Ultraviolet Raman spectroscopy characterization of sulfated zirconia catalysts: fresh, deactivated and regenerated

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Received 3 August 1995; accepted 11 October 1995

Ultraviolet Raman spectroscopy (UVRS) has been demonstrated to be a powerful new tool for catalysis and surface science studies. UVRS can successfully avoid the surface fluorescence which frequently occurs in normal Raman spectra of many catalysts. Fresh, deactivated and regenerated sulfated-zirconia catalysts have been characterized using this new method. The UV Raman spectrum of the fresh sample is dominated by the tetragonal phase, however, the spectrum of deactivated sulfated zirconia is nearly identical to that of the monoclinic phase of pure zirconia. A regeneration of the deactivated catalyst restores the spectrum back to that of the fresh sample. In addition, a new band at 750 cm^{-1} associated with the fresh sample attenuates with the deactivation process. This band is tentatively assigned to the surface $[ZrO_4]^{4-}$ unit which is assumed to bond to the surface sulfate group. The results indicate that the surface phase of sulfated zirconia is reconstructed from tetragonal to monoclinic phase during the deactivation process while the bulk remains in the tetragonal phase after the deactivation. It is proposed that the surface tetragonal phase is stabilized by sulfate groups, and is associated with the catalytic activity.

Keywords: UV Raman spectroscopy; zirconia; sulfated zirconia; deactivation; surface phase transformation

1. Introduction

Raman spectroscopy is potentially one of the most powerful techniques for characterizing catalysts [1,2]. However, conventional Raman spectroscopy using visible laser excitation often suffers from two limitations in catalysis studies, inherently low Raman scattering signals and strong fluorescence which often obscures the weak Raman signal. One technique to avoid interference from fluorescence is to employ ultraviolet excitation because the fluorescence of most molecules and surfaces occurs in the visible region. Asher et al. [3–5] have demonstrated that fluorescence does not interfere with the Raman spectrum for a number of systems when an ultraviolet laser was used as the excitation source. However, there have been no reports to date of catalyst characterization using UV Raman spectroscopy. In principle, UV Raman can not only diminish the fluorescence interference but also greatly increase the Raman signal when the laser frequency falls in an absorbance region of the system giving rise to the resonance Raman phenomenon [6]. Using UV excitation, we have detected the surface Raman signal for several kinds of catalysts, e.g., coked cracking catalysts, sulfated zirconia and even grease-contaminated catalyst samples, all of which are difficult to characterize by normal Raman spectroscopy because of strong fluorescence.

Sulfated zirconia has attracted considerable attention in recent years as a solid acid catalyst [7–12]. Sulfated zirconia shows very high initial activity for alkane isomerization and has been designated as a superacid catalyst. Unfortunately this catalyst deactivates very rapidly. This fact has motivated many researchers to study the nature of the catalytic reactions on sulfated zirconia and extensive catalyst characterization has been made by various techniques in order to understand this deactivation phenomenon [13–18]. Despite this effort the nature of the catalysis is still unclear, and there is no definitive identification of either the active site or the active surface phase. In this contribution we report the UV Raman spectra of sulfated zirconia before and after testing for butane isomerization, together with those of the regenerated catalyst. The UV Raman spectra clearly show a surface phase change associated with the deactivation. This result may shed light into the nature of the catalysis on sulfated zirconia catalysts.

2. Experimental

A previous paper has showed an overview of the UV Raman spectrometer [19]. The frequency doubled output of a 12 W argon ion laser was used as the 257.2 nm excitation source. The power of the 257.2 nm line can be as large as 30 mW, but in this study, the power delivered to the sample was kept below 5 mW to avoid thermal decomposition. The Raman scattering from the sample surface was collected using a backscattering geometry by an $AlMgF_2$ coated ellipsoidal reflector, and focused

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into a single grating spectrograph through a notch filter. The detector is an imaging multichannel photomultiplier tube (IPMT) with a spectral window of 2100 cm^{-1}. The slit width used in fig. 2 is 200 μm and 100 μm in fig. 3. Catalyst samples were formed into pressed discs. The measurements can be performed both in air and in situ in a quartz reactor cell at room temperature. The sample in the quartz cell can be treated over a wide temperature range, r.t.–1000°C.

