Surface and related studies in sulphated oxides of zirconium

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Zirconium oxide superacids with different sulphate ion contents were prepared from $Zr(SO_4)_2$ using *urea* as precipitating agent. These oxides were subjected to different heating temperatures. Characterization was carried out by means of infrared spectroscopy, X-ray diffraction and nitrogen adsorption studies. The surface acidity was determined by the method described by Boehm [1]. Infrared results confirmed the presence of the sulphate ions and suggested the gradual lowering through heat-treatment of the symmetry of the sulphate ions by complex formation. Surface acidity was favored when the sulphate ions were in a bidentate state of ligation. The latter ligands seemed in turn to be stabilized by water. The strongest acidity was displayed in systems where a *high concentration of bidentated sulphate ions* was present in conjunction with *high surface areas* and *micropore volumes*. © *2004 Kluwer Academic Publishers*

1. Introduction
Sulphated zirconium oxides with high surface area are of much interest to catalytic research as they have proven to be active catalysts in a large number of processes, such as isomerization of hydrocarbons, esterification and alkene polymerization [2–12].

These sulfate promoted zirconium oxides are generally prepared by impregnation with sulphuric acid or ammonium sulphate [13–16], then calcining at different temperatures and are believed to be effective catalysts because they are *superacidic* [17–21]. Some workers however have claimed that the acidity of the sulphated zirconia is not stronger than 100% sulfuric acid [22] and more recent researchers [23] have indicated that the high catalytic activity of the sulfated zirconia arose not from its superacidity but from its ability to stabilize a transition state complex of the organic reactants on the surface and was favored by the *tetragonal* zirconia as opposed to the *monoclinic* zirconia.

Vera *et al.* [24] have indicated that sulfated zirconia prepared from $Zr(OH)_4$ and H_2SO_4 solutions when calcined at temperatures higher than 375°C were crystalline and adsorbed sulphate groups but were catalytically inactive. The catalytic activity was found to increase with increasing concentration of (OH) groups on the surface. These authors showed that sulphate anions, in order to become anchored to the surface of zirconia and form bidentate sulpho bridges, needed the presence of adjacent hydroxyls. Babou *et al.* [25] corroborating the work of Vera *et al.* showed that samples of sulfated zirconia, prepared from zirconium hydroxide which was contacted with a sulphuric acid solution and further dried at 120°C, exhibited in their infrared spectra bands belonging to the bidentate SO_4^{2-} ion in

C_{2v} symmetry and that the surface sites on sulphated zirconia may need small quantities of water to be active.

The present work aims at complementing such previous work through a study of zirconium oxide superacids prepared from $Zr(SO_4)_2$ using *urea* as precipitating agent. In light of previous work the following questions need to be addressed:

(a) Does such a preparative route lead to sulfated zirconia with sulphate ions in the same state of coordination as in the case of impregnation of ZrO_2 in sulfuric acid?

(b) What is the effect of the sulphate content on the surface acidity and do the textural characteristics of the zirconium dioxide so prepared have any effect on the observed acidity?

(c) Does water or hydroxyl ions play any significant role with respect to the stabilization of the sulphate ions as in the case of previous work?

2. Experimental
2.1. Materials
The hydrous zirconium oxide was prepared by heating a 1 M solution of $Zr(SO_4)_2$ prepared in 0.1 M H_2SO_4 (99.99% pure, Aldrich and A.R. grade respectively) to about 325 K in a water bath . Just enough NH_4OH (A.R. grade, Fischer) was added to the solution to bring the pH to 8.8. For every 25 g of salt used, about 300 g of urea (Fluka-Garantie, Harnstoff Pursum, p-a) were added. This was carried out in batches and each batch was stirred until dissolution before the following batch was added. During this process the temperature was kept at 340 K. Once all of the urea was added, the temperature of the water bath was adjusted to 365 K, and a milky

| Washing | Heat treatment | | | | |
	Original temperature	150°C	300°C	650°C	700°C
Washed with 100 ml of water	100T1	100T2	100T3	100T4	100T5
Washed with 150 ml of water	150T1	150T2	150T3	150T4	150T5
Washed with 300 ml of water	300T1	300T2	300T3	300T4	300T5
Washed free of sulphate ions	FREET1	FREET2	FREET3	FREET4	FREET5

dense precipitate was formed. It was left to settle for two hours, after which the solution was cooled to room temperature and the precipitate left in contact with the mother liquor for two days.

