Heterogeneous Catalysis

DOI: 10.1002/anie.200700499

Real-Time Control of a Catalytic Solid in a Fixed-Bed Reactor Based on In Situ Spectroscopy**

*Simona M. Bennici, Bas M. Vogelaar, T. Alexander Nijhuis, and Bert M. Weckhuysen**

Large-scale reactors loaded with catalytic solids are employed in a wide variety of chemical plants all over the world for the production of transportation fuels, bulk and fine chemicals, and pharmaceutical intermediates. These reactors are commonly controlled by monitoring the chemicals that are leaving the catalytic process. Once the product composition deviates from the desired one, process-control actions are taken to correct for this change. Important parameters for running most economically large-scale industrial reactors based on heterogeneous catalysis for bulk chemicals production are the reaction temperature and pressure, as well as the chemical composition and physical properties of the reaction mixture. Often such corrective scenarios are based on empirical models, which are obtained from plant test runs.[1]

A better approach is to monitor online the physicochemical phenomena of the catalyst material in the reactor by in situ spectroscopy,[2–5] and if possible to develop an "expert system" based on such spectroscopic measurements. Examples include coke formation (e.g., leading to active-site blocking), catalyst reduction (e.g., over-reduction of the catalyst surface), change of catalyst dispersion (e.g., metal-oxide clustering), migration of the oxide phase into the oxide support (e.g., metal-ion migration into the support oxide), and change of phase (e.g., solid-phase transformation during a redox reaction).[6–10] With such an expert system, it should be possible to make corrective actions once a spectroscopically visible change occurs in the catalyst material. This procedure is faster than monitoring the off-specification product leaving the reactor. In particular, for catalytic processes in which the catalyst is operated with alternating reactive and regenerative cycles, the use of in situ spectroscopy will have specific advantages. Indeed, monitoring the catalyst allows the possibility of dynamically tuning the cycles while the process runs. In an industrial context, where the feedstock composition of a process is not always identical and process disturbances are a reality, it would be especially advantageous to adapt the cycle times to the actual state of the "catalyst health" measured online with a robust in situ spectroscopic tool.

The use of online spectroscopic techniques to obtain data for process trend monitoring has already been applied in polymer science,[11,12] whereas to the best of our knowledge the only catalytic process in which in situ spectroscopy is applied as a means of process control is the production of 1,3-propanediol, which makes use of a homogeneous catalyst.[13] The novelty of the present work is linked to the use of in situ spectroscopy for the online control of different heterogeneous catalytic systems. Herein, we illustrate for the first time the concept of reactor control by online spectroscopy, by making use of two examples: an industrial-like supported chromium oxide (Cr/Al_2O_3) catalyst for propane dehydrogenation and an industrial-like vanadium phosphorus oxide (VPO) catalyst for the selective oxidation of *n*-butane to maleic anhydride.

In many industrial catalytic processes, coke deposition is the primary cause of catalyst deactivation.[6,14] Therefore, any means of directly measuring the amount of coke on the catalyst surface would be welcomed, especially for the purpose of online control of a chemical process. In this manner, one can keep the catalyst material in its optimal state in terms of activity, selectivity, and stability. For this reason, as a first example we have chosen a methodology to perform real-time quantitative coke analysis on a catalytic solid by using combined in situ Raman–UV/Vis spectroscopy with online calibration. The studied process is based on the Catofin propane dehydrogenation reaction over Cr/Al_2O_3 catalyst.[15–17] In this process, the catalyst dehydrogenates propane in a reactive cycle, during which coke is deposited on the catalyst and some of the chromium is reduced. In a regenerative cycle the chromium is reoxidized and the coke is burned with air. Currently, for the industrial Catofin process, the real state of the catalyst material is not taken into consideration and the cycle times are based on the overall performance of the unit. In this manner, gradual catalyst deactivation is compensated by an increase of the reaction temperature to maintain the desired conversion level. The gradual recovery of the activity declines during the lifetime of the catalyst as a result of migration of chromium (as Cr^{3+}) into

