



Alkene dicarbonyl complexes of Ru in a zeolite matrix Formation and catalytic properties

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

The surface chemistry of well-defined Ru carbonyl complexes on dealuminated Y zeolites has been studied by in situ FTIR spectroscopy coupled with on-line analysis of the gas phase. Coordinatively unsaturated Ru subcarbonyls (mono- and dicarbonyls), obtained by a controlled decarbonylation of Ru tricarbonyl on the surface, react with olefins as ethylene and propylene in the gas phase and form well-defined olefin dicarbonyl complexes. The IR wavenumbers of the dicarbonyl $[\text{Ru}^{\text{II}}(\text{CO})_2]^{2+}$ are shifted from 2084 to 2017 cm^{-1} in the uncoordinated dicarbonyl to 2064 and 1994 cm^{-1} in the ethylene complex $[\text{Ru}^{\text{II}}(\text{CO})_2(\text{C}_2\text{H}_4)]^{2+}$ and to 2060 and 1993 cm^{-1} in the propylene complex $[\text{Ru}^{\text{II}}(\text{CO})_2(\text{C}_3\text{H}_6)]^{2+}$. The olefin carbonyl complexes are active and highly selective catalysts for the dimerization of ethylene to *n*-butene. At 170 °C the selectivity to *n*-butene is >95%.

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1. Introduction

As a catalytically active noble metal, ruthenium has attracted considerable attention for long time. It has been used, for the hydrogenation of CO and CO₂ (see e.g. [1]), the photo-catalytic splitting of water and, recently, it has been found to be a promising candidate for the ammonia production from molecular nitrogen and hydrogen. Ru complexes are also active catalysts in olefin reactions as selective di- or oligomerization, metathesis reactions, and hydroformylation [2,3]. An investigation of well-defined surface complexes of Ru active in these reactions might be helpful for charac-

terization and optimization of the catalysts. With this intention, Ugo and coworkers have studied the surface chemistry of well-defined Ru carbonyl complexes on silica [4].

Highly dealuminated Y zeolite (US-Ex, DAY) has been found to be a unique material to stabilize well-defined cationic surface complexes of transition metals [5]. These complexes are probably localized at cation positions in the supercage near the remaining Al atoms in the zeolite framework. Due to the high Si:Al ratio, the complexes are isolated from each other like in a matrix and there are no water or other cations in the micropores to interact with. These properties result in unusually sharp ($\nu_{1/2} \leq 5 \text{ cm}^{-1}$) infrared bands of the attached complexes, which allows a detailed structural characterization.

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As an example we obtained [6,7] well-defined surface complexes of Rh^{I} with molecular nitrogen, that are stable in a flow of nitrogen at temperatures up to 250 °C. The dinitrogen complexes were characterized as a Rh bis-dinitrogen complex $[\text{Rh}^{\text{I}}(\text{N}_2)_2]^+$ and a mixed carbonyl dinitrogen complex $[\text{Rh}^{\text{I}}(\text{CO})\text{N}_2]^+$.

The chemistry of ruthenium compounds in dealuminated zeolites is considerably more abundant than that of rhodium compounds [8,9]. Similar to the homogeneous complex chemistry, Ru forms well-defined tricarbonyls with meridional and facial structure on the surface and their mutual conversion in dependence on the experimental conditions could be followed IR-spectroscopically. As for Rh, upon decarbonylation, coordinatively unsaturated subcarbonyls (mono- and dicarbonyls) are formed, which are highly reactive and form well-defined complexes with different ligands. bis-Dinitrogen, $[\text{Ru}^{\text{II}}(\text{N}_2)_2]^{2+}$ ($\nu(\text{N}_2) = 2207$ and 2173 cm^{-1}), and mixed carbonyl dinitrogen complexes, $[\text{Ru}^{\text{II}}(\text{CO})(\text{N}_2)]^{2+}$ ($\nu(\text{N}_2) = 2218$, $\nu(\text{CO}) = 2023 \text{ cm}^{-1}$), are found to be stable in a nitrogen atmosphere at 250 °C. In addition to these complexes, Ru forms further dinitrogen complexes stable at room temperature. In particular, a *trans*-dicarbonyl dinitrogen complex, $[\text{Ru}^{\text{II}}(\text{CO})_2(\text{N}_2)]^{2+}$ ($\nu(\text{N}_2) = 2231$, $\nu(\text{CO}) = 2129$ and 2061 cm^{-1}), is stable even in the presence of CO and the absence of N_2 in the gas phase. These surface dinitrogen complexes do not have precedents in the complex chemistry.

