

A Novel Internally Heated Au/TiO₂ Carbon-Carbon Composite Structured Reactor for Low-Temperature CO Oxidation

Nina Hammer, Sarka Zarubova, Ingvar Kvande, De Chen and Magnus Rønning*

Department of Chemical Engineering, NTNU, N-7491 Trondheim, Norway

* ronning@chemeng.ntnu.no, Phone: +47 73 59 41 21

Abstract

A compact, internally heated, catalytic reactor is demonstrated for the low-temperature oxidation of carbon monoxide. Carbon nanofibres were grown on carbon felt and used as a support material for Au/TiO₂ catalysts. The carbon composite plays two roles; as a support material for the catalyst and for providing heat to the reaction by the Joule effect. The internal heating offers a stable reactor system with quick temperature response at relatively low energy input. Comparison between external and internal heating shows higher conversion of CO in the low-temperature range when using internal heating. The Au/TiO₂ catalyst supported on the carbon-carbon composite shows good stability at 250°C.

Introduction

Graphitic carbon materials such as carbon felt (CF) and carbon nanofibres (CNF) have relatively high thermal conductivity. It is therefore possible to utilise the material as an electrical conductor between two electrodes. Introduction of a current in the material causes ohmic heating by the Joule effect (1,2). This paper reports the synthesis of a carbon-carbon (CC) composite consisting of CNF grown onto a CF and the preparation of Au/TiO₂ catalysts. The CC composite material is used for direct heating of the catalyst in a structured chemical reactor. The CNF/CF composite thus has two purposes; as a structured reactor and support for the Au-based catalyst and as a direct internal heating source for the microreactor. Results from CO oxidation with external and internal heating are presented.

Highly dispersed gold nanoparticles in association with a partially reducible oxide have been shown to exhibit high catalytic activity in oxidation reactions such as CO oxidation (3). There are three main factors governing the activity and selectivity; i.e. strong interaction of Au particles with the support, careful selection of support material and control of particle size (4).

In this research CNF was utilised as a support material for the TiO₂ and Au was subsequently deposited selectively onto the oxide. The deposition of highly dispersed noble metals on carbon is not a trivial task due to the tendency towards agglomeration. Gold supported on activated carbon has been used for liquid-phase reactions, although the activity of these catalysts is highly sensitive to the preparation method (5,6). Bulushev et al. (7) have used woven fabrics of activated carbon as support material for gold. The optimal size for the gold particles was reported to be 2-5 nm and they were highly active for CO oxidation at room temperature.

The structure and morphology of the oxide support material seems to be very important for catalytic activity (8). High catalytic activity is achieved by keeping the particle sizes of both the Au and the oxide below 10 nm. Small catalyst particles are a concern in catalytic reactors due to the pressure drop and the formation of fines. The problem can be avoided by anchoring the nanoparticles onto a macroscopic substrate. Carbon nanofibres are promising catalyst support materials due to their unique physical and chemical properties (9). CNF as a support have mainly been used in powder form (10,11). However, CNF can be directly grown on macroscopic substrates such as carbon felt (12,13), monoliths (14,15) and nickel foam (16). Carbon felt with CNF displays a relative high surface area > 100 m²/g, essentially arising from the external CNF surface and hence virtually free of bottled pores encountered with traditional supports such as alumina and silica (17). The high external surface area provides excellent accessibility of the reactants to the deposited active phase and accordingly improves the catalytic properties of the carbon nanostructure-containing catalysts.