---

[*] Dr. S. M. Bennici,[+] Dr. Ir. B. M. Vogelaar,[$] Dr. Ir. T. A. Nijhuis,[#]
Prof. Dr. Ir. B. M. Weckhuysen
Inorganic Chemistry and Catalysis Group
Department of Chemistry
Utrecht University
P.O. Box 80083, 3508 TB Utrecht (The Netherlands)
Fax: (+31) 30-251-1027
E-mail: b.m.weckhuysen@chem.uu.nl

[+] Current address:
IRCELYON, UMR 5256 CNRS/Université Lyon 1
2 avenue Albert Einstein, 69626 Villeurbanne Cedex (France)

[$] Current address:
Albemarle Catalysts
P.O. Box 37650, 1030 BE Amsterdam (The Netherlands)

[#] Current address:
Department of Chemical Engineering
Technische Universiteit Eindhoven
P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

[**] The ASPECT (ACTS) and CW-VICI (NWO) funding schemes are kindly acknowledged for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

the alumina support, which occurs at the high temperatures commonly found in the hot spots of the reactor bed. In particular, the risk of permanent deactivation is very high during the regeneration step, as the exothermic coke combustion process may lead to hot spots in the catalyst bed.

An example of the controlled coke burn-off procedure is illustrated in Figure 1, in which coke and propane conversion levels are plotted versus time on stream, and the upper coke level set-point is also indicated. A clear relation was found between the presence of a certain amount of coke and the maximum propane conversion of the catalyst. The reaction and regeneration cycle times were automatically optimized as a function of reaction temperature and deactivation or coking rate: coke buildup appeared to be slower in the last two cycles at 550 and 560 °C, with a consequential increase of the reaction cycle time. This slower kinetics in the formation of coke could be related to the permanent catalyst deactivation after exposure at high temperature. The approximately 20 minutes necessary to regenerate the catalyst in the controlled coke burn-off step was slightly longer than the cycle time currently used in the chemical industry. However, the time during which propane could be dehydrogenated at conversions >20 % was much longer than in industrial practice (1 to 3 h in dependence on the reaction temperature). Note that in industrial reactors cycle times are typically shorter because of heat consumption by the endothermic reaction. The cycles performed at the highest temperatures (590 and 600 °C) presented some coke-level overshoots, which are related to the delay between the flushing and regeneration steps.

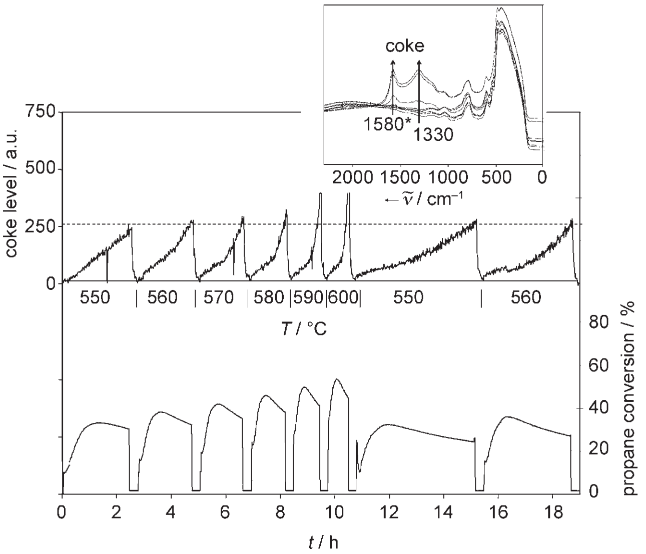

Figure 1. Real-time control of a Cr/Al_2O_3 propane dehydrogenation catalyst by online in situ Raman–UV/Vis spectroscopy. Propane conversion levels and amounts of coke are reported versus time on stream *t* for different reaction cycles and temperatures. The control system continues the reaction step until a given coke limit is reached (-----), after which the catalyst is automatically regenerated. Inset: in situ Raman spectra indicative of increasing amounts of coke during a propane dehydrogenation step.