Catalyst samples used in this work were kindly provided by Professor Sachtler's group, and a description of the sample preparation has been given elsewhere [10]. Sulfated zirconia, SO_4^{2-}/ZrO_2, was prepared from sulfated zirconium hydroxide by calcination at 650°C in a flow of dry air. The sulfur content was measured to be 1.1 wt% by inductively coupled plasma (ICP) analysis. Zirconia, ZrO_2, was prepared by calcining zirconium hydroxide, $Zr(OH)_4$, at 650°C in dry air. The catalyst was tested at 180°C for isomerization of *n*-butane to isobutane. The catalyst after 1 h at reaction conditions is called the used or deactivated catalyst. The deactivated catalyst has an activity less than 10% of the fresh catalyst. Catalyst regeneration was carried out by oxidizing the used sample disc at 500°C in a flow of dry air for the data shown in fig. 2 and pure O_2 for fig. 3 respectively. X-ray diffraction (XRD) patterns show that the sulfated zirconia is mainly tetragonal phase and pure zirconia is mainly monoclinic phase. This is in good agreement with that reported in ref. [20].

As shown in fig. 1, the Raman spectrum of pure zirconia recorded using normal visible excitation ($\lambda = 514.5$ nm) is characteristic of the monoclinic phase [21], while there is no detectable Raman signal for fresh and used sulfated zirconia because of strong background of fluorescence. The resolution of the normal Raman spectrum is superior to the UV Raman at present because the resolving power of the spectrograph in the UV region is less than in the visible region. Therefore the bands in the UV Raman spectra are relatively broad.

3. Results and discussion

Fig. 2 displays four UV Raman spectra recorded in the 300–1700 cm^{-1} region for zirconia, fresh sulfated zirconia, used sulfated zirconia and regenerated sulfated zirconia as indicated. Apparently, the fluorescence background is successfully avoided in these UV Raman spectra, so that structural characterization of the catalyst can be performed whether the catalyst is fresh or used. The UV Raman spectrum of pure zirconia gives strong bands at 475, 630, and 750 cm^{-1}, and weak bands at 560 and 690 cm^{-1}. The main bands in this region are very similar to those in fig. 1 except for the lower resolution. The band at 475 cm^{-1} is fairly narrow but the bands at 630 and 750 cm^{-1} are actually composed of several overlapping bands. There are at least two bands near 630 cm^{-1}, i.e., 610 and 630 cm^{-1}. The intensities of the lower frequency bands should be stronger than shown in fig. 2 because the notch filter attenuates the Raman signal close to the exciting line. In the region exhibited above,

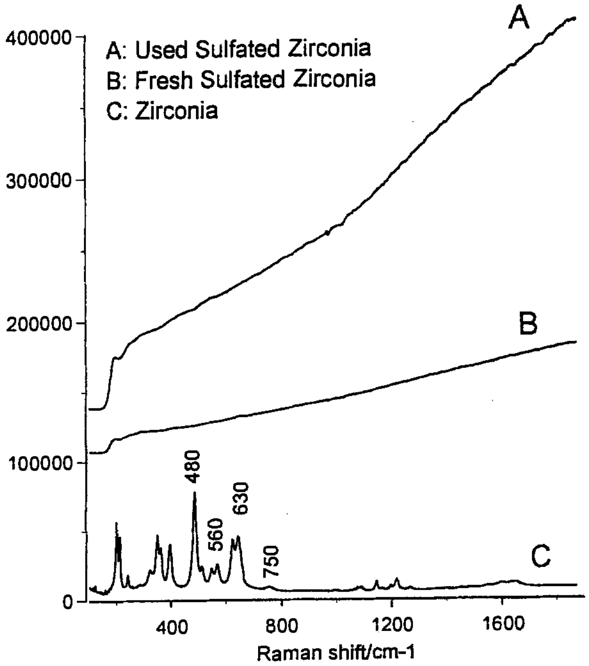


Fig. 1. Normal Raman spectra of pure zirconia, fresh and used sulfated zirconia ($\lambda = 514.5$ nm; laser power, 100 mW).