This was then filtered and the hydrous oxide was divided into four portions which were washed with different volumes of distilled water with the purpose of varying their sulphate content. These constituted sample series T1, comprising samples 100T1, 150T1 and 300T1 resulting from washing with 100, 150 and 300 ml of distilled water respectively, and sample FREET1, which was continuously washed until no traces of sulphate ions in the filtrate were detected by using barium chloride. The four samples were then dried to constant weight at 325 K.

The T1 samples were then subjected to heat treatment at different temperatures, chosen according to the thermal behavior of the oxide,* namely: 150°C giving sample series T2 (*devoid of free or interstitial water*), 300°C giving sample series T3 (*containing no coordinated water*), 650°C giving sample series T4, and 700°C giving sample batch T5. The preparation conditions for the different samples are presented in Table I.

2.2. Techniques
The *infrared studies* were carried out using a FTIR Paragon 1000 Perkin Elmer spectrophotometer. Solid samples were prepared in the form of KBr pellets, for which two milligrams of the compound were mixed with approximately 200 mg of KBr (spectroscopic grade), and the mixture then subjected to a pressure of about 200 lb/inch^2 in a hydraulic press.

Adsorption measurements were carried out at 77 K using a conventional volumetric technique. Typically, the sample was outgassed overnight at room

*Work in progress on similar systems has indicated the following:

– The endotherm at 150°C corresponds to the loss of *free* or *interstitial* water
– The endotherm at 320°C corresponds to the loss of coordinated water and some ionic sulphate
– The endotherm at 625°C–670°C corresponds to the loss of differently bound sulphato ligands
– The exotherm at 650°C corresponds to the development of crystallinity
– No more weight losses or phase changes are detected at 700°C

temperature to residual pressures of $\sim 25 \times 10^{-4}$ torr. The gas pressures were measured on a mercury manometer. The time required for each point of the adsorption or desorption isotherm to attain equilibrium was between 15–20 min.

Adsorption isotherms obtained by the adsorption of sodium hydroxide or phosphoric acid from solution were determined by shaking, overnight, about 0.2 g of the solid compound in 10 ml of the base or acid of known normality. A series of different concentrations, ranging between 0.2 N and 0.005 N, was used. A blank run was carried out first on the base or acid alone. The difference between the blank run and that with the sample gave the amount adsorbed. In the case of the adsorption of H_3PO_4, the PO_4^{3-} was estimated photometrically.

The *X-ray diffraction patterns* were determined using a Philips X-ray diffraction analyzer system, PW1840, using nickel filtered Cu K_α radiation.

3. Results and discussion
3.1. Infrared studies
Infrared studies carried out on the T1 samples revealed in all cases peaks at 3430, 3320, 2350, 2230, 1660, 1630, 1400 and 1430 cm^{-1}. The 3430, 3320, 2350, 1660 and 1430 cm^{-1} bands are attributed to undecomposed urea [26] whereas the 1400 and 1630 cm^{-1} bands are related to NH_4^+ ions and to the bending mode of molecular water respectively [27–29]. Additional weak bands were observed at 1110, 975 and 625 cm^{-1} for samples 100T1, 150T1 and 300T1 and are attributed to the ν_3, ν_1 and ν_4 vibrational modes of the free sulphate ion in T_d symmetry. Furthermore these samples also displayed weak bands at 1250, 1140, 1040 and 980 cm^{-1} which belong to a bridging bidentate sulphate ion and correspond to the gradual lowering, through heat treatment of the T_d symmetry of the sulphate ion to C_{2v} by complex formation [30]. Sample FREET1 did not display any bands belonging to the free sulphate ion but clearly displayed the bands belonging to the bridging bidentate sulphate ion.