In the developed methodology, the catalytic solid is automatically regenerated when the amount of coke exceeds a predefined level (determined from the intensity of the Raman peak at 1580 cm^{-1}, see insert in Figure 1).[15,16] The regeneration cycle is stopped automatically when the coke level drops below a given level. Furthermore, the oxygen concentration is gradually increased in four stages during regeneration, based on the actual level of coke. This results in a controlled coke burn-off, which reduces the formation of hot spots during catalyst regeneration and maintains the small amount of coke that seems to have a positive effect on the activation of the catalyst.[18] In the expert-system "control algorithm" used in this experiment, the coke level on the catalyst ("coke") was the control variable. The first propane dehydrogenation cycle (see Figure 1) was carried out at 550 °C until the coke level exceeded a predefined limit (250 in these experiments). Then, after a flushing step (1 min, 20 $mL\,min^{-1}$ He), the feed gas was switched to a diluted oxygen stream (2 % O_2/He) to kinetically limit the rate of coke burn-off until the coke level reached a second predefined limit (100 in these experiments). The regeneration procedure was prolonged at increasing oxygen concentrations of 4, 10, and 20 % to reach a lower coke limit in each stage (for the subsequent three regeneration stages the coke limit was fixed at 50, 20, and 10, respectively). After the last stage of regeneration a new propane dehydrogenation cycle was performed at increased temperature (>10 up to 600 °C) to verify the robustness of the proposed methodology by checking how it would behave in different conditions. Further details on the developed methodology can be found in the Supporting Information.

To illustrate the beneficial effect of controlled coke burn-off on the catalyst temperature, a series of experiments was performed in which the reaction temperature was measured online for "standard" and "controlled" activation procedures (see Figure 2). Ten reaction–regeneration cycles are reported for temperatures in the range of 550–600 °C. The regeneration

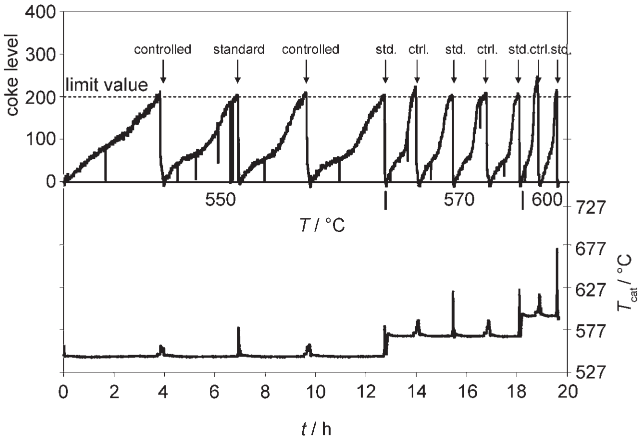

Figure 2. Beneficial effect of online spectroscopic control of a Cr/Al_2O_3 propane dehydrogenation catalyst. Catalyst temperature T_{cat} and coke buildup during ten reaction–activation cycles, with alternating "standard" regeneration (fixed duration, 20 % O_2) and "controlled" regeneration (gradually increasing O_2 concentration until the coke is removed), are shown.

procedure was alternated between controlled burn-off (as in Figure 1) and a standard regeneration procedure in air, which is currently employed in industrial propane dehydrogenation plants. In each case, at the beginning of the regeneration step we noticed a sharp increase in the temperature of the catalyst bed. During the controlled burn-off, the increment in this temperature was three times smaller than in the standard regeneration procedure (increments of 25 and 75 °C, respectively). The lower temperature reached during regeneration by controlled burn-off (Figure 2) proves the benefits of this regeneration procedure; the possibility of reducing the formation of hot spots in an industrial reactor, and thus suppressing the irreversible deactivation of the catalyst (that is, migration of Cr^{3+} into the Al_2O_3 support), could offer a simple way to extend the catalyst lifetime.