In the present work, the reactivity of the zeolite attached Ru complexes towards alkenes has been studied.

2. Experimental

The support DAY (DEGUSSA, Germany) is a Y zeolite with a Si:Al ratio ≥ 100 , dealuminated by exchange of the Al atoms in the framework by treating the NaY with SiCl_4 . The sample Ru/DAY (1 wt.% Ru) has been prepared by impregnation of the support with the appropriate amount of RuCl_3 in ethanolic solution and drying the sample at 80 °C in air. Additional pretreatment was performed directly in the infrared cell. It consisted usually in a carbonylation in a flow of 5% CO/Ar at 250 °C. A chlorine free sample Ru_3/DAY (1 wt.% Ru) has been obtained for comparison by im-

pregnation of the support with $\text{Ru}_3(\text{CO})_{12}$ in ethanolic solution and drying the sample at 60 °C in air.

Transmission IR studies were performed with self-supported wafers using a special infrared cell made from stainless steel for in situ measurements up to 400 °C and 5000 kPa, connected to a gas flowing system, which allows a fast variation of the feed gas. The IR cell was used as catalytic reactor, thus allowing the simultaneous characterization of the surface species. The gas flow through the cell was controlled using electronic flow controllers. The gases used were of high purity (AGA Gas GmbH) and were additionally purified by OXYSORB units (Messer Griesheim GmbH). The spectra were recorded with a Perkin-Elmer Paragon 1000 FTIR spectrometer at a resolution of 2 cm^{-1} . To obtain a sufficient signal-to-noise ratio, 10–50 scans were co added.

The gas phase has been analysed after the reaction in the infrared cell both in a pulse regime with an quadruple mass spectrometer (Balzers QMS 125) for fast response and at stationary conditions using a gas chromatograph (Shimadzu GC-17A) equipped with a gas sampling system, a Porabond Q capillary column and a FID detector.

3. Results and discussion

3.1. Formation of unsaturated reactive Ru carbonyl intermediates

The carbonylation of Ru/DAY and the subsequent controlled decarbonylation have been described previously [9]. During carbonylation in a CO containing atmosphere at elevated temperature a Ru tricarbonyl is formed with IR-bands at 2147, 2087 and 2084 cm^{-1} (Fig. 1a), in which the CO ligands are arranged in a facial structure [9]. The smaller band at 2046 cm^{-1} is assigned to a tricarbonyl isomer with meridional structure, that can be reversibly formed from the facial tricarbonyl [9].

As the first step in the decarbonylation process, a well-defined dicarbonyl with wavenumbers at 2084 and 2017 cm^{-1} is formed on the surface (Fig. 1b). Intensity and sharpness of the bands allow the resolution of the ^{13}C O satellite band at 1986 cm^{-1} even with the 1.1% ^{13}C O from natural abundance. Upon further decarbonylation in a hydrogen containing atmosphere

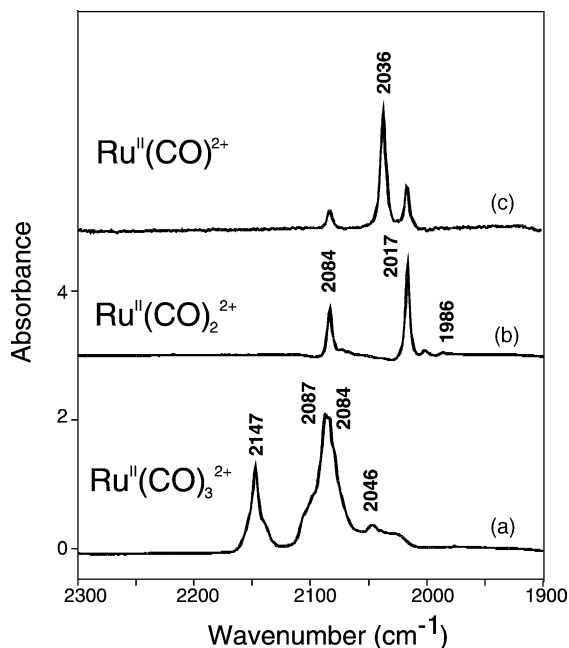


Fig. 1. FTIR spectra of Ru/DAY after carbonylation in 5% CO/Ar at 250 °C (a) after a subsequent decarbonylation in 50% H₂/N₂ at 300 °C and (b) after further decarbonylation in 100% H₂ at 250 °C (c).