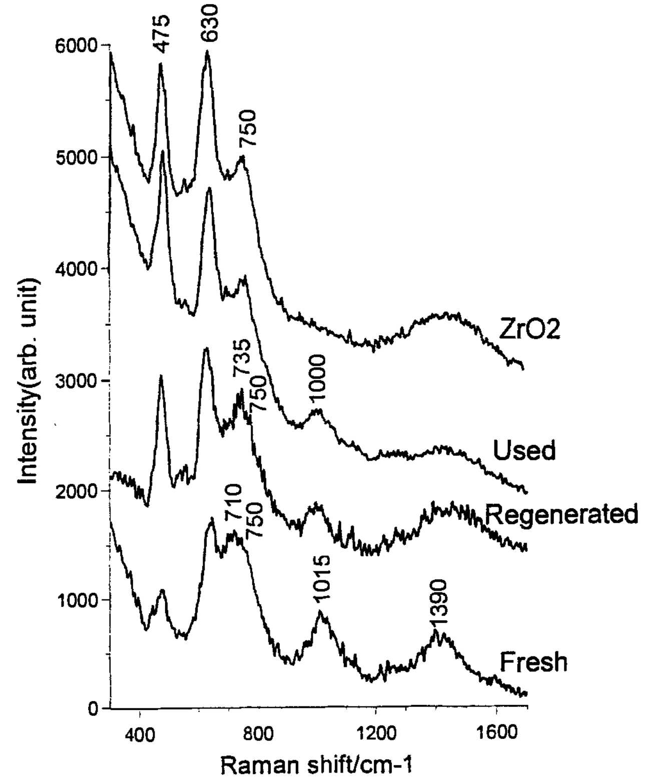


Fig. 2. UV Raman spectra of zirconia, fresh, used and regenerated sulfated zirconia ($\lambda = 257.2$ nm; laser power, 5 mW). The regeneration was made at 500°C, in flowing dry air for 2 h.

there are two main differences in the Raman spectra for monoclinic and tetragonal phases of zirconia [21]. The band at 475 cm^{-1} is stronger than the 630 cm^{-1} band for the monoclinic phase and the reverse for tetragonal phase and there are small bands in between 475 and 630 cm^{-1} for monoclinic phase that are absent for the tetragonal phase. Obviously, the Raman spectrum of pure zirconia is dominated by the monoclinic phase as XRD patterns showed that the pure zirconia contains primarily the monoclinic phase.

A fresh catalyst sample shows quite a different spectrum from that of pure zirconia, as seen in fig. 2. The bands near 1015 and 1390 cm^{-1} originate from the sulfate groups on the zirconia surface. These bands can be readily assigned to the stretch vibrations of S–O (1015 cm^{-1}) and S=O (1390 cm^{-1}) of sulfate groups [14]. The bands in the low frequency region (<800 cm^{-1}) are mainly from zirconia. By comparison to the spectrum of pure zirconia, a significant difference can be clearly observed in the zirconia region of the spectrum for the fresh catalyst. First, the relative intensity of the band at 475 cm^{-1} is reduced dramatically; second, the weak band at 560 cm^{-1} disappears, and third, the band at 750 cm^{-1} becomes much stronger and shifts slightly toward lower frequency. These features are strong evidence that the structure of zirconia in the sulfated form is really different from that of pure zirconia. By comparison to the spectra reported by Mercera et al. [21], the spectrum of the fresh sample is clearly due to the tetragonal phase.

The band at 750 cm^{-1} has not been reported before. This band does not appear to be from the bulk but from the surface since its frequency is very close to the ν_1 mode of ZrO_4^{4-} anions in the tetra-oxo-complex [22]. The top layer of zirconia may be similar to the ZrO_4^{4-} unit in the tetra-oxo-complex, but in any case the band at 750 cm^{-1} is likely due to localized bonds giving higher frequencies than those from the bulk. This band may vary in frequency and intensity for sulfated zirconia because of the interactions between surface ZrO_4^{4-} units and sulfate groups. Indeed, new structure in the 750 cm^{-1} region does develop and shift to lower frequencies around 710 cm^{-1}. This suggests that the bands in the 710–750 cm^{-1} region are from surface moieties like ZrO_4^{4-} and SO_4^{2-}–ZrO_4^{4-}. The fact that the band near 750 cm^{-1} is more intense for sulfated zirconia than for zirconia means that the interaction between sulfate groups and the zirconia surface is strong enough to change the properties of surface ZrO_4^{4-}.