In a second example, we explored the selective oxidation of *n*-butane to maleic anhydride over an industrial-like VPO catalyst. This reaction is presently the only industrial process of light alkane oxidation on a large scale. The great importance of this reaction and the unique chemical–physical properties of the VPO-based catalysts make this system a hot research topic.[19] To better understand and improve the existing catalyst material and catalytic processes involved in maleic anhydride production, different and complementary physicochemical techniques have been used to provide information on the bulk and surface properties of the VPO system.[20–25] Among them, Raman spectroscopy demonstrated its power in detecting the transformation of the VPO precursor into the active VPO catalyst.[26–31] For this reason, the second example is based on the use of in situ Raman spectroscopy as a tool for the online control of the catalyst performance of the VPO system.

Two series of experiments were performed at a constant temperature of 400 °C, one devoted to control of the phase changes occurring by alternating reaction (React, $He/O_2/C_4H_{10} = 77:21:2$), oxidizing (Ox, $He/O_2 = 79:21$), and reducing (Red, $He/C_4H_{10} = 98:2$) steps, and the other to real-time control of the reversible transformation between $(VO)_2P_2O_7$ and $VOPO_4$ polymorphs, representative of five-valence vanadium.[22,32–35] In Figure 3 A and B, the Raman peak intensity at 989 cm^{-1} and the maleic anhydride concentration trends are reported as a function of the reaction time. Examples of Raman spectra acquired under different reaction conditions are reported in Figure 3 C, while the Raman spectra of the relatively pure phases present on the catalyst are shown in Figure 3 D.[26,28] The experiment was carried out by alternating the reaction, oxidizing, and reducing conditions for five React-Ox-React-Red cycles, as shown schematically at the bottom of Figure 3, where the presence/absence of butane and/or oxygen is reported. The increased/decreased intensity of the 989 cm^{-1} Raman peak was clearly reversible and, after each Ox or Red step, the maleic anhydride concentration could be rapidly reestablished when the catalyst was reexposed to React conditions.

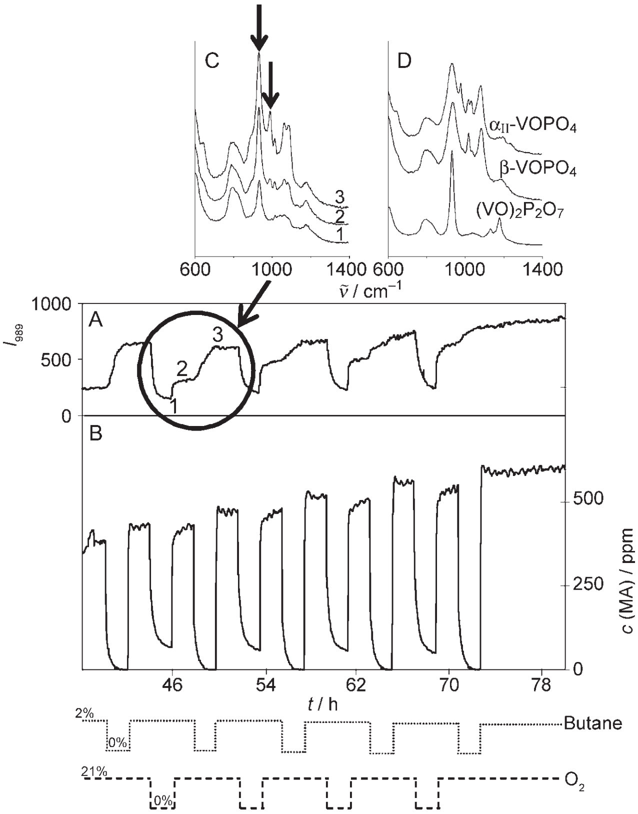

Figure 3. Catalytic performances and related in situ Raman spectra of a VPO catalyst as a function of feed gas composition. Raman intensities I_{989} of the 989 cm^{-1} peak (A) and maleic anhydride (MA) concentration (B) are shown as a function of time on stream during alternating reaction, oxidizing, and reduction conditions (indicated at the bottom). Examples of Raman spectra C) acquired 1) in the absence of oxygen, 2) during reaction, and 3) in the absence of butane, and D) of the pure-phase components acquired at 400 °C. The 932 and 989 cm^{-1} peaks are indicated with arrows.

