15**, № 1–2. -P. 63—73.
24. *Watson J.M., Ozkan U.S.* // J. Catal. -2002. -**210**, № 2. -P. 295—312.
25. *Watson J.M., Ozkan U.S.* // J. Molecular Catal. -2003. -**192**, № 1–2. -P. 79—91.
26. *Shimokawabe M., Okumura K., Ono H., Takezawa N.* // React. Kinet. Catal. Lett. -2001. -**73**, № 2. -P. 267—274.
27. *Okumura K., Shimokawabe M., Takezawa N.* // Ibid. -2002. -**77**, № 1. -P. 181—188.
28. *Mariscal R., Rojas S., Gomez-Cortes A. et al.* // Catal. Today. -2002. -75, № 1–4. -P. 385—391.
29. *Gutierrez L., Boix A., Petrunchi J.* // Ibid. -1999. -**54**, № 4. -P. 451—464.
30. *Kikuchi E., Yogo K.* // Ibid. -1994. -**22**, № 1. -P. 73—86.
31. *Kikuchi E., Ogura M., Aratani N. et al.* // Ibid. -1996. -**27**, № 1–2. -P. 35—40.
32. *Kikuchi E., Ogura M.* // Catal. Surveys. -1997. -**1**, № 2. -P. 227—237.
33. *Heinisch R., Jahn M., Yalamas C.* // Chem. Eng. Technol. -1999. -**22**, № 4. -P. 337—341.
34. *Cowan A.D., Cant N.W., Haynes B.S., Nelson P.F.* // J. Catal. -1998. -**176**, № 2. -P. 329—343.
35. *Cant N.W., Cowan A.D., Doughty A. et al.* // Catal. Lett. -1997. -**46**, № 3, 4. -P. 207—212.
36. *Ohtsuka H., Tabata T.* // Appl. Catal. -1999. -**21**, № 2. -P. 133—139.
37. *Ploense L., Salzar M., Gurau B., Smotkin E.S.* // Solid State Ionics. -2000. -**136–137**. -P. 713—720.
38. *Tsiplakides D., Neophytides S.G., Enea O. et al.* // J. Electrochem. Soc. -1997. -**144**, № 6. -P. 2072—2078.
39. *Pacchioni G., Illas F., Neophytides S., Vayenas C.G.* // J. Phys. Chem. -1996. -**100**, № 41. -P. 16653—16661.
40. *Thevenin P.O., Menon P.G., Jaras S.G.* // Cattech. -2003. -**7**, № 1. -P. 10—22.
41. *Yogo K., Tanaka S., Ono T. et al.* // Microporous Materials. -1994. -**3**, № 1–2. -P. 39—46.
42. *Balint I., Miyazaki A., Aika K.* // J. Catal. -2002. -**207**, № 1. -P. 66—75.
43. *Regalbuto J.R., Zheng T., Miller J.T.* // Catal. Today. -1999. -**54**, № 4. -P. 495—505.
44. *Li Y., Slager T.L., Armor J.N.* // J. Catal. -1994. -**150**, № 2. -P. 388—399.
45. *Qingfeng L., Bjerrum N.J.* // Battery Bimonthly. -2002. -**32**, № 3. -P. 174—177.
46. *Qingfeng L., Hjuler H.A., Bjerrum N.J.* // Electrochem. Acta. -2000. -**45**, № 25–26. -P. 4219—4226.
47. *Ji-An Gao*, Department of Chemistry, Technical University of Denmark , Lyngby, by personal communication.

Technical University of Denmark, Lyngby

Received 20.05.2005

---

УДК 546.824

**V.N. Nemykin, M. McGinn, A.Y. Koposov, I.N. Tretyakova, E.V. Polshin, N.M. Loim, N.V. Abramova** *

# ASSESSING OF THE MIXED-VALENCE STATES IN ZINC MESO-FERROCENYLPORPHYRIN: EXPERIMENTAL AND THEORETICAL DATA

The formation of the stable at room temperature mixed-valence state in the zinc 5,10,15,20-tetra(ferrocenyl)porphyrin has been investigated by UV-VIS-NIR, Mössbauer, NMR, electrochemical, and theoretical (DFT) methods. On the basis of experimental and theoretical data it has been concluded that the first oxidation process involves

---

* V.N. Nemykin (В.Н.Немыкин) — канд. хим. наук (1995), работает с С.В. Волковым с 1993 г.; I.N. Tretyakova (И.Н.Третьякова) — мл. науч. сотр., работает в отделе С.В. Волкова с 1996 г.