Experimental

Preparation of the carbon-carbon composite

Carbon felt (Carbon Lorraine Company) with a surface area of approximately $1 \text{ m}^2/\text{g}$ has been used. The CF was oxidised for 2 hours in nitric acid under reflux. The sample was filtered off, washed in distilled water until the pH of the filtrate levelled out at 6, and dried overnight at 100°C . Due to the hydrophobic character of the material, ethanol was used as solvent when the CF was impregnated with a nickel nitrate solution. The material was dried at 100°C overnight. The amount of nickel corresponds to 2 weight percent (wt%) of the total weight. The material was calcined in air at 300°C for 2 hours. The reduction of nickel oxide was performed *in situ* at 600°C for 2 hours in 25 ml/min H_2 and 75 ml/min N_2 . CNF synthesis was performed in a tubular flow reactor at 650°C for 5 hours, using a reactant mixture of 30 ml/min ethane and 50 ml/min H_2 .

Preparation of the gold catalysts

The Au/TiO_2 catalysts supported on the CNF/CF composite have been prepared in two steps: i.e. deposition of TiO_2 onto the CNF/CF followed by deposition of gold. TiO_2 was prepared by hydrolysis of a TiCl_4 solution and subsequent addition of polyethyleneimine (PEI). The mixture was covered in aluminium foil and kept at 70°C . After 40 minutes the white precipitate began to appear and the CNF/CF was added. The mixture was stirred and refluxed at 70°C for another 2 hours. The suspension was then filtered, washed with ethanol and dried for 12 hours at 100°C (18). The Au sol was prepared by reduction of chloroaurate(III) ions by a partially hydrolysed tetrakis(hydroxymethyl)phosphonium chloride (THPC) solution, following a procedure reported by Duff et al. (19). NaOH (0.2 M) and THPC (1.2 ml of 80 wt.% THPC in water diluted to 100 ml) were dissolved in continuously stirred

distilled water. After 2 minutes a HAuCl_4 (43 mM) solution was added. When the gold(III) solution was added to the alkaline THPC mixture a rapid colour change from yellow to dark brown-orange was observed, indicating the formation of a gold sol. The $\text{TiO}_2/\text{CNF/CF}$ was dispersed in 50 ml water and the Au sol was added dropwise. The pH was adjusted to 2 by HNO_3 (0.2 M) and the solution was stirred for 1 hour. The catalysts were filtered and washed in ethanol until no traces of Cl^- could be detected in the colourless filtrate by addition of AgNO_3 . All catalysts were finally dried at 100°C for 12 hours.

Catalyst characterisation

Temperature programmed oxidation (TPO) was performed in a Perkin-Elmer TGA7 thermogravimetric analyser. The samples were heated from room temperature to 800°C at a heating rate of 10°C/min . The total gas flow (air) was 80 ml/min .

X-ray diffraction (XRD) studies were performed using a Siemens D500 diffractometer using monochromatic $\text{Cu K}\alpha$ radiation.

The surface area and the pore properties were determined by N_2 adsorption in a Micromeritics Tristar 3000 instrument. The samples were evacuated and dried at 150°C prior to analysis. The surface area was calculated from the Brunauer-Emmett-Teller (BET) equation.

Scanning electron microscope (SEM) images of the composite material were recorded using a Hitachi S4300 field emission microscope. A piece of the CC composite was cut and fixed to the sample holder by carbon tape. The average diameter of the CNF was measured from the SEM images.

Elemental analysis (X-ray fluorescence, XRF) was performed to determine the sample composition and the catalyst loading.