Examples of the characteristic Raman spectra acquired in the different steps are reported in Figure 3 C. The possibility of acquiring real-time Raman spectra of the catalyst surface and at the same time analyzing the reaction products permitted observation of behavior peculiar to the VPO system: when the butane was removed from the reactant mixture (Ox condition), as expected the maleic anhydride concentration rapidly decreased to zero, while in the case of the Red condition (no O_2 present) the maleic anhydride concentration diminished to a value of only 60 ppm. This could be related to the fact that VPO operates as an oxidation catalyst by a Mars–van Krevelen mechanism, that is, in the absence of oxygen in the feed, the butane reacts to give maleic anhydride by reacting with lattice oxygen.[36,37] This behavior could also be deduced by observing the trend in maleic anhydride concentration during the React steps (Figure 3). In the React steps that followed the Ox treatments, the activity of the VPO catalyst was immediately reestablished and showed a constant trend, whereas after the Red treatments, an increasing trend in the maleic anhydride concentration could be observed that was related to the time request to reoxidize the catalyst and replace the lattice oxygen, in accordance with the reaction model presented by Gascón et al.[38]

The possibility of controlling the phase composition of the VPO catalyst by online in situ Raman spectroscopy is illustrated in Figure 4, which shows the intensity ratios of

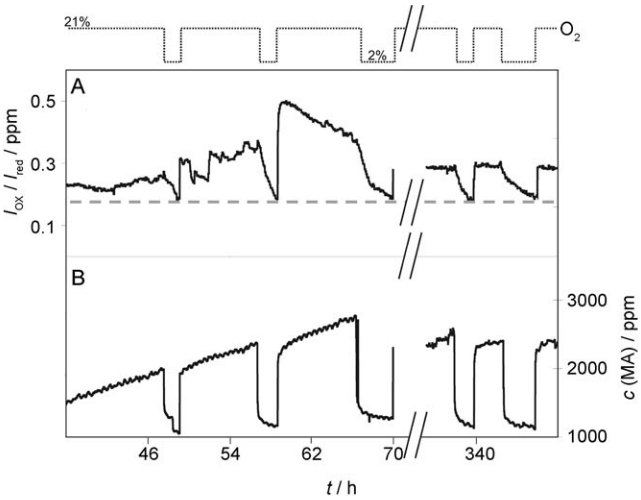

Figure 4. Real-time control of a VPO catalyst by online in situ Raman spectroscopy. Intensity ratios of the 989 and 932 cm^{-1} Raman peaks (A) and maleic anhydride (MA) production (B) are shown as a function of time on stream. The control system alternates reaction and lean oxygen conditions (indicated at the top) until the given I_{ox}/I_{red} limit is reached (-----).

the Raman bands at 989 and 932 cm^{-1} (I_{ox}/I_{red}, related to V^{5+} and V^{4+} phases, respectively)[39] for alternating reaction conditions, as shown schematically for the oxygen concentration as a function of time on stream. The lean oxygen steps were maintained until an arbitrarily chosen I_{ox}/I_{red} value of 0.19 was reached. Once this lower-limit value was obtained, the lean oxygen step was automatically terminated and the reaction condition restored. The first three cycles were affected by the changing of phases as a result of catalyst activation that, after 24 hours, was not yet complete,[40] as demonstrated by the global increasing trend in the maleic anhydride concentration (Figure 4B). After ten days of activation (400 °C, 30 mL min^{-1}, He/O$_2$/C$_4$H$_{10}$ = 77:21:2) the transformation towards $(VO)_2P_2O_7$ was complete, and the I_{ox}/I_{red} ratio and maleic anhydride concentration in the reaction steps showed a constant trend. The benefit of this online control of phase composition can be applied to prolong the life of the VPO catalyst, thus avoiding in time any dramatic phase changes that could not only decrease the catalyst performance, but also result in permanent catalyst deactivation, as explained above for the Cr/Al$_2$O$_3$ catalyst system.

