Catalysis Letters Vol. 96, Nos. 1–2, July 2004 (© 2004)

Synthesis and microscopic characterization of dendrimer-derived Ru/Al_2O_3 catalysts

Gwendoline Lafaye, Christopher T. Williams*, and Michael D. Amiridis**

Department of Chemical Engineering, Swearingen Engineering Center, University of South Carolina, Columbia SC 29208

Received 27 January 2004; accepted 14 April 2004

Fourth generation poly(amidoamine) dendrimers have been used to template and stabilize Ru nanoparticles in solution. UV-visible spectroscopic results indicate that Ru^{3+} ions from a $RuCl_3$ precursor can complex with functional groups within the dendrimer structure. Subsequent reduction of the Ru^{3+} ions yields finely dispersed Ru nanoparticles with a narrow particle size distribution. These dendrimer-stabilized nanoparticles were deposited onto an alumina support and thermally activated to remove the dendrimer "shell", as indicated by *in situ* Fourier transform infrared (FTIR) spectroscopic measurements. High resolution transmission electron microscopy (HRTEM) measurements indicate that the resulting Ru/Al_2O_3 catalyst has a smaller mean metal particle size and a narrower particle size distribution than a similar catalyst prepared by a traditional wet impregnation from the same $RuCl_3$ precursor.

KEY WORDS: PAMAM dendrimer; ruthenium; nanoparticles; catalysts.

1. Introduction

Supported catalysts play a central role in industrial chemical processes, as well as in pollution abatement. In such catalysts, the average particle size and particle size distribution of the supported nanoparticles is often critical for controlling the catalytic performance (i.e., activity and/or selectivity). Recently, dendrimers have been successfully used to template and stabilize metal nanoparticles in solution [1–5]. Dendrimers are a special class of hyperbranched polymers with a specific molecular structure and controllable size. To date, poly(amidoamine) (PAMAM) dendrimers have been the most widely used dendrimers for nanoparticle synthesis. PAMAM dendrimers contain interior tertiary amine groups that can effectively chelate metal ions. Such metal ions may be subsequently reduced to form encapsulated metal particles that can be highly stable in solution [2,3]. Since the same number of chelating sites is present in all dendrimer molecules, this process should in principle yield monodispersed metal particles.

The use of dendrimers as vehicles for synthesis of supported nanoclusters of metals and metal oxides has been reported in the literature [6,7]. For example, fifth generation poly(propylene)imine dendrimers have been successfully used as macrochelating agents to produce well-dispersed CuO nanoclusters embedded in a silica sol–gel matrix [6]. More recently, PAMAM dendrimer-stabilized platinum nanoparticles have been used as synthetic precursors for Pt/SiO_2 catalysts [8]. In this case the Pt nanoparticles were delivered intact to the support after dendrimer removal, resulting in catalysts that were active for CO oxidation and toluene hydrogenation. Supported Ru catalysts are also well known to be active for a variety of important applications [9–13], and in principle the dendrimer synthetic route could provide a means of controlling Ru particle size. However, there are very few studies that have investigated the interaction of Ru with PAMAM dendrimers. Crooks and collaborators have demonstrated that Ru^{3+} from an $[Ru(NH_2Cl]Cl_2$ precursor can be complexed with the interior amine groups of hydroxyl-terminated PAMAM dendrimers [2,3]. However, there was no evidence provided to suggest that such complexed Ru^{3+} could be effectively reduced to form monodisperse nanoparticles. Furthermore, it is unclear whether such Ru nanoparticles would exhibit long-term stability in solution, as is now well established for dendrimer-stabilized Pt nanoparticles [1–3,8].

In the present study, we utilize Ru nanoparticles stabilized in fourth generation hydroxyl-terminated PAMAM dendrimers to synthesize a Ru/Al_2O_3 catalyst. Ultraviolet–visible (UV–vis) and Fourier transform infrared (FTIR) spectroscopies are used to monitor the Ru-dendrimer complexation step and supported catalyst activation procedure, respectively. The mean Ru particle size and particle size distribution are determined through analysis of high resolution transmission electron microscopy (HRTEM) images. The results show for the first time that this approach can be used to produce monodispersed Ru nanoparticles in solution, and that these nanoparticles can be delivered to a typical catalyst support surface. The resulting catalysts exhibit a smaller

---

*To whom correspondence should be addressed.
E-mail: willia84@engr.sc.edu
**To whom correspondence should be addressed.
E-mail: amiridis@engr.sc.edu

1011-372X/04/0700–0043/0 © 2004 Plenum Publishing Corporation

mean particle size and a narrower particle size distribution than what is obtained via a traditional wet impregnation synthesis using the same Ru salt precursor.