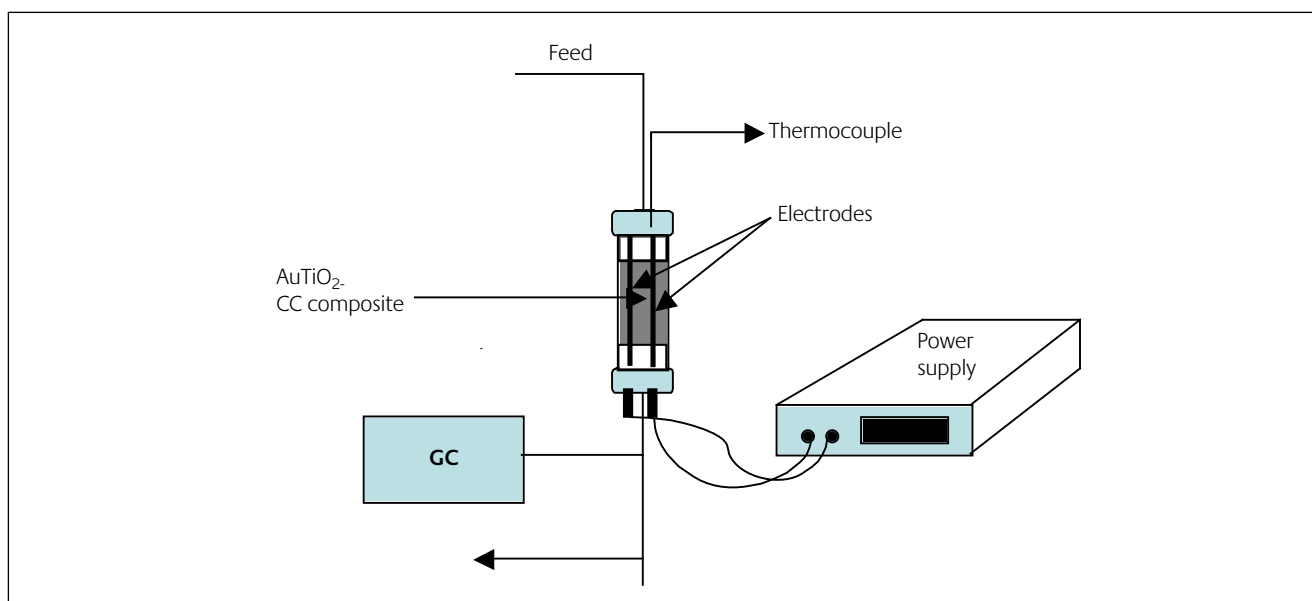


Figure 1

Sketch of the reactor set-up for CO oxidation with internal heating. The carbon-carbon composite containing the catalyst is placed inside a quartz tube and connected by two electrodes. A power supply is used to heat the material by the Joule effect

The transmission electron microscopy (TEM) analysis was performed in a JEOL 2010F electron microscope at an acceleration voltage of 200 kV. The sample powder was suspended in ethanol using an ultrasonic bath. The sample was spread onto a Cu-grid coated with holy carbon film.

CO oxidation measurements

The catalytic activity measurements were performed in a fixed bed reactor at atmospheric pressure in the temperature range 25 – 250°C. A sketch of the reactor set-up is given in Figure 1. The AuTiO₂/CNF/CF pieces are placed inside a quartz tube and connected by two stainless steel electrodes. By applying a potential over the electrodes, the material is instantaneously heated by the Joule effect. The reactor was fed with 10 ml/min CO, 20 ml/min O₂, and 70 ml/min N₂ at a total gas hourly space velocity of (GHSV) 632 h⁻¹. The analytical grade of the gases was 99.999% with no further purification. The product stream was analysed using an Agilent micro gas chromatograph. The catalyst was oxidised at 200°C for 1 hour followed by reduction at 200°C for 1 hour prior to the reaction. The stability of the catalysts was studied at 250°C using the same conditions as stated above. Two different heating methods have been used: 1) Direct heating with an external heating jacket and 2) Internal heating by the Joule effect.

Results and discussion

Supported nickel catalysts are well known to be active catalysts for CNF production through a catalytic decomposition route (9). The CNF are of the fishbone type with the graphite sheet stacked at a given angle with respect to the central axis. The carbon to nickel growth ratio in the present work is 45 g/g_{Ni}*h. Ledoux et al. (17) have reported a growth ratio of 50 g/g_{Ni}*h. However, they used 1 wt% Ni compared to 2 wt% in the present work. The CNF diameter was determined by SEM to be approximately 50 nm. The narrow peak observed in temperature programmed oxidation of the CF shows that the felt is highly crystalline with an oxidation temperature of 720°C. After introduction of CNF in the CF the TPO curve shows that the oxidation temperature for CNF is approximately 600°C. After the nitric acid treatment the combustion temperature is almost unchanged and XRD confirms that the graphite structure has not been affected.