On the basis of both examples it is clear that in situ spectroscopy of a catalytic solid can be used to control online the amount of a specific catalyst material as well as that of coke deposits during a reaction process. Based on this input the catalyst performance and its long-term stability can be automatically controlled. We expect that the developed methodology will be of general use for developing "catalyst diagnostics" strategies, in cases where catalyst deactivation processes are related to the blocking of active sites by coke, as well as by the formation of catalyst phases that contain less active and/or selective active sites. More specifically, based on the promising results for the two examples discussed, catalyst users and producers have now decided to perform test experiments in pilot-scale reactors, thus illustrating the potential industrial impact of this new spectroscopic approach.

Experimental Section

The first example dealing with propane dehydrogenation was conducted with a flow setup similar to the one already described by Nijhuis et al.,[15,16] at atmospheric pressure, in which Cr/Al$_2$O$_3$ catalyst (0.3 g) was positioned in a quartz fix-bed reactor and tested in cycles at different reaction temperatures (550–600 °C). The gas stream during the reaction step was composed of propane and He (2 and 20 mL min^{-1}, respectively). After each cycle of reaction the catalyst was regenerated in a flow of O$_2$/He, in which the concentration of O$_2$ was varied from 2 to 20 % in relation to the control system already described, or by standard regeneration in air. UV/Vis spectra of the catalyst surface were collected (with a time resolution of 1 s) by an Avantes AvaSpec-4 analyzer with four high-temperature diffuse reflectance probes (Ocean Optics/Micropack), focused at different heights on the catalyst bed. At the same time, a Kaiser RXN Raman spectrometer, equipped with a 532-nm diode laser and a noncontact objective, was used to analyze the sample with a total recording time of about 3 min (ten accumulations with a 3-s exposure time). The reactor outlet stream was analyzed online using an Interscience compact gas chromatography (GC) system, equipped with Porabond-Q and Molsieve 5A columns, capable of performing analyses within 1.3 min.

In the second example, the home-made VOHPO$_4$·0.5 H$_2$O catalyst precursor was prepared in organic medium[26] and activated in situ (reaction conditions: 400 °C, total flow: 30 mL min^{-1}, molar ratio: He/O$_2$/C$_4$H$_{10}$ = 77:21:2, 24 h) to form the activated VPO catalyst (mainly $(VO)_2P_2O_7$). The setup was the same as that described for the first example (see also the Supporting Information). However, the analysis of the product gases was performed within 170 s with an online Interscience compact GC system equipped with three capillary columns (Rtx-1.5u, PorbondU, and PorbondQ) and two different detectors (flame ionization and thermal conductivity detectors). All the pipes, starting from the exit of the reactor to the end of the catalytic line, were constantly heated at 100 °C to avoid condensation of the maleic anhydride. Ten Raman spectra were accumulated within 6 s exposure time for a total spectral recording time of about 5 min. A second series of experiments was performed on 0.3 g of catalyst, by alternating reaction condition (molar ratio: He/O$_2$/C$_4$H$_{10}$ = 77:21:2) and lean oxygen steps (molar ratio: He/O$_2$/C$_4$H$_{10}$ = 77:3:2).

Received: February 4, 2007
Revised: March 12, 2007

Keywords: heterogeneous catalysis · process control · Raman spectroscopy · supported catalysts · UV/Vis spectroscopy

---

[1] J. S. Lin, S. S. Jang, S. S. Shieh, M. Subramaniam, *Ind. Eng. Chem. Res.* **1999**, *38*, 4700.