Samples of the T2 and T3 series somewhat displayed the similar behavior with a notable decrease in the bands belonging to urea and a greater predominance of the bands belonging to the bridging bidentate sulphate ion. Representative infrared spectra for the T2 samples are shown in Fig. 1. The sharpness of the band belonging to molecular water is noteworthy.

Furthermore, the 1400 cm^{-1} band attributed to NH_4^+ was seen to decrease considerably for samples of the T3, T4 and T5 series, suggesting the probable elimination of nitrogen in the form of NH_3 as a result of heat-treatment. For samples of the T4 series, only sample 100T4 displayed weak bands belonging to the free sulphate and coordinated sulphate ions. These virtually disappeared on washing. Finally, samples of the T5 series displayed extremely weak bands belonging to urea and did not display any bands belonging to the sulphate ions.
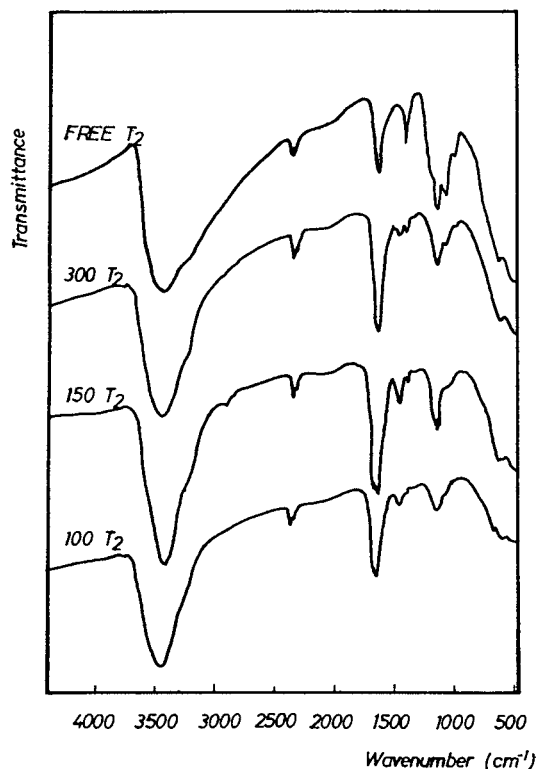
Figure 1 Representative infrared spectra for samples 100T2, 150T2, 300T2, and FREET2.

3.2. X-ray diffraction studies
The X-ray diffraction studies were carried out on all samples. Samples of T1, T2 and T3 series were found to be amorphous, while samples of T4 and T5 series were found to be in the *tetragonal* modification of zirconium oxide.

3.3. Adsorption studies
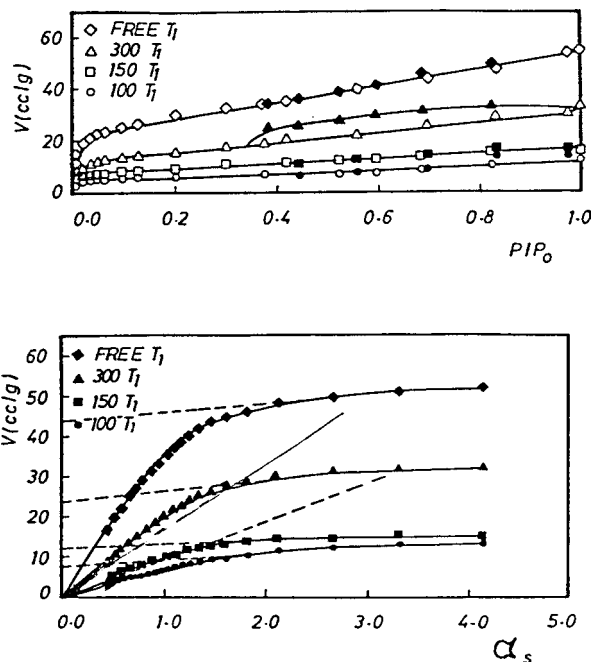Table II summarizes all of the adsorption results obtained in this study, as well as the calculated surface

Figure 2 Representative adsorption isotherms and α_s-plots for samples 100T1, 150T1, 300T1, and FREET1.

areas and pore volumes. The values of the B.E.T. surface areas are based on the assumption that each nitrogen molecule occupies 0.162 nm^2. S_s values have been calculated from the slope of the original part of the α_s-plot.