XRD measurements were performed after each preparation step mainly to identify the phases present in the titania and to check the crystallinity of the CNF. The titania was identified to be predominantly anatase. The Au and TiO₂ loadings based on the total weight of the CC-composite material were determined from XRF to be 0.7 wt% and 7 wt%, respectively.

TEM images confirm that the CNF are not completely covered by the oxide and that the titania is attached as clusters to the surface of CNF/CF. The Au particles are selectively deposited on the TiO₂ surface. A selective deposition is achieved by lowering the pH below the isoelectric point of

titania. At pH=2 the titania has a positive charge whereas the CNF/CF is negatively charged in the entire pH range of the synthesis (20). The average Au particle size is 5 nm determined from TEM images (Figure 2).

The surface area of the carbon felt increases from 1 m²g⁻¹ to 91 m²g⁻¹ after CNF growth and further to 106 m²g⁻¹ after oxidation. The surface area was maintained after deposition of the oxide but minor changes in the pore structure could be observed. The proportion of mesopores of size 3.5 nm increased at the expense of pores in the region between 15 and 45 nm. Guzman and Corma (21) have demonstrated that the structure of Y₂O₃ supports strongly influence the activity for CO oxidation and a higher activity was achieved for nanocrystalline and mesostructured supports compared to powder with low pore volume.

The reactor system requires an input of 12 W to reach 250°C when the reactor is loaded with 1.34 g of the composite material. However, the amount of the active component for CO oxidation (AuTiO₂) corresponds to 103 mg. The resistance of the CF and CNF/CF decreases with increasing temperature, which is typical for carbon materials (2). The heating rate can be easily controlled by gradually increasing the current through the material. The system shows excellent thermal stability and provides a constant and reproducible temperature.

The catalytic activity was measured in temperature cycles from room temperature up to 250°C. The reaction rates for the catalyst are presented in Figure 3. The reaction rate increases for the three first cycles before it levels out, indicating that a further thermal pre-treatment is necessary to activate the catalyst. The increase is most pronounced between the first and second cycle. Park and Lee (22) have reported that the catalytic activity depends on the activation at different calcination temperatures and that the gaseous atmosphere during activation also plays a role.