[2] Examples of relevant textbooks are: a) *In Situ Spectroscopy in Heterogeneous Catalysis* (Ed.: J. F. Haw), Wiley-VCH, Weinheim, **2002**; b) *In Situ Spectroscopy of Catalysts* (Ed.: B. M. Weckhuysen), American Scientific, Stevenson Ranch, **2004**; c) J. W. Niemansverdriet, *Spectroscopy in Catalysis: An Introduction*, VCH, Weinheim, **1993**.

[3] For examples of relevant review papers, see: a) M. Hunger, J. Weitkamp, *Angew. Chem.* **2001**, *113*, 3040; *Angew. Chem. Int. Ed.* **2001**, *40*, 2954; b) B. M. Weckhuysen, *Chem. Commun.* **2002**, 97; c) B. M. Weckhuysen, *Phys. Chem. Chem. Phys.* **2003**, *5*, 4351; d) H. Topsøe, *J. Catal.* **2003**, *216*, 155; e) M. A. Banares,

Catal. Today **2005**, *100*, 71; f) I. E. Wachs, *Catal. Today* **2005**, *100*, 79.
[4] G. Mestl, *J. Mol. Catal. A* **2000**, *158*, 45.
[5] a) S. Bordiga, A. Damin, F. Bonino, G. Ricchiardi, C. Lamberti, A. Zecchina, *Angew. Chem.* **2002**, *114*, 4928; *Angew. Chem. Int. Ed.* **2002**, *41*, 4734; b) E. Groppo, C. Prestipino, F. Cesano, F. Bonino, S. Bordiga, C. Lamberti, P. C. Thune, J. W. Niemantsverdriet, A. Zecchina, *J. Catal.* **2005**, *230*, 98.
[6] E. H. Wolf, A. Alfani, *Catal. Rev. Sci. Eng.* **1982**, *24*, 329.
[7] C. H. Bartholomew, *Appl. Catal. A* **2001**, *202*, 17.
[8] M. L. Occelli, J. P. Olivier, A. Auroux, *J. Catal.* **2002**, *209*, 385.
[9] I. Rossetti, E. Bencini, L. Trentini, L. Forni, *Appl. Catal. A* **2005**, *292*, 118.
[10] J. Aßmann, D. Crihan, M. Knapp, E. Lundgren, E. Loffler, M. Muhler, V. Narkhede, H. Over, M. Schmid, A. P. Seitsonen, P. Varga, *Angew. Chem.* **2005**, *117*, 939; *Angew. Chem. Int. Ed.* **2005**, *44*, 917.
[11] P. D. Coates, S. E. Barnes, M. G. Sibley, E. C. Brown, H. G. M. Edwards, I. J. Scowen, *Polymer* **2003**, *44*, 5937.
[12] A. Tuchbreiter, J. Marquardt, B. Kappler, J. Honerkamp, M. O. Kristen, R. Mülhaupt, *Macromol. Rapid Commun.* **2003**, *24*, 47.
[13] P. R. Weider, J. B. Powell, K. D. Allen, J. Knifton, *Examination of the Hydroformylation of Ethylene Oxide by In Situ IR and the Development of a Commercial Route to 1,3-Propanediol*, presented at the 1st Conference on Operando Spectroscopy, Lunteren (The Netherlands), **2003**.
[14] J. R. Rostrup-Nielsen, *Catal. Today* **1997**, *37*, 225.
[15] T. A. Nijhuis, S. J. Tinnemans, T. Visser, B. M. Weckhuysen, *Phys. Chem. Chem. Phys.* **2003**, *5*, 4361.
[16] S. J. Tinnemans, M. H. F. Kox, T. A. Nijhuis, T. Visser, B. M. Weckhuysen, *Phys. Chem. Chem. Phys.* **2005**, *7*, 211.