Representative nitrogen adsorption isotherms and the α_s-plots for samples of T1 series are shown in Fig. 2, whereas representative nitrogen adsorption isotherms and the α_s-plots for samples of T2 series are shown in Fig. 3. In the construction of each α_s-plot the volume of nitrogen is plotted against the reduced adsorption α_s as measured on a nonporous reference ZrO_2 [31]. As explained elsewhere [32], α_s is defined as the (amount adsorbed/amount adsorbed at $P/P_0 = 0.4$).

TABLE II Analysis of the nitrogen adsorption data of the surface of ZrO_2 sulfated samples

Sample	Temp. (°C)	V_m (ml)	BET C-const	S_{BET} (m^{2}g^{-1})	S_s (m^{2}g^{-1})	Total pore volume (ml g^{-1})	Micro-pore volume (ml g^{-1})	Porosity	Amount of acidic sites in (μmol g^{-1})
FREET1	orig	24.1	188	105	104	0.082	0.069	Micro	2500
300T1	orig	13.1	197	57.0	56.8	0.050	0.043	Micro + Meso	2500
150T1	orig	6.7	164	29.1	29.7	0.024	0.021	Micro + Meso	2100
100T1	orig	4.6	246	20.2	20.1	0.021	0.016	Micro + Meso	1900
FREET2	150	20.8	214	90.6	90.1	0.067	0.060	Micro + Meso	1600
300T2	150	21.2	164	92.2	92.7	0.072	0.065	Micro	2500
150T2	150	11.0	178	47.9	47.4	0.046	0.035	Micro + Meso	1700
100T2	150	6.9	152	29.8	29.1	0.029	0.023	Micro + Meso	1700
FREET3	300	16.1	245	70.1	68.4	0.052	0.048	Micro	1700
300T3	300	12.8	240	55.7	55.3	0.044	0.037	Micro	1700
150T3	300	18.5	415	80.3	77.3	0.069	0.047	Micro + Meso	1900
100T3	300	24.4	216	106	108	0.078	0.068	Micro	2100
FREET4	650	12.1	168	52.6	52.2	0.045	0.040	Micro	800
300T4	650	8.9	198	38.8	38.6	0.032	0.028	Micro	650
150T4	650	6.3	108	27.4	27.2	0.027	0.020	Micro	380
100T4	650	7.1	118	31.1	31.1	0.030	0.023	Micro	430
FREET5	700	6.8	317	29.6	29.7	0.037	0.030	Micro + Meso	200
300T5	700	4.6	66	20.2	20.9	0.019	0.013	Micro + Meso	240
150T5	700	4.5	81	19.6	19.6	0.021	0.013	Micro	100
100T5	700	6.1	125	26.5	27.1	0.029	0.018	Micro	140

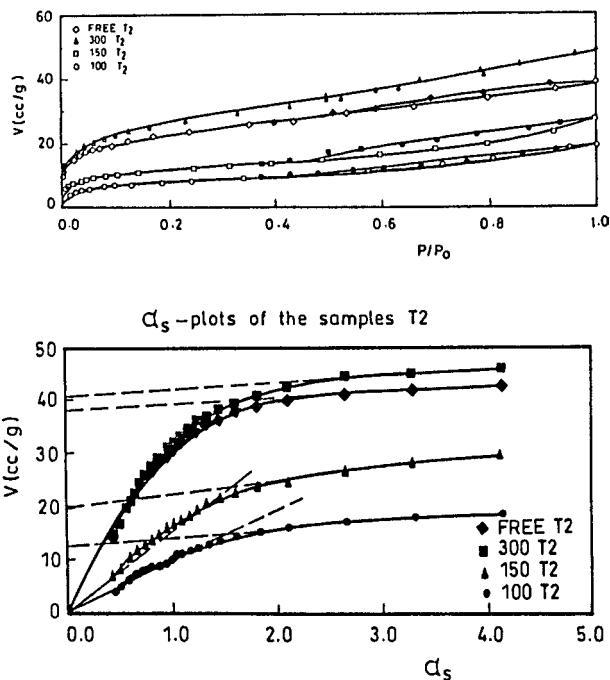*Figure 3* Representative adsorption isotherms and α_s-plots for samples 100T2, 150T2, 300T2, and FREET2.