2. Experimental

2.1. Materials

Hydroxyl-terminated fourth-generation (G_4OH) poly(amidoamine) (PAMAM) dendrimer was obtained as 10 wt% methanol solution (Aldrich). Prior to use, the methanol was removed under N_2 flow at room temperature. $RuCl_3$ was purchased from Alfa Aesar and used as received. Water purified to 18 MΩ cm (Milli-Q) was used to prepare all the aqueous solutions. The γ-alumina support (Alfa Aesar, surface area = 45 $m^2\ g^{-1}$) was calcined in air for 4 h at 500 °C prior to its use.

2.2. UV–visible spectroscopy

UV–vis spectra were acquired using a Shimadzu UV-2101PC scanning spectrophotometer. 18 MΩ cm water was used as a reference for all measurements.

2.3. Electron microscopy

HRTEM studies were performed on a Philips CM 120 instrument operating at 120 kV. The Ru-G_4OH PAMAM solution was dried onto a copper grid with a carbon support film. The Ru/Al_2O_3 catalyst particles were ultrasonically dispersed in ethanol prior to their deposition onto the copper grid. Energy dispersive X-ray (EDX) analysis of ruthenium was carried out in the nanoprobe mode, with a probe diameter of 5.0–7.0 nm.

2.4. Fourier transform infrared (FTIR) spectroscopy

In situ FTIR spectra were recorded using a Nicolet Nexus 670 spectrometer, with a resolution of 2 cm^{-1} (64 scans). Catalyst samples were prepared as self-supporting wafers with a diameter of 12 mm and a thickness of approximately 40 mg/cm^2 . These samples were placed in a variable temperature gas flow transmission cell (length of 10 cm) that has been described in detail elsewhere [14]. Total gas flowrates were maintained at 70 mL/min.

3. Results and discussion

The preparation of dendrimer-stabilized Ru nanoparticles was performed under an inert atmosphere (i.e., flowing N_2) in order to avoid the oxidation of Ru. The aqueous $RuCl_3$ precursor solution was added to a dilute aqueous solution of fourth-generation, hydroxyl-terminated (G_4OH) PAMAM dendrimer. The total metal-ion-per-dendrimer ratio in the mixed solution was fixed at 40 : 1 resulting in dendrimer and $RuCl_3$ concentrations of 9.35×10^{-5} and 3.74×10^{-3} mol L^{-1}, respectively. UV–vis studies were performed in order to follow the reaction between these two compounds. Prior to analysis the mixture needed to be diluted by almost a factor of two. Figure 1 shows the UV–vis absorption spectra of the $RuCl_3$ solution in the absence (1a) and presence (1b) of the dendrimer. In the absence of the dendrimer, the spectrum of the freshly prepared aqueous solution of $RuCl_3$ consists of two peaks at 316 and 415 nm. These two peaks can be assigned to ruthenium complexed with water and/or chlorine, in agreement with the work of Seddon and Seddon [15]. They reported that upon hydrolysis $RuCl_3$ may yield a large number of different ruthenium complexes, with characteristic UV–vis peaks in the 270–500 nm range.

