

Characterization and evaluation of ZrO_2 supported hydrotreating catalysts

S.K. Maity^{*}, M.S. Rana, B.N. Srinivas, S.K. Bej, G. Murali Dhar, T.S.R. Prasada Rao

Indian Institute of Petroleum, Dehradun 248005, India

Received 9 April 1999; received in revised form 16 July 1999; accepted 9 August 1999

Abstract

A series of zirconia supported molybdenum catalysts were prepared and characterized by BETSA, XRD, TPR, FTIR, XPS and oxygen chemisorption. Thiophene, cyclohexene and tetrahydrofuran were taken as model compounds for evaluating their hydrodesulfurization (HDS), hydrogenation (HYD) and hydrodeoxygenation (HDO) activities, respectively. The XRD results indicate that Mo is present as a monolayer up to 6 wt.% loading, whereas MoO_3 crystalline growth is observed beyond this loading. O_2 -uptake and catalytic activities also increase up to 6 wt.% Mo-loading but above this loading both start decreasing. There are good correlations between O_2 uptake and all catalytic activities. TPR and FTIR results indicate that at lower loading, MoO_3 is present as tetrahedra form and at moderate loading, both tetrahedral and octahedral forms are found. XPS results reveal that the electron transfer is taking place from support to molybdenum. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: XRD; TPR; FTIR; XPS; Oxygen chemisorption; HDS; HYD; HDO

1. Introduction

The legislative pressure on the specification of different petroleum products is increasing day by day to protect the environment. Out of all these restrictions, the sulfur content of the transportation fuels is being tightened more strictly. For example, the maximum sulfur content in atmospheric gas oil is presently restricted to 500 ppm in different parts of the world, which is going to be reduced further (e.g., 350 ppm in Europe) by the beginning of the 21st century. The hydrodesulfurization (HDS) of gas

oil over Al_2O_3 based CoMo/NiMo catalysts are used commercially for reducing sulfur content. Though there are a number of process variables which can be attempted to produce diesel having sulfur level of 500 ppm or lower, but mostly all these variables show trade-off. For example, increasing temperature will help in desulfurization but at the expense of cycle life of the catalyst and producing bad color product. Similarly, reducing space velocity will require a higher reactor and catalyst volume causing more capital investment. Increasing hydrogen pressure as well as adopting new process line-up will also require additional capital investment. The only option, which does not have any negative effect, is to utilize a better catalyst

^{*} Corresponding author.

having higher activity and life. Support plays an important role in this direction. Traditional improvement in catalyst performance of conventional Al_2O_3 based catalyst has mostly levelled off. The new horizon, which can show some light, may be by the development of catalyst using novel support and some breakthrough in dispersing active metals on the support. In the last decade, there has been considerable interest on support effects due to the realization that these data may be useful in preparing improved catalysts. With this view in mind, Zirconium oxide (ZrO_2) has been selected as a support for studying different hydrotreatment reactions.

ZrO_2 has been attracting attention of researchers as catalyst as well as catalyst support in recent years. Higher thermal stability, extreme hardness, high specific mass of zirconia are the advantages for its use as catalyst and as support. It has both acidic and basic properties. Zirconia was used as support for hydrotreating catalysts by many research workers [1–7]. Though many studies have been conducted using ZrO_2 as support, the effect of support on catalytic functionalities for hydrotreating reactions and structure–activity relationship are not yet fully understood. Therefore, this study has been carried out in a systematic way to elucidate some of these aspects.

2. Experimental

The catalysts were prepared by incipient impregnation method over a commercial (Harshaw) zirconia support having a surface area of $43 \text{ m}^2 \text{ g}^{-1}$. The impregnated catalysts were dried in air overnight at 120°C and then calcined in air at 450°C for 6 h. The particle size of the support used was 18–40 mesh. Oxygen chemisorption was measured at -77°C in a high vacuum glass unit on catalyst sulfided at 400°C for 2 h using CS_2/H_2 mixture. X-ray diffractograms were recorded on a Rigaku model D-Max 111B. Temperature programmed reduction (TPR) was carried out in the range of 0 – 900°C at a heating

rate of 10 K min^{-1} using 5% H_2/N_2 mixture. Catalyst weight was taken constant for each TPR experiment. For the FTIR study, Perkin Elmer 1700X model was used for surface characterization of molybdenum oxide catalysts. Self-supported discs were prepared with KBr. A vacuum Generator ESCALAB MK11 Spectrometer with Mg K_α radiation (1253.6 eV) was used for the measurement of molybdenum oxidation states by XPS. The data were collected and analyzed on an Apple 11e (48k) microcomputer.

The catalytic functionalities of molybdenum sulfide catalysts were tested using different model compounds, viz. thiophene for HDS, cyclohexene for hydrogenation (HYD) and tetrahydrofuran for hydrodeoxygenation (HDO). The reactions have been carried out at 400°C temperature and atmospheric pressure. The oxide precursors were sulfided in situ at 400°C for 2 h by passing a mixture of CS_2 and H_2 (at the rate of 40 ml min^{-1}) before reaction. Reaction products were analyzed by an on-line GC.