TABLE III Results of elemental analyses

	100	150	300	Free	100	150	300	Free
	T1 series				T2 series			
S	2.05	2.15	2.89	3.38	2.60	2.87	3.15	3.35
C	9.63	7.60	4.86	1.33	8.63	6.25	4.02	2.09
H	3.65	3.41	2.49	2.22	3.22	2.49	2.32	1.77
N	20.8	16.28	9.21	0.53	16.54	9.18	2.45	0.70
	T3 series				T4 series			
S	4.13	4.30	4.90	4.42	2.25	3.02	3.30	3.60
C	2.95	2.07	1.15	1.12	9.26	5.51	3.50	1.56
H	1.49	1.24	1.03	1.04	3.45	2.46	2.03	1.73
N	2.80	1.56	0.51	0.37	18.72	9.68	5.38	3.60
	T5 series							
S	0.32	0.58	0.69	0.55				
C	0.57	0.47	0.59	1.03				
H	0.26	0.09	0.28	0.38				
N	0.16	0.58	<0.1	0.20				

Consideration of the main features of the isotherms and α_s-plots allowed us to conclude that all samples were predominantly microporous. A small amount of mesoporosity was detected in the case of samples 150T3, 300T5 and FREET5.

The generally observed trend is an increase in surface areas and micropore volumes with increased washing of samples of T1, T2, T4 and T5 series. A reversed trend is observed in the case of samples of T3 series. It suggests that at relatively low temperatures the observed variations in surface areas may be somehow related to the coordinated water ligands. Indeed, as mentioned earlier samples of T3 series, as opposed to samples of T1 and T2 series, had lost all of their coordinated water. At higher heating temperatures sintering phenomena may be responsible for the observed variations in the areas. The highest areas for each series was obtained for samples FREET1, 300T2, 100T3, FREET4 and FREET5, respectively.

An interesting observation here is the closeness between the values of the surface areas obtained by the BET method S_{BET} and the values of the areas obtained by the α_s method S_s. Thus suggesting that these calculated areas are real and not apparent areas.

3.4. Elemental analysis

Elemental tests were carried out for S, N, H, and C on all of the samples. The results of the analyses are reported in Table III.

It is seen that, in general, for samples of T1, T2, T3 and T4 series, contrary to expectations, the sulfur content increases with increased washing, whereas the reverse is true for the hydrogen, nitrogen and carbon contents. Also of significance, is the percent decrease of hydrogen content with increased washing, which is significantly less for these samples than the percent

content decrease of the other elements. This suggests that the depletion of hydrogen is being controlled by some given mechanism within the sulphated zirconia matrix, and that hydrogen is possibly retained in the form of water or surface hydroxyls. In turn, this water, or hydroxyl ions, may be playing a role in stabilizing the sulfur within the zirconia structure.

3.5. Surface acidity

The total number of acidic sites was determined from the saturation values of the neutralization-adsorption isotherms of NaOH. The latter were Langmuir-like in shape. The total number of basic groups was determined by phosphoric acid adsorption from solution. These were found to be negligible in number. The number of acidic sites is indicated in Table II in μmol/g.

It is noteworthy that in the prepared T1, T2 and T3 series the highest number of acidic sites is observed for the sulphated zirconium samples with *highest areas*, *micropore volumes*, and with greatest evidence, in their infrared spectra, of *bridging bidentate sulphate ions*. The *concomitant* effect of these three parameters seems to be the crucial parameter in determining the extent of acidity in these sulphated zirconium oxides. Indeed, samples FREET1, 300T2, 100T3 displaying high surface areas, high micropore volumes *and* a high concentration of sulphate ions in a bidentate state of ligation exhibited the most pronounced acidic behavior. The observed decrease in acidic sites for the samples of the T4 series and more so for the samples of the T5 series (shown to be devoid of sulphate ions) confirms that the high acidities observed in the case of samples of T1, T2 and T3 series are closely related to the sulphate ions, and more specifically when the latter are in a bridging bidentate state of ligation.