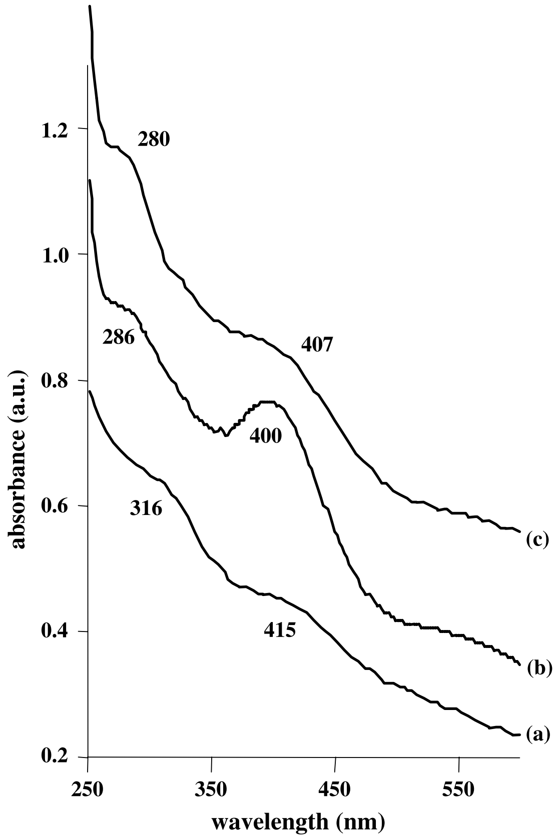

Figure 1. UV–vis spectra of: (a) aqueous 2×10^{-3} mol/L $RuCl_3$ solution, (b) aqueous 2×10^{-3} mol/L $RuCl_3$ and 4.95×10^{-5} mol/L G_4OH-PAMAM dendrimer solution immediately after initial mixing, (c) same solution as (b) maintained under an inert atmosphere 3 days after initial mixing.

Upon addition of the G_4OH PAMAM dendrimer to the $RuCl_3$ solution, the two peaks at 316 and 415 nm disappear within minutes, while two new peaks emerge at 286 and 400 nm. With increased time, the peak at 400 nm decreases slowly in intensity and shifts to 407 nm, while the peak at 286 nm increases in intensity and shifts to 280 nm. A characteristic absorption peak at 277 nm has been previously assigned to a $Ru(NH_3)_6^{3+}$ complex [2].

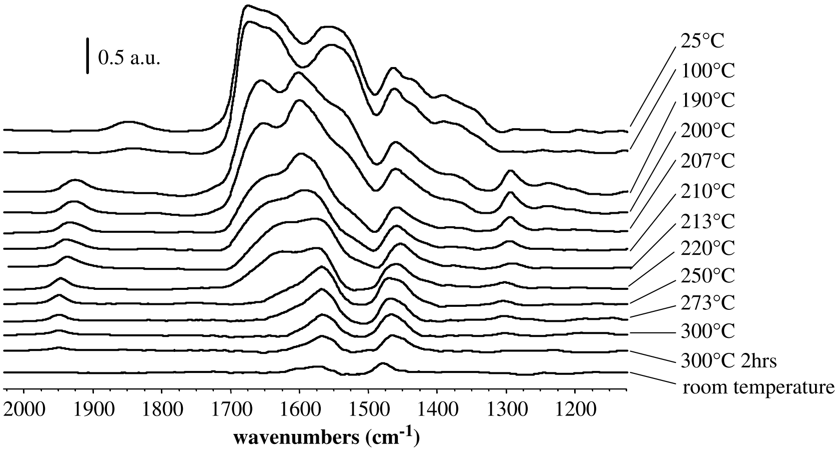

Figure 2. Fourier-transform infrared spectra of the dendrimer-derived 1% Ru/Al_2O_3 catalyst obtained at elevated temperatures in flowing H_2. See text for details.

Consequently, the 280 nm peak can be assigned to a Ru-amine type of complex formed within the dendrimer structure. The additional peak at approximately 400 nm suggests the presence of a second ligand in the complex (probably water). These results indicate that most of the Ru^{3+} ions in the initial solution are extracted into the dendrimer interiors and complex with the available amine groups, in agreement with previous literature reports [2,3]. The spectral changes observed suggest that this process is taking place in two steps. The first is fast and is completed within the first few minutes, while the second takes approximately 3 days.

After completion of the complexation process (i.e., 3 days) under inert atmosphere, a reduction of the Ru ions was performed by bubbling hydrogen through the solution for 1 h at room temperature. No precipitates were observed during this step and the reduced solution was stable (under inert atmosphere) for at least 30 days. In contrast, control experiments involving the reduction of a non-dendrimer containing aqueous solution of $RuCl_3$ led to visible black precipitates of metallic Ru. These results are consistent with the notion that most Ru^{3+} ions in the original solution were complexed inside the dendrimer structure.