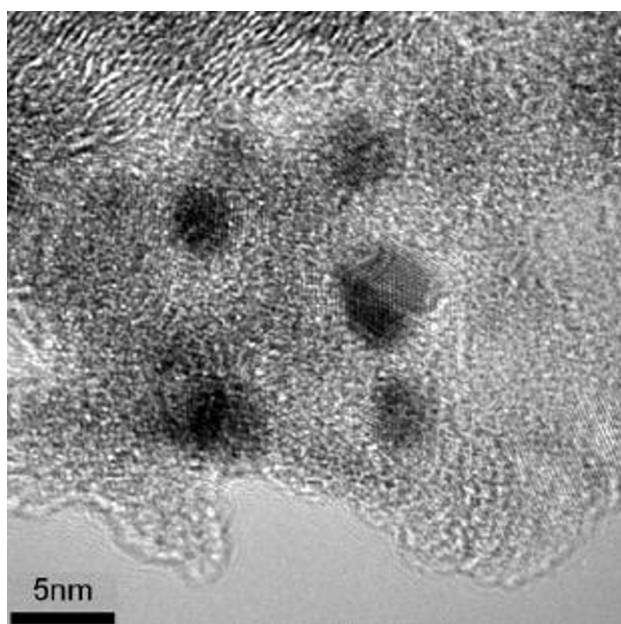


Figure 2

TEM image showing Au particles deposited on the TiO₂ surface

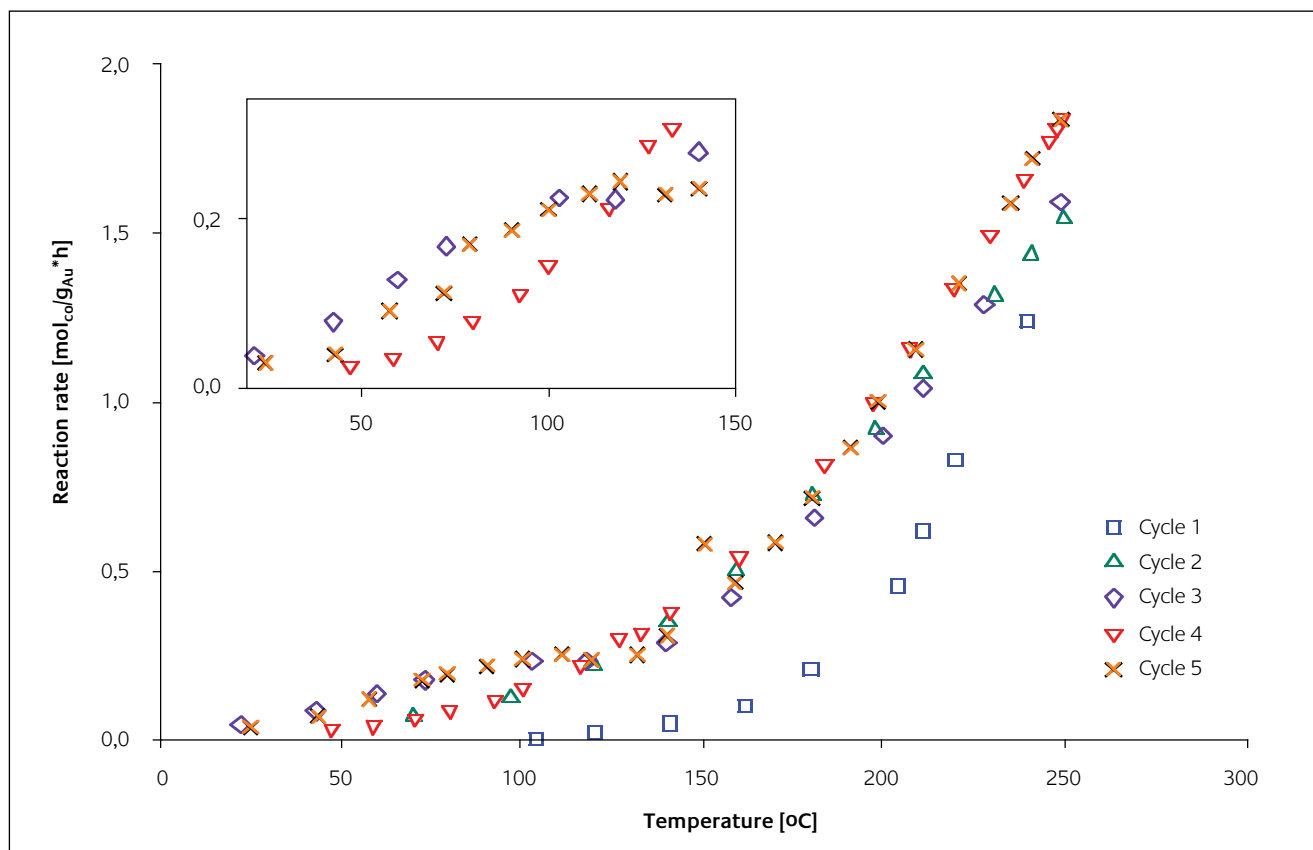


Figure 3

Reaction rates for CO oxidation as a function of temperature during cyclic operation. External heating is used for cycle 4. The other cycles are performed using internal heating. The highlighted window shows an expanded low-temperature region where the conversion is significantly higher with internal heating