It is also noteworthy that our present results seem to suggest that such a state of ligation of the sulphate ions is dependent on the presence of small amounts of either water or hydroxyl ions. In a manner akin to that described by Saur [33] for sulphated titania, one possible interpretation is that the presently prepared sulphated

zirconias have the structure $(Zr-O)_3$-S=O which upon the addition of water leads to:
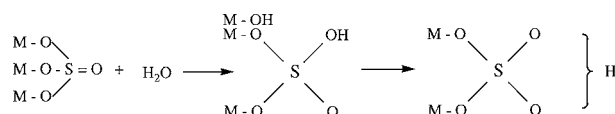
Such a scheme would account for the increase in the stability of the bidentated sulfur as a result of washing and for the increase in the observed acidities.

Another interpretation based on quantum chemistry calculations which was made by Babou *et al*. [25] is that sulphated zirconia may be considered as a sulphuric acid molecule grafted to the surface of zirconia (as below) so that water stabilizes this grafted state. These authors also showed that to become catalytically active the surface sites on the sulphated zirconia needed small amounts of water.
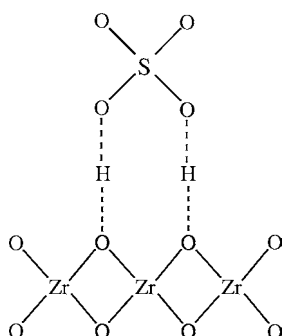
Corroborating such interpretations, and as mentioned earlier, Vera *et al*. [24] determined the quantity of surface (OH) groups and showed that surface anions need the presence of adjacent hydroxyls in order to become anchored to the surface of zirconia and form sulpho-bridges, and that the depletion of such surface hydroxyl groups hampered the possibility of the sulpho-bridge formation. Water is the most probable source of such hydroxyl groups.

All of the above interpretations emphasize the role of water in stabilizing the bidentated sulphate and account for the observed trends in the acidity of the presently prepared sulphated zirconias. Furthermore high acidities are expected to be particularly perceived in systems displaying extensive surface areas which would allow for the presence of a large number of surface sulphate groups. In this connection, Tichit *et al*. [34] found a close correlation between the catalytic activities of sulfated zirconias and their specific surface areas: the higher these areas the higher was the activity of the catalyst.

In addition, a high micropore volume is also expected to enhance the stability of the surface sulphate ions. Indeed as pointed out by Gregg and Sing [35] in the case of microporosity the overlap of the potential fields from opposite walls in the pore would increase the attractive force acting on any chemisorbed or physisorbed species (sulphate ions in the present study) as compared with the force on an open surface.

It is therefore expected that high specific areas and high micropore volumes would enhance the

accessibility of the suphate ions to the surface and their stability there. This would, in turn, account for the high acidities observed in the presently studied high area sulphated zirconias displaying also high micropore volumes.

4. Conclusions

Sulphated oxides of zirconium prepared using *urea* as precipitating agent exhibit strong surface acidity. The latter is favored when the sulfur ions are in a bidentated state of ligation. Water appears to have a stabilizing effect on the formed sulphur complex. Strong acidity is particularly displayed in systems exhibiting *high surface areas* and *micropore volumes*. High surface areas allow a greater *accessibility* of the *bidentated sulphate ions* to the surface, whereas high micropore volumes increase the *stability* of the adsorbed bidentate sulphate species on the surface.