this dicarbonyl transforms in to a monocarbonyl with a carbonyl band at 2036 cm⁻¹. The first decarbonylation step to the dicarbonyl is accelerated by hydrogen, but occurs also in an inert gas flow. On the other hand, the

formation of the monocarbonyl requires a participation of hydrogen. The mass-spectroscopic on-line analysis of the gas phase allowed an insight into the chemical reaction during this decarbonylation. As main products CO, CO₂ and, especially during the formation of the monocarbonyl, CH₄ could be identified. Apart from desorption, CO is disproportionated to CO₂ and hydrogenated to CH₄.

The subcarbonyls are coordinatively unsaturated and highly reactive. They are, therefore, the starting point to the formation of other well-defined surface species as dinitrogen complexes [8,9] or olefin carbonyl complexes as outlined in the following paragraph.

3.2. Formation of olefin carbonyl complexes

The interaction of olefins with the well-defined surface complexes of Ru was followed IR spectroscopically to study the formation and the properties of new surface complexes. As an example, Fig. 2 shows the results of the interaction of C₂H₄ with a Ru/DAY sample subsequent to the formation of Ru dicarbonyl (2084 and 2017 cm⁻¹) and Ru dinitrogen carbonyl complex [Ru^{II}(CO)(N₂)]²⁺ (2219 and 2024 cm⁻¹) on the surface (Fig. 2a). Already one pulse C₂H₄ (1 ml to the nitrogen flow of 100 ml/min) results in a significant decrease of the intensity of the dicarbonyl bands and a new doublet at 2064 and 1994 cm⁻¹ appears

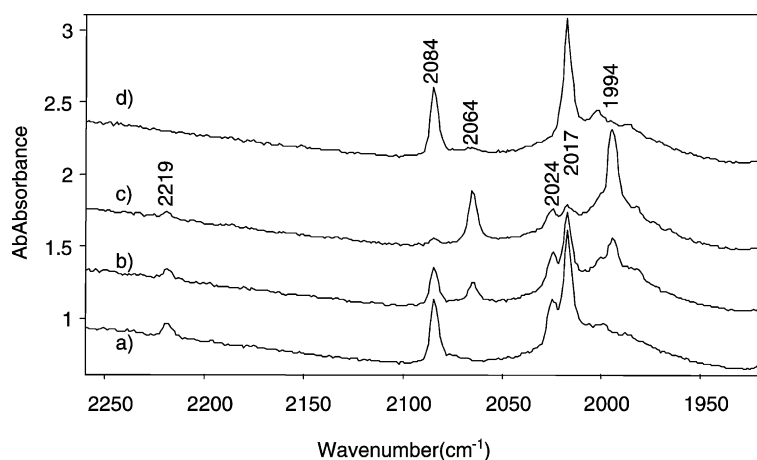


Fig. 2. FTIR spectra of Ru/DAY in a flow of 100 sccm nitrogen at 150 °C after the formation of the mixed carbonyl dinitrogen complex, [Ru^{II}(CO)(N₂)]²⁺ (a), the subsequent addition of one pulse (1 ml) (b) and two pulses (c) C₂H₄ to the flow of nitrogen, and after additional 20 min flow of nitrogen (d).

(Fig. 2b). The intensity of the bands due to the dinitrogen carbonyl complex changes, at the same time, only marginally. After two pulses C_2H_4 the initial dicarbonyl doublet is almost completely substituted by the new one, whereas the band intensity of the dinitrogen carbonyl decreases without the formation of new species (Fig. 2c). It is interesting to note that only the dicarbonyl reacts with the olefin, whereas the dinitrogen carbonyl complex does not add ethylene. The reason for the different behavior is not obvious. The two CO ligands in the dicarbonyl are arranged in a local C_{2v} symmetry with an estimated bond angle of about 113° [9], and the addition of C_2H_4 does not change this angle significantly. The structure of the dinitrogen carbonyl complex is, on the other hand, not known, but possibly the dinitrogen ligand is differently arranged and/or saturates more coordinative vacancies. The transformation of the dicarbonyl is reversible: in an nitrogen flow without further C_2H_4 addition the original Ru-dicarbonyl is formed again (Fig. 2d). As no additional CO is admitted during the experiment, one can conclude that the olefin does not react with the co-ordinated CO at these conditions. The same reversible transformation of the dicarbonyls is observed also in a flow of hydrogen.