The fourth cycle was carried out using external heating. Internal heating gives higher reaction rate in the low temperature region (50 – 120°C) compared to external heating as indicated in the highlighted window in Figure 3. The enhanced activity of the catalysts may be due to a change in the electronic structure of the active phase caused by the introduced current. Miremadi et al. (23) observed a similar behaviour for electrically activated In-Sn oxide catalysts during hydrogen production from methanol. They suggest that the enhanced reaction rate could be caused by creation of regions having higher temperature than the thermocouple due to the localised heating, and that grain boundaries may have higher resistance leading to increased ohmic heating in microscopic hot spots. The gas flow in the present system may effectively remove heat from the reactor (and hence the thermocouple) whereas the material close to the active sites is heated by the Joule effect and maintains a higher temperature. At higher temperatures, the heat load in the system attenuates this effect and the difference disappears. The temperature is measured in the middle of the reactor, not locally on the ohmically heated active material. The temperature is measured at exactly the same position with external and internal heating. The thermocouple is not moved between the cycles and the only difference is the external heating jacket around the reactor for supplying the external heating.

The activation energies (E_a) were calculated from data obtained in the temperature region from 25 to 80°C (differential conditions). The apparent E_a is 24 kJ/mol for internal heating and 32 kJ/mol for external heating. The values are comparable with results obtained in other studies (4). It is reported that three different regions exist where different kinetics are operating and where the rate and apparent activation energies are different (4). The reaction rate at 50°C for cycle 5 is $2 \times 10^{-5} \text{ mol}_{\text{CO}} \text{ s}^{-1} \text{ g}_{\text{Au}}^{-1}$, which is comparable with what is reported by Guzman and Corma (21). They used 1 vol% CO in the feed whereas in the present work 10 vol% is used.

Stability measurements were performed after the activity measurements and are presented as cycles in Figure 4. The reaction rate increases during the first three cycles before it levels out at a conversion of approximately 70%. The relatively high stability of the system is a result of the strong interaction between the TiO_2 particles and the CNF-support which are preventing further agglomeration of the Au particles (20). Deactivation of Au-based catalysts due to agglomeration of Au particles from residual Cl^- has been reported (24). The system presented in this work contains 0.23 wt.% Cl^- . This suggests the existence of a strong interaction between Au and the support. The influence of the mesopores in the titania and subsequent stabilisation of the surface functional groups on the carbon may also contribute.