Analysis of HRTEM images of the reduced Ru particles deposited on the copper grid directly from the aqueous Ru-G_4OH PAMAM solution (figure 3a) indicates a narrow particle size distribution and a roughly spherical shape. Measurements of 200 randomly selected particles yield a mean diameter of 1.2 nm. EDX analysis of the individual particles unambiguously identifies them as consisting of ruthenium. To our knowledge, this is the first direct evidence that the dendrimer synthetic approach can lead to Ru nanoparticles with high monodispersity.

The Ru-G_4OH PAMAM nanocomposites were deposited onto a calcined alumina support via wet impregnation at room temperature. In order to expose the Ru nanoparticles, the dendrimer "shell" is removed by thermal treatment. It has been shown in the literature that oxidation followed by reduction with H_2 results in sintering of Ru particles on the support [16–21]. As a result we have used a direct hydrogen treatment for the present studies. The treatment temperature in H_2 was chosen based on results of *in situ* FTIR spectroscopic measurements conducted during thermal removal of the dendrimer. Figure 2 shows spectra obtained during heating of a freshly impregnated sample to progressively higher temperatures in flowing H_2. The spectra are referenced to the background taken at room temperature of the dendrimer-free support.

The absorption bands observed in the 1500–1700 cm^{-1} region at room temperature can be assigned unambiguously to vibrations of functional groups present in the G_4OH dendrimer. The pear of overlapping peaks at around 1640 and 1670 cm^{-1} correspond to C=O stretching (i.e., amide I) vibrations [22], while the peak centered at approximately 1550 cm^{-1} is assigned to the C–N stretching/C–N–H bending (amide II) vibration [23,24]. In addition, the features clustered around 1450 cm^{-1} are assigned to CH_2 scissoring vibrations [23–25]. When the temperature is increased, the split amide I peaks join into one peak centered at 1650 cm^{-1}. In addition, one peak around 1290 cm^{-1} appears, which corresponds to a secondary amide (amide III) vibration [23,24]. This compound is quickly removed from the surface. Thus, the spectra indicate that the amide bonds of the PAMAM dendrimers are destroyed when the temperature reaches 250 °C, while few coke-type species (coke band ~1580–1540 cm^{-1} [26,27]; aliphatic residue ~1470 cm^{-1} [28]) remain on the support surface after 2 h of hydrogen treatment at 300 °C.

Given the results of the infrared studies, the 1 wt% Ru/Al_2O_3 catalyst was reduced under flowing hydrogen for 2 h at 300 °C in order to ensure maximum removal