Fig. 3 shows the IR spectra in the carbonyl stretching region during a continuous addition of ethylene or propylene to the Ru dicarbonyl in a nitrogen or hydrogen flow. With both ethylene and propylene

the new carbonyl band doublet appears, with only a small shift to lower wavenumbers for propylene (2060 and 1993 cm^{-1}) as compared to ethylene (2064 and 1994 cm^{-1}). This indicates the formation of well-defined olefin carbonyl complexes on the surface. Related olefin carbonyl complexes are known also in the homogeneous complex chemistry of Ru, with carbonyl bands of the propylene complex shifted by $5\text{--}10\text{ cm}^{-1}$ to lower wavenumbers as compared to the ethylene complex [10,11]. The band doublet at 2064 and 1994 cm^{-1} is assigned, consequently, to an ethylene carbonyl complex and the doublet at 2060 and 1993 cm^{-1} to a propylene carbonyl complex of Ru^{II} on the surface of Ru/DAY. Similar to the related olefin carbonyl complexes of Ru in solution [10,11], the surface complexes do not show direct IR-bands ($\nu(C=C)$) from the coordinated olefin ligand, probably because of symmetry restrictions.

3.3. Ethylene dimerization

It has been shown in the previous paragraph, that the Ru dicarbonyl is reversibly formed from the olefin dicarbonyl complex in an inert atmosphere free of additional olefin. To follow the fate of the olefin, the gas phase during the pulse experiments as outlined in the previous paragraph (see Fig. 2) has been analysed by on-line QMS analysis. The results clearly indicated the formation of butene as the major product, but a clear

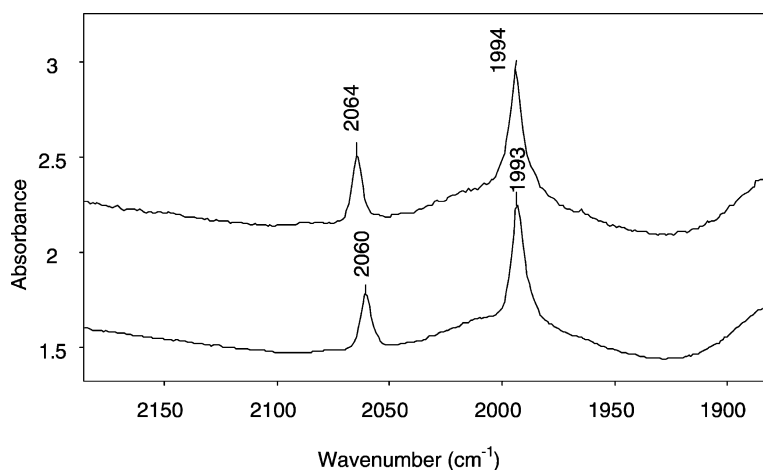


Fig. 3. FTIR spectra of Ru/DAY in a flow of $100\text{ sccm N}_2 + 10\text{ sccm C}_2\text{H}_4$ at 150°C (top), and $100\text{ sccm N}_2 + 35\text{ sccm C}_3\text{H}_6$ at 150°C (bottom).

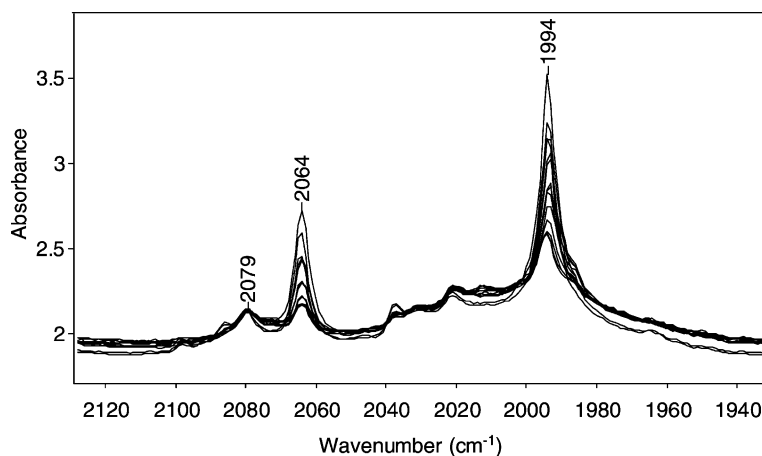


Fig. 4. FTIR spectra of Ru/DAY during the ethylene dimerization reaction in a flow of Ar (20 and 100 sccm) with 0.5 and 1% C_2H_4 at 140–200 °C.