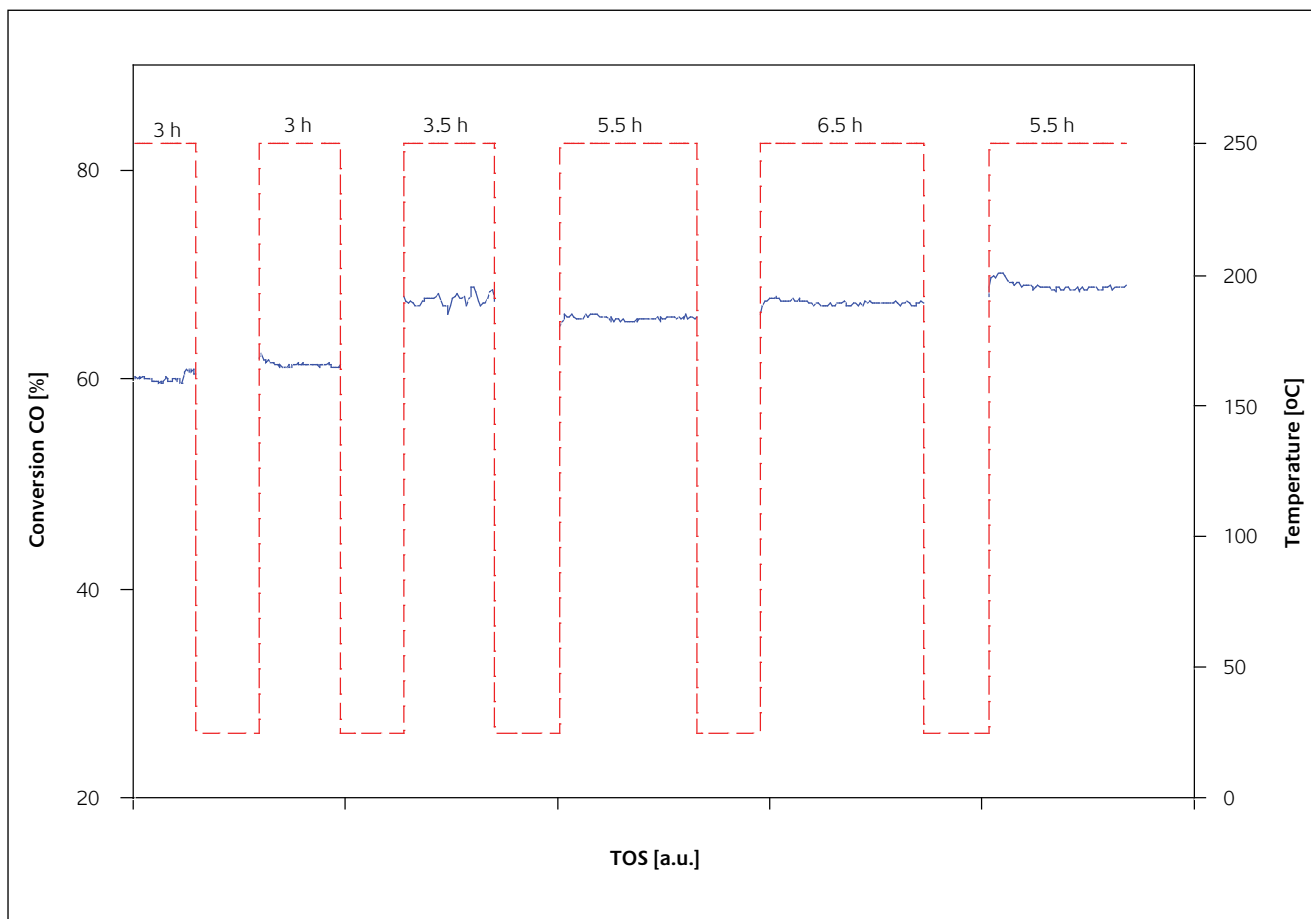


Figure 4

Stability measurements at 250°C during cyclic operation. The temperature is plotted as a function of time on stream (TOS, dashed red line). All measurements except number 3 (TOS=3.5 h) are performed with internal heating (by the Joule effect)

Conclusions

A novel concept for a compact internally heated structured reactor for CO oxidation has been demonstrated. The reactor system with internal heating gives a stable and rapid temperature response and a modest power input is needed to raise the temperature to 250°C. The catalytic activity increases during cyclic operation before it stabilises, suggesting that further thermal pre-treatment is required to activate the catalyst. The catalyst displays slightly higher conversion in the low temperature range when the heating is provided by the Joule effect compared to external heating. The Au/TiO₂ catalyst supported on the carbon-carbon composite exhibits promising stability at 250°C and the activity is maintained after several temperature cycles.

Acknowledgements

Dr. John C Walmsley, SINTEF, is greatly acknowledged for supplying the TEM image. The Norwegian University of Science and Technology is acknowledged for financial support.