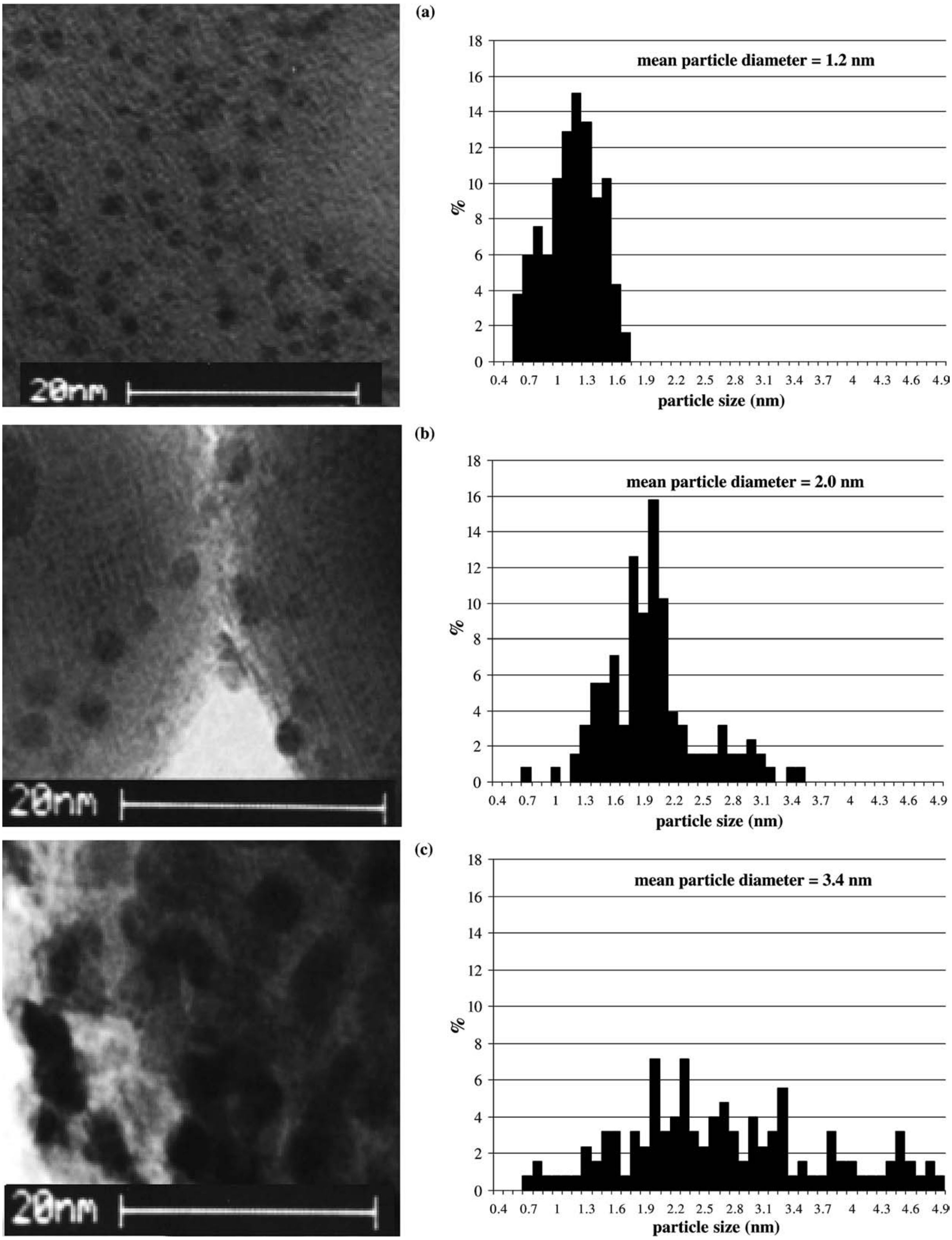

Figure 3. HRTEM images and metal particle size distributions of (a) the Ru-G_4OH PAMAM dendrimer nanocomposite precursor, (b) a 1%wt Ru/Al_2O_3 catalyst prepared from the Ru-G_4OH PAMAM dendrimer nanocomposite precursor and reduced for 2 h at 300 °C and (c) a 1%wt Ru/Al_2O_3 catalyst prepared directly from a $RuCl_3$ precursor and reduced for 2 h at 300 °C.

of dendrimer. For comparison with the dendrimer-derived catalyst, a 1 wt% Ru/Al_2O_3 catalyst was also prepared by a traditional wet impregnation method using the same $RuCl_3$ precursor and reduced under the same conditions. HRTEM images of these two catalysts are shown in figure 3b and c. The dendrimer-derived sample consists of small well-dispersed particles (mean diameter = 2.0 nm) on the alumina surface (figure 3b). The Ru particles maintain a narrow size distribution and a roughly spherical shape. Nevertheless, the mean particle size is approximately 50% larger than obtained for the dried Ru-G_4OH PAMAM solution (figure 3a), indicating that some sintering is taking place during the hydrogen treatment step needed for the dendrimer removal. A significantly larger mean particle size (3.4 nm) and a much wider particle size distribution was observed with the conventionally prepared Ru/Al_2O_3 catalyst (figure 3c).

4. Conclusions

Dendrimer-stabilized Ru nanoparticles have been used to prepare an alumina-supported ruthenium catalyst. This material exhibits a smaller mean particle size and a much narrower particle size distribution than a corresponding catalyst prepared through a conventional wet impregnation procedure directly from the same $RuCl_3$ precursor. No attempt was made at this point to optimize the dendrimer removal procedure, which in the present case resulted in mild aggregation of the Ru nanoparticles on the support. Nevertheless, the present findings suggest that the dendrimer route to nanoparticle synthesis provides a novel means for the preparation of supported ruthenium catalysts, and offers superior control of the size characteristics of the resulting supported metal particles when compared to conventional wet impregnation.