discrimination of the different butene isomers was not possible in that way. After these preliminary experiments, therefore, an on-line GC analysis at stationary conditions was used to get more detailed information on the dimerization reaction. The IR spectra obtained simultaneously allow a correlation between the surface species characterized spectroscopically and the reaction products.

Fig. 4 shows the FTIR spectra of Ru/DAY obtained in the presence of ethylene during the reaction at different conditions. The spectra are almost identical, with only different intensities of the bands at 2064 and 1994 cm^{-1} , that we have assigned to ethylene dicarbonyl species. We have used the intensities of the band at 2064 cm^{-1} as a measure of the concentration of the ethylene dicarbonyl on the surface of the catalyst and related them to the simultaneously obtained catalytic activity. Fig. 5 shows as an example the results obtained for 170 °C at two space velocities and at different time on stream. A significant relation is obvious between the activity and the surface concentration of Ru ethylene dicarbonyl as expressed in terms of the corresponding band absorbencies. This is a strong argument in favor of the surface complexes as the active sites for dimerization of ethylene. The dependence of the conversion on the space velocity as shown in Fig. 5 is expected for a surface site controlled catalytic reaction.

We performed an additional test to identify the active sites: a Ru/DAY sample without preliminarily

formed Ru carbonyl species on the surface was used in the same reaction. As result, a significant smaller conversion of ethylene and a different product distribution with more light by-products as ethane and propene instead of butenes was found.

Another interesting point is the stability of the surface complexes during the reaction. Without additional dosing of CO the complexes are stable over hours of reaction.

The dimerization of ethylene has been followed at temperatures between 140 and 200 °C. Fig. 6 shows the Arrhenius plot of the reactivity. To have an unified

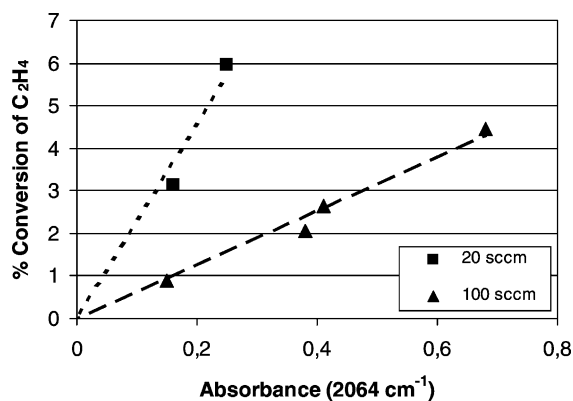


Fig. 5. Ethylene conversion during the dimerization to butene in dependence on the integral absorbencies of the carbonyl band at 2064 cm^{-1} . Amount of Ru/DAY about 40 mg, space velocity 30,000 h^{-1} (20 sccm N_2) and 150,000 h^{-1} (100 sccm N_2).

Table 1

Distribution of products of the dimerization of 0.5% ethylene in N₂ on Ru-ethylene-dicarbonyl/DAY, space velocity 30,000 h⁻¹

Temperature (°C)	Selectivity (%)					
	Ethane	Propene	<i>n</i> -Butene	1-Butene	<i>trans</i> -2-Butene	<i>cis</i> -2-Butene
150	4.0	0.5	95.5	9.1	56.4	30.0
170	4.1	0.5	95.4	10.4	54.8	30.2
200	8.4	2.8	88.8	12.4	48.3	28.1

basis for comparison, the productivity has been normalized with respect to the actual concentration of active sites, i.e. to the concentration of Ru ethylene dicarbonyl species on the surface as expressed by the absorbencies of the corresponding IR-bands. From the Arrhenius plot an activation energy of 36 kJ/mol K ($\pm 10\%$) can be estimated.