The spectrum of the sulfated zirconia is remarkably different after catalytic testing by the isomerization of *n*-butane at 180°C. To our surprise, the spectrum of the used catalyst is nearly identical to that of pure zirconia except for the weak bands near 1000 cm^{-1} associated with surface sulfate groups. The features of the tetragonal phase disappear while the monoclinic phase appears. This is clear evidence to demonstrate that the phase of the sulfated zirconia transformed from tetragonal to monoclinic during the deactivation process. The band intensities of surface sulfate groups at 1015 and 1390 cm^{-1} are also reduced. However, an elemental analysis indicated that the sulfur content did not change significantly before and after the reaction. This result suggests that a change in geometry or symmetry of the surface sulfate groups is responsible for the lower Raman intensities because the Raman cross section is very sensitive to the symmetry of the scattering species. It also seems likely that the changes in sulfate groups must be responsible for or related to the transformation from tetragonal to monoclinic phase because the pure zirconia surface without sulfate groups shows mainly the monoclinic phase in the Raman spectrum.

The spectrum of a regenerated sulfated zirconia seems to be intermediate between the spectra of fresh and deactivated samples. The regeneration was performed by treating the pressed sample disc in dry air flow at 500°C for 2 h. The band at 750 cm^{-1} grows and the bands due to sulfate groups at 1000 and 1390 cm^{-1} recover somewhat also. The spectrum indicates that the sample has been partially restored from the monoclinic to the tetragonal phase. Since the sample is in a pressed disc form and the diffusion of O_2 is much more difficult in the compact sample than in the powder used for reaction, the regeneration is incomplete even after 2 h. On the other hand, a fully regenerated sample may not be exactly the same as the fresh sample even though the reaction activity has been restored.

Fig. 3 presents a series of UV Raman spectra which were recorded stepwise during the regeneration. These spectra were recorded with a spectrometer slit width of 100 μm, therefore their spectral resolution is better than in fig. 2 where a slit width of 200 μm was used. The deactivated catalyst shows bands at 630, 480, 380 and 335 cm^{-1}. The bands at 380 and 335 cm^{-1} are related to the monoclinic phase according to the standard spectra reported by Mercera et al. [21]. After treatment for 1 h, the bands at 630 and 750 cm^{-1} increased, and two new bands at 420 and 460 cm^{-1} appeared while the bands at 380 and 480 cm^{-1} attenuated. After further treatment for 3 h, the spectrum changed dramatically. The band at 480 cm^{-1} disappeared, meanwhile the band at 460 cm^{-1} grew further. The band at 630 cm^{-1} becomes stronger, but the bands at 380 and 335 cm^{-1} become much weaker.

A striking change can be seen in the spectrum when the deactivated sample was oxidized at 500°C for 9 h. The bands at 750 and 685 cm^{-1} are nearly restored to the intensities of the fresh sample shown in fig. 2, meanwhile, the band at 630 cm^{-1} becomes stronger than the band at 480 cm^{-1}. The features at 335 and 385 cm^{-1} are gone, but two new bands are produced at 325 and 265 cm^{-1} which are signatures of the tetragonal phase [21]. All these facts strongly suggest that the catalyst surface changed from monoclinic to tetragonal phase after the regeneration treatment. From the evolution in the 200–

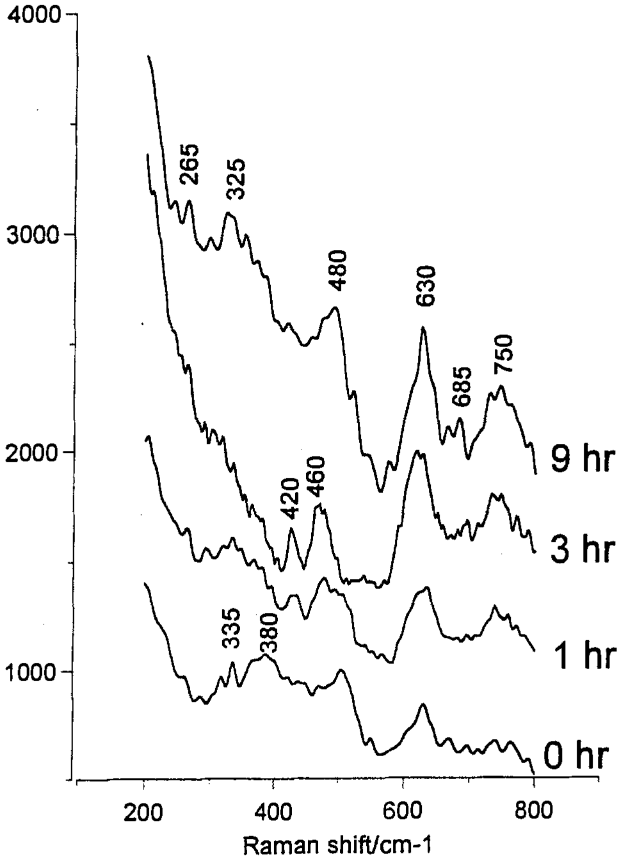


Fig. 3. UV Raman spectra recorded after the regeneration of deactivated sulfated zirconia at 500°C in flowing O_2 for different times.