About the authors

Magnus Ronning is an Associate Professor at the Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU). His research work is mainly concerned with aspects of heterogeneous catalysis applied to natural gas conversion, hydrogen production and synthesis and characterisation of new catalyst materials. De Chen is Professor of Chemical Engineering (Catalysis) at NTNU, Trondheim. He previously headed the group of petrochemical technology at the Shanghai Institute of Petrochemical Technology, SINOPEC, China. His main research areas are natural gas conversion, deactivation of heterogeneous catalysts, microkinetic modelling of surface reactions, application of oscillating microbalance (TEOM), and production and applications of carbon nanofibres/nanotubes. Nina Hammer is a PhD student at NTNU working on gold-based catalysts related to hydrogen production. Ingvar Kvande is a PhD student at NTNU working on synthesis and applications of carbon nanofibres. Sarka Zarubova is currently a Master degree student at the Institute of Chemical Technology, Prague.

References

- 1 A. Subrenat and P. Le Cloirec, *J. Environ. Eng.*, 2003, **129(12)**, 1077
- 2 A. Subrenat, J. N. Baleo, P. Le Cloirec and P. E. Blanc, *Carbon*, 2001, **39**, 707
- 3 M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet and B. Delmon, *J. Catal.*, 1993, **144**, 175
- 4 M. Haruta, *Cattech*, 2002, **6**, 102
- 5 C. Bianchi, F. Porta, L. Prati and M. Rossi, *Top. Catal.*, 2000, **13**, 231
- 6 L. Prati and G. Martra, *Gold Bull.*, 1999, **32**, 96
- 7 D. A. Bulushev, I. Yuranov, E. I. Suvorova, P. A. Buffat and L. Kiwi-Minsker, *J. Catal.*, 2004, **224**, 8
- 8 Q. Fu, S. Kudriavtseva, H. Saltsburg and M. Flytzani-Stephanopoulos, *Chem. Eng. J.*, 2003, **93**, 41
- 9 P. Serp, M. Corrias and P. Kalck, *Appl. Catal. A*, 2003, **253**, 337
- 10 A. Chambers, T. Nemes, N. Rodriguez and R. Baker, *J. Phys. Chem. B*, 1998, **102**, 2251
- 11 C. Pham-Huu, N. Keller, G. Ehret, L. Charbonniere, R. Ziessler and M. Ledoux, *J. Mol. Catal. A: Chem.*, 2001, **170**, 155
- 12 R. Vieira, C. Pham-Huu, N. Keller and M. J. Ledoux, *Chem. Commun.*, 2002, 954
- 13C. Pham-Huu, R. Vieira, M. Ledoux, L. Charbonniere and R. Ziessler, US Patent Application, US 2005/0103990A1
- 14 E. Garcia-Bordejé, I. Kvande, D. Chen and M. Rønning, *Adv. Mater.*, 2006, **18**, 1589
- 15 N. Jarrah, J. G. van Ommen and L. Lefferts, *J. Mater. Chem.*, 2004, **14**, 1590
- 16 N. A. Jarrah, J. G. van Ommen and L. Lefferts, *J. Mater. Chem.* 2005, **15**, 1946
- 17 M.-J. Ledoux and C. Pham-Huu, *Catal. Today*, 2005, **102-103**, 2
- 18 J. Sun, M. Iwasa, L. Gao and Q. Zhang, *Carbon*, 2004, **42**, 885
- 19 D. G. Duff, A. Baiker and P. P. Edwards, *J. Chem. Soc. Chem. Commun.*, 1993, 96
- 20 N. Hammer, I. Kvande, V. Gunnarsson, B. Tøtdal, X. Xu, D. Chen and M. Rønning, (submitted to *Catal. Today* 123 (2007) 245)
- 21 J. Guzman and A. Corma, *Chem. Commun.*, 2005, 743
- 22 E. D. Park and J. S. Lee, *J. Catal.* 1999, **186**, 1
- 23 B. Miremedi, T. Yadav, J. Z. Zhang and J. L. Falconer, *Chem. Commun.*, 2000, 1875
- 24 H.-S. Oh, H. Yang, C. K. Costello, Y. M. Wang, S. R. Bare, H. H. Kung and M. C. Kung, *J. Catal.* 2002, **210**, 375