[17] M. M. Bhasin, J. H. McCain, B. V. Vora, T. Imai, P. R. Pujadó, *Appl. Catal. A* **2001**, *221*, 397.
[18] S. T. Korhonen, S. M. K. Airaksinen, A. O. I. Krause, *Catal. Today* **2006**, *112*, 37.
[19] N. Ballarini, F. Cavani, C. Cortelli, S. Ligi, F. Pierelli, F. Trifirò, C. Fumagalli, G. Mazzoni, T. Monti, *Top. Catal.* **2006**, *38*, 147.
[20] G. W. Coulston, E. A. Thompson, N. Herron, *J. Catal.* **1996**, *163*, 122.
[21] M. P. Casaletto, G. Mattogno, M. A. Massucci, *Appl. Surf. Sci.* **2003**, *211*, 216.
[22] M. A. Carreon, V. V. Guliants, *Catal. Today* **2003**, *78*, 303.
[23] L. O'Mahony, T. Curtin, D. Zemlyanov, M. Mihov, B. K. Hodnett, *J. Catal.* **2004**, *227*, 270.
[24] M. Hävecker, A. Knop-Gericke, H. Bluhm, E. Kleimenov, R. W. Mayer, M. Fait, R. Schlögl, *Appl. Surf. Sci.* **2004**, *230*, 272.
[25] T. Giornelli, A. Löfberg, E. Bordes-Richard, *Thin Solid Films* **2005**, *479*, 64.
[26] F. Ben Abdelouahab, R. Olier, N. Guilhaume, F. Lefebvre, J. C. Volta, *J. Catal.* **1992**, *134*, 151.
[27] H. Knözinger, *Catal. Today* **1996**, *32*, 71.
[28] Z. Y. Xue, G. L. Schrader, *J. Phys. Chem. B* **1999**, *103*, 9459.
[29] F. J. Cabello Sanchez, R. P. K. Wells, C. Rhodes, J. K. Bartley, C. J. Kiely, G. J. Hutchings, *Phys. Chem. Chem. Phys.* **2001**, *3*, 4122.
[30] N. Topsøe, M. Anstrom, J. A. Dumesic, *Catal. Lett.* **2001**, *76*, 1.
[31] M. V. Martínez-Huerta, X. Gao, H. Tian, I. E. Wachs, J. L. G. Fierro, M. A. Bañares, *Catal. Today* **2006**, *118*, 279.
[32] R. Mallada, S. Sajip, C. J. Kiely, M. Menéndez, J. Santamaría, *J. Catal.* **2000**, *196*, 1.
[33] M. Conte, G. Budroni, J. K. Bartley, S. H. Taylor, A. F. Carley, A. Schmidt, D. M. Murphy, F. Girgsdies, T. Ressler, R. Schlögl, G. J. Hutchings, *Science* **2006**, *313*, 1270.
[34] X. Huang, B. Chen, B. Liu, P. L. Silveston, C. Li, *Catal. Today* **2002**, *74*, 121.
[35] D. Wang, H. H. Kung, M. A. Barteau, *Appl. Catal. A* **2000**, *201*, 203.
[36] M. J. Lorences, G. S. Patience, R. Cenni, F. Díez, J. Coca, *Catal. Today* **2006**, *112*, 45.
[37] M. Ruitenbeek, A. J. van Dillen, F. M. F. de Groot, I. E. Wachs, J. W. Geus, D. C. Koningsberger, *Top. Catal.* **2000**, *10*, 241.
[38] J. Gascón, R. Valenciano, C. Téllez, J. Herguido, M. Ménendez, *Chem. Eng. Sci.* **2006**, *61*, 6385.
[39] M. Abon, J. M. Herrmann, J. C. Volta, *Catal. Today* **2001**, *71*, 121.
[40] V. V. Guliants, J. B. Benziger, S. Sundaresan, N. Yao, *Catal. Lett.* **1995**, *32*, 379.