400 cm^{-1} region of the spectrum, it seems that the transformation from monoclinic to tetragonal proceeds through some transition states. The bands at 420 and 460 cm^{-1} which are features of the transition state appear at the beginning of the oxidation treatment and disappear eventually when the tetragonal phase is regenerated.

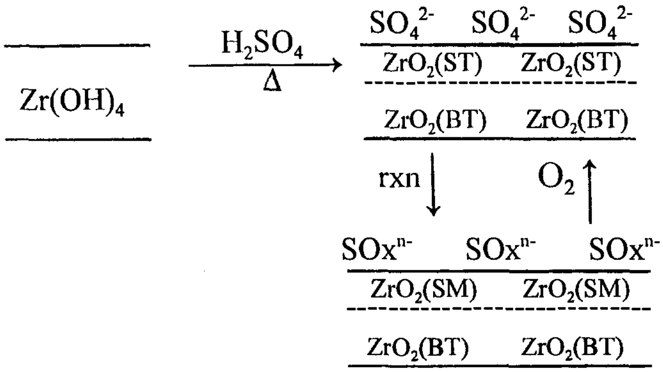
Generally speaking, Raman scattering comes from both the surface and bulk of the solid sample. However, since the signal from the bulk is attenuated with depth, the Raman spectra contain more information from the top region of sample. In particular, the fact that most oxides strongly absorb UV light makes UV Raman spectroscopy more surface-sensitive. This feature allows us to resolve information about the surface phase. In contrast, it is hard to distinguish information solely from surface phases using X-ray diffraction which produces signal mainly from the bulk of the sample. The XRD patterns of fresh and used samples show pretty much the same results, i.e., mainly tetragonal phase. We conclude that the surface phase which can be detected more easily by UV Raman spectroscopy is principally correlated with the catalytic activity of this catalyst, and the deactivation of the catalyst is accompanied by changes mainly in the surface phase. The tetragonal phase in sulfated zirconia has also been reported previously [20,23,24], but there has been no previous report which identified the change of surface phase for the sulfated zirconia catalyst during the reaction.

Tanabe and co-workers [25] proposed that the tetragonal phase is the catalytically active one in sulfated zirconia. But they did not show the phase transformation during the deactivation and regeneration process. From the UV Raman spectra reported here, the activated surface phase, tetragonal, is produced on top of a tetragonal bulk phase when surface sulfate groups are present. The tetragonal phase is a metastable phase at low temperatures, and it can be maintained in bulk but appears to be unstable near the surface. The monoclinic phase is favored if the surface sulfate groups are absent. The tetragonal phase is stabilized on the surface of the fresh catalyst because of the presence of the surface sulfate groups. When the catalyst is deactivated, the chemical nature of the sulfate groups must be dramatically changed, either they are partially reduced or their coordination geometry on the surface is altered. As a consequence, the surface tetragonal phase is transformed into the monoclinic phase. The UV Raman spectra clearly reflect the variation of the surface zirconia phase together with the changes of the sulfate groups after the isomerization reaction.

Fig. 4 depicts the surface phase transformation of sulfated zirconia during the deactivation process. It is assumed that the surface phase can be easily affected by the surface sulfate groups. We concur with the view that the sulfate group on the fresh sample coordinates to zirconia surface in a multiple bonding configuration [14,18,26] which must be strong enough to stabilize the tetragonal phase. For the deactivated sample, either the chemical identity or the coordination geometry of the sulfate groups must be altered. Accordingly, the bonding between the sulfate groups and the surface of zirconia is softened, and as a result, the surface phase transforms from tetragonal to monoclinic. An oxidation treatment regenerates the surface sulfate groups, restores the original bonding configuration with the zirconia surface, and the surface phase is reconstructed back to the tetragonal structure. It is worthwhile to point out that the phase transformation from monoclinic to tetragonal is thermodynamically difficult at 500°C, however, the regeneration of surface sulfate groups could induce the surface phase change.