Supported nickel catalysts are active materials for the oligomerization of ethylene and it has been found [12] that their activity and selectivity are significantly influenced by the support and the promoters added. A high selectivity to *n*-butenes can be obtained with zeolites as supports [13,14] or with specially modified Ni/ZrO₂ catalysts [15]. Especially at higher conversions, by-products as *iso*-butene, hexene, propane, butane are formed.

The selectivity towards *n*-butenes obtained in our experiments was >95% at 170 °C and about 90% at 200 °C. As by-products we found ethane and propene. Higher hydrocarbons were not found. Table 1 provides

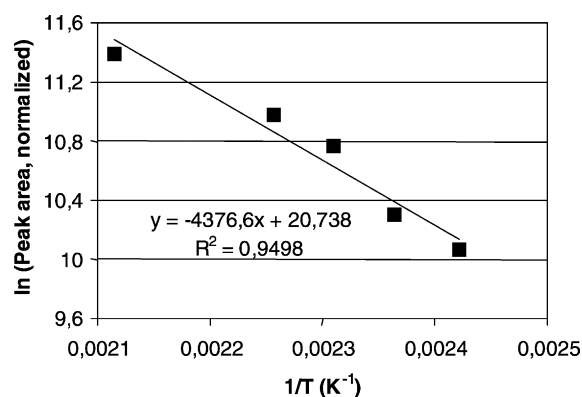


Fig. 6. Temperature dependence of the dimerization of 0.5% ethylene in N₂ at 140–200 °C and a space velocity of 30,000 h⁻¹. The areas of the product chromatogram are normalized with respect to the intensities of the in situ obtained IR carbonyl bands as in Fig. 4.

some representative results on the selectivity in our studies. The distribution of *n*-butenes corresponds to the thermodynamic equilibrium.

4. Conclusions

- Ru mono- and dicarbonyl species are formed on the surface of dealuminated Y zeolite during a controlled decarbonylation of Ru tricarbonyl.
- These Ru subcarbonyls are coordinatively unsaturated and react reversibly with olefins as ethylene and propylene in the gas phase and form well-defined olefin dicarbonyl complexes.
- The olefin dicarbonyl complexes are active and highly selective catalysts for the dimerization of ethylene to *n*-butenes.

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References

- [1] R. Ugo, R. Psaro, J. Mol. Catal. 20 (1983) 53.
- [2] E. Cesarotti, A. Fusi, R. Ugo, G.M. Zanderighi, J. Mol. Catal. 4 (1978) 205.
- [3] A. Fusi, E. Cesarotti, R. Ugo, J. Mol. Catal. 10 (1981) 213.
- [4] D. Roberto, R. Psaro, R. Ugo, J. Organomet. Chem. 451 (1993) 123.
- [5] H. Miessner, I. Burkhardt, D. Gutschick, A. Zecchina, C. Morterra, G. Spoto, J. Chem. Soc., Faraday Trans. 1 (85) (1989) 2113.
- [6] H. Miessner, J. Chem. Soc., Chem. Commun. (1994) 927.
- [7] H. Miessner, J. Am. Chem. Soc. 116 (1994) 11522.

- [8] H. Miessner, K. Richter, *Angew. Chem., Int. Ed. Engl.* 37 (1998) 117.
- [9] H. Miessner, K. Richter, *J. Mol. Catal. A: Chem.* 146 (1999) 107.
- [10] Y.-M. Wu, J.G. Bentsen, C.G. Brinkley, M.S. Wrighton, *Inorg. Chem.* 26 (1987) 530.
- [11] E. Lindner, R.-M. Jansen, W. Hiller, R. Fawzi, *Chem. Ber.* 122 (1989) 1403.
- [12] J. Heveling, C.P. Nicolaidis, M.S. Scurrall, *Appl. Catal. A: Gen.* 173 (1998) 1.
- [13] F.T.T. Ng, D.C. Creaser, *Appl. Catal. A: Gen.* 119 (1994) 327.
- [14] M. Hartmann, L.J. Kevan, *Chem. Soc., Faraday Trans.* 92 (1996) 1429.
- [15] J.R. Sohn, H.W. Kim, M.Y. Park, E.H. Park, J.T. Kim, S.E. Park, *Appl. Catal. A: Gen.* 128 (1995) 127.