References
 1. H. P. BOEHM, *Discuss. Faraday Soc*. **52** (1971) 264.
 2. K. YAMAGUSHI, T. JIN and K. TANABE, *Mater. Chem. Phys*. **17** (1987) 3.
 3. K. ARATA, *Appl. Catal. A: Gen*. **146** (1996) 3.
 4. G. K. CHUAH, S. JAENIKE, S. A. CHEONG and K. S. CHANG, *ibid*. **145** (1996) 267.
 5. X. SONG and A. SAYARI, *Chemtech*. (1995) 27.
 6. M. WAQUIF, J. BACHELIER, O. SAUR and J. C. LAVALLAY, *J. Mol. Catal*. **72** (1992) 127.
 7. J. M. PARERA, *Catal. Today* **15** (1992) 481.
 8. T. YAMAGUSHI, *Appl. Catal*. **61** (1990) 1.
 9. R. SRINVASAN, D. TAULBEE and B. H. DAVIS, *Catal. Lett*. **9** (1991) 1.
10. K. ARATA and M. HINO, *Mater. Chem. Phys*. **26** (1990) 213.
11. M. T. TRAN, N. S. GNEP, G. SZABO and M. GUISNET, *Appl. Catal. A: Gen*. **171** (1998) 207.
12. W. STICHERT and F. SCHUTH, *J. Catal*. **174** (1998) 242.
13. M. HINO, S. KOBAYASHI and K. ARATA, *J. Amer. Chem. Soc*. **101** (1979) 6439.
14. V. PARVULESCU, S. COMAN, P. GRANGE and V. I. PARVULESCU, *Appl. Catal. A: Gen*. **176** (1999) 27.
15. E. PLATERO and P. MENTRUIT, *Mater. Lett*. **14** (1992) 318.
16. B. H. DAVIS, R. A. KEOGH and R. SRINIVASAN, *Catal. Today* **20** (1994) 219
17. C. ZHANG, G. MENG, D. HAN and X. ZENG, *Cailiao Yanjiu Xuebao* **9** (1995) 259.
18. E. E. PLATERO, M. P. MENTRUIT, C. O. AREAN and A. ZECCHINA, *J. Catal*. **162** (1996) 268.
19. K. ARATA, M. HINO and N. YAMAGATA, *Bull. Chem. Soc. Jpn*. **63** (1990) 244.
20. T. RIEMER, D. SPIELBAKER, M. HUNGER, G. A. H. MEKHEMER and H. KNOZINGER, *J. Chem. Soc. Chem. Commun*. (1994) 1181.
21. F. GARIN, L. SEYFRIED, P. GIRARD, G. MAIRE, A. ABDULSAMAD and J. SOMMER, *J.Catal*. **151** (1995) 26.
22. 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, *ibid*. **151** (1995) 364.

23. W. STICHERT, F. SCHUTH, S. KUBA and H. KNOZINGER, *ibid.* **198** (2001) 277.
24. C. A. VERA and J. M. PARERA, *ibid.* **165** (1997) 254.
25. F. BABOU, G. COUDURIER and J. C. VEDRINE, *ibid.* **152** (1995) 341.
26. K. NAKAMOTO, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" (Wiley, New York, 1986).
27. M. L. HAIR, *J. Phys. Chem.* **74** (1970) 1290.
28. J. RAGAI, *J. Chem. Tech. Biotech.* **40** (1987) 143.
29. N. D. PARKYNS, "Chemisorption and Catalysis" (Hepple Publications, London, 1970).
30. K. NAKAMOTO, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" (Wiley, New York, 1978) p. 239.
31. J. RAGAI and K. S. W. SING, *J. Colloid Interf. Sci.* **101** (1984) 369.
32. S. J. GREGG and K. S. W. SING, "Adsorption, Surface Area and Porosity" (Academic Press, London, 1982) p. 98.
33. O. SAUR, M. BENSITEL, A. B. M. SAAD, J. C. LAVALLEY, C. P. TRIPP and B. A. MORROW, *J. Catal.* **99** (1986) 104.
34. D. TICHIT, D. ELALAMI and F. FIGUERAS, *ibid.* **163** (1996) 18.
35. S. J. GREGG and K. S. W. SING, "Adsorption, Surface Area and Porosity" (Academic Press, London, 1982) p. 195.