Acknowledgments

We gratefully acknowledge the National Science Foundation (NSF Award CTS-0103135) for financial support of this work. We thank Eric Gautron, from the Service de Microscopie Electronique of the University of Poitiers (France), who conducted the HRTEM measurements. G. Lafaye also expresses her gratitude to the French Government for the financial support provided through the Lavoisier Postdoctoral Grant.

References

[1] R.M. Crooks, M. Zhao, L. Sun, V. Chechik and L.K. Yeung, Acc. Chem. Res. 34 (2001) 181.
[2] M. Zhao, Ph.D. Dissertation, Texas A&M University, December 1999.
[3] R.M. Crooks, B.I. Lemon, III, L. Sun, L.K. Yeung and M. Zhao, Top. Curr. Chem. 21 (2001) 81.
[4] Y.M. Chung and H.K. Rhee, Catal. Lett. 85 (2003) 159.
[5] R.W.J. Scott, A.K. Datye and R.M. Crooks, J. Am. Chem. Soc. 123 (2003) 3708.
[6] R. Velarde-Ortiz and G. Larsen, Chem. Mater. 14 (2002) 858.
[7] A.S.H. King and L.J. Twyman, J. Chem. Soc. Perkin Trans. 1 (2002) 2209.
[8] H. Lang, R.A. May, B.L. Iversen and B.D. Chandler, J. Am. Chem. 125 (48) (2003) 14832.
[9] P. Gallezot and D. Richard, Catal. Rev. 40 (1998) 81.
[10] A. Wörner, C. Friedrich and R. Tamme, Appl. Catal. A 245 (2003) 1.
[11] S. Sayan, M. Kantcheva, S. Suzer and D.O. Uner, J. Mol. Struc. 480 (1999) 241.
[12] E. Guglielminotti, F. Boccuzzi, M. Manzoli, F. Pinna and M. Scarpa, J. Catal. 192 (2000) 149.
[13] E. Kikuchi, M. Matsumoto, T. Takahashi, A. Machino and Y. Morita, Appl. Catal. 10 (1984) 251.
[14] D.K. Captain and M.D. Amiridis, J. Catal. 184 (1999) 377.
[15] E.A. Seddon and K.R. Seddon, *The Chemistry of Ruthenium* (Elsevier, Amsterdam 1984).
[16] L.C. Hoang, J.C. Menezo, C. Montassier and J. Barbier, Bulletin de la Société chimique de France 4 (1991) 491.
[17] J. Wellenbuscher, M. Muhler, W. Mahdi, U. Sauerlandt, J. Schutze, G. Ertl and R. Schlogl, Catal. Lett. 25 (1–2) (1994) 61.
[18] G.C. Bond and J.C. Slaa, J. Mol. Catal. 89 (1–2) (1994) 221.
[19] G.C. Bond and J.C. Slaa, J. Mol. Catal. 96 (1995) 163.
[20] V. Mazzieri, F. Coloma-Pascual, A. Arcoya, P.C. L'Argentière and N.C. Fígoli, Appl. Surf. Sci., 210 (3–4) (2003) 222.
[21] C. Elmasides, D.I. Kondarides, W. Grünert and X.E. Verykios, J. Phys. Chem. B 103 (1999) 5227.
[22] K.P. Ishida and P.R. Griffiths, Appl. Spectrosc. 47 (5) (1993) 584.
[23] D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli, *Infrared and Raman Characteristic Frequencies of Organic Molecules* (Academic Press, 1991).
[24] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd ed. (Wiley, Chichester, 2001).
[25] A. Manna, T. Imae, K. Aoi, M. Odada and T. Yogo, Chem. Mater. 13 (2001) 1674.
[26] B.W.L. Southward, J.S. Vaughan and C.T. O'Connor, J. Catal. 153 (1995) 293.
[27] J. Datka, Z. Sarbak and R.P. Eischens, J. Catal. 145 (1994) 544.
[28] J. Yang, P.G. Stansberry, J.W. Zondlo and A.H. Stiller, Fuel Process. Technol. 79 (2002) 207.