4. Conclusions

Sulfated zirconia has been studied by UV Raman spectroscopy in order to avoid fluorescence which obscures normal Raman spectra. The UV Raman spectra indicate that the surface phase of sulfated zirconia changed during the deactivation process, from the tetragonal phase of the fresh sample to the monoclinic phase of the deactivated sample, even though the bulk phase maintains the tetragonal phase before and after the reac-



ST: surface tetragonal; SM: surface monoclinic; BT: bulk tetragonal.

Fig. 4. Proposed mechanism for the deactivation of sulfated zirconia.

tion test. A regeneration treatment of the deactivated sample results in a recovery of the Raman spectrum back to the tetragonal phase. It is concluded that the surface tetragonal phase together with the sulfate groups is associated with the catalytic activity, and that the deactivation is due to the loss of this active phase.

Acknowledgement

The samples were kindly provided by V. Adeeva in Professor Sachtler's group, thanks also to Professor Sachtler for his helpful discussion. Special thanks to Maritoni Litorja for measuring the spectra in fig. 1. Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research. This project was also supported by the Center for Catalysis and Surface Science of Northwestern University.

References

[1] J.M. Stencel, *Raman Spectroscopy for Catalysis* (Van Nostrand Reinhold, New York, 1990).
[2] A. Campion, in: *Vibrational Spectroscopy of Molecules on Surfaces*, eds. J.T. Yates Jr. and T.E. Madey (Plenum Press, New York, 1987) p. 345.
[3] C.R. Johnson and S.A. Asher, Anal. Chem. 56 (1984) 2261.
[4] S.A. Asher, Anal. Chem. 65 (1993) 201A.
[5] R.W. Bormett and S.A. Asher, J. Appl. Phys. 77 (1995) 5916.
[6] S.A. Asher, Anal. Chem. 65 (1993) 57A.
[7] T. Yamaguchi, T. Jin, T. Ishida and K. Tanabe, Mater. Chem. Phys. 17 (1987) 3.
[8] M. Waqif, J. Bachelier, O. Saur and J.C. Lavalley, J. Mol. Catal. 72 (1992) 127.
[9] C. Morterra, G. Cerrato, C. Emanuel and V. Bolis, J. Catal. 142 (1993) 349.
[10] V. Adeeva, J.W. de Haan, J. Janchen, G.D. Lei, V. Schunemann, L.J.M. van de Ven, W.M.H. Sachtler and R.A. van Santen, J. Catal. 151 (1995) 364.
[11] D.A. Ward and E.I. Ko, J. Catal. 150 (1994) 18.
[12] R. Srinivasan, R.A. Keogh, D.R. Milburn and B.H. Davis, J. Catal. 153 (1995) 123.
[13] F.R. Chen, G. Coudurier, J.-F. Joly and J.C. Vedrine, J. Catal. 143 (1993) 616.
[14] T. Riemer, D. Spidbauer, M. Hunger, G.A.H. Mekhemer and H. Knözinger, J. Chem. Soc. Chem. Commun. (1994) 1181.
[15] C. Morterra, G. Cerrato, F. Pinnar and M. Signoretto, J. Phys. Chem. 98 (1994) 12373.
[16] L.M. Kustov, V.B. Kazansky, F. Figueras and D. Tichit, J. Catal. 150 (1994) 143.
[17] J.R. Sohn and H.J. Jany, J. Mol. Catal. 64 (1991) 349.
[18] E. Escalona Platero and M. Peñarroya Mentruit, Catal. Lett. 30 (1995) 31.
[19] G.H. Smudde Jr. and P.C. Stair, Surf. Sci. 317 (1994) 65.
[20] R.A. Comelli, C.R. Vera and J.M. Parera, J. Catal. 151 (1995) 96.
[21] P.D.L. Mercera, J.G. van Ommen, E.B.M. Doesburg, A.J. Burggraaf and J.R.H. Ross, Appl. Catal. 57 (1990) 127.
[22] F. Gonzalez-Vilehez and W.P. Griffith, J. Chem. Soc. Dalton Trans. (1972) 1416.
[23] R. Srinivasan, D. Taulbee and B.H. Davis, Catal. Lett. 9 (1991) 1.
[24] J.R. Sohn and H.W. Kim, J. Mol. Catal. 52 (1989) 361.
[25] T. Ishida, T. Yamaguchi and K. Tanabe, Chem. Lett. (1988) 1869.
[26] M. Bensitel, O. Saur, J.C. Lavalley and B.A. Morrow, Mater. Chem. Phys. 19 (1988) 147.