3. Results

3.1. X-ray diffraction

Pure ZrO_2 and $\text{MoO}_3/\text{ZrO}_2$ catalysts with varying Mo-loading have been examined by X-ray diffraction technique. The X-ray diffractograms are shown in Fig. 1. Pure ZrO_2 support exists in tetragonal ($d_{11} = 2.94 \text{ \AA}$) and monoclinic ($d_{11} = 3.16$ and 2.834 \AA) forms. Addition of molybdenum causes partial transformation of the monoclinic phase to the tetragonal phase. It is observed from the peak areas of the spectrum that with addition of 10 wt.% Mo on the support, the tetragonal phase is increased from 39.5% (for pure ZrO_2) to 44% (for Mo/ZrO_2). No reflection due to molybdenum oxide is observed up to 6 wt.% Mo. Above 6 wt.% loading, lines due to molybdenum oxides are observed.

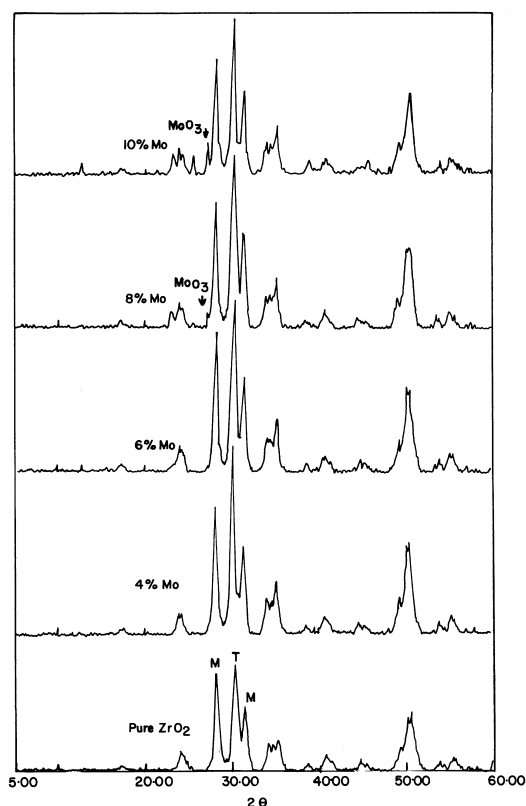


Fig. 1. X-ray diffractograms of $\text{MoO}_3/\text{ZrO}_2$ catalysts at different loadings.

3.2. Temperature programmed reduction (TPR)

TPR profiles are given in Fig. 2. It can be noticed from the figure that pure zirconia shows a broad reduction feature at a very high temperature around 726°C . With the addition of 2 wt % of molybdenum, the temperature maxima (T_m) drops to 544°C . No reduction of ZrO_2 is observed in this procedure, indicating that presence of Mo is decreasing reducibility of pure ZrO_2 . The TPR peak becomes very broad for the sample having 4 wt.% of molybdenum and it is clear that this broad peak is the sum of two peaks whose T_m are around 542°C and 621°C . In addition, with further molybdenum loading, the T_m is shifted to a higher temperature and peak pattern becomes broader. It is well known that at lower Mo-loading, molybdenum oxide is present mainly as tetrahedral species, which is

difficult to reduce due to strong interaction with support. At moderate loading, both tetrahedral and octahedral species are present, and compared to tetrahedral species, the octahedral species are easily reducible. Two peaks were observed at 4 wt.% Mo-loading, the low temperature peak (542°C) can be assigned to the reduction of octahedral species, whereas the high temperature peak (621°C) may be due to reduction of tetrahedral species. Both octahedral and crystalline MoO_3 are expected to be present at much higher Mo-loading. But, due to the broadness of TPR profiles, it is not possible to distinguish both these species. The difficulty in distinguishing these two species can also be attributed to weak interaction of molybdenum with ZrO_2 support. It is also noticed that at 2 wt.% Mo-loading, the reduction of MoO_3 starts at temperature around 498°C . But the temperature at which the reduction starts gradually shifts toward lower temperature with increasing Mo-loading. These results are in agreement with results observed by Bond et al. [8].

3.3. FTIR spectroscopy

The IR spectra of molybdenum oxide supported on zirconia was carried out using KBr pellet technique and the spectra are presented in Fig. 3. It can be seen that pure MoO_3 has bands in the region of $400\text{--}1050\text{ cm}^{-1}$. There are bands around 560 , 860 and 992 cm^{-1} (Fig. 3). The region at $1050\text{--}900\text{ cm}^{-1}$ represents terminal $\text{Mo}=\text{O}$ and $800\text{--}700\text{ cm}^{-1}$ represents the region of antisymmetric Mo-O-Mo or O-Mo-O stretching vibration or both. But the band around 820 cm^{-1} is the characteristic band for bulk MoO_3 [9]. It can be noticed from Fig. 3 that pure zirconia has a broad band concentrated around 505 cm^{-1} . No IR band is observed due to molybdenum species up to 4 wt.% Mo-loading. Bands due to polymolybdates species appear in the region of $950\text{--}980\text{ cm}^{-1}$ at 6 wt.% Mo-loading and the bands positions are shifted to a higher region from 950 to 992 cm^{-1} as Mo-loading is increased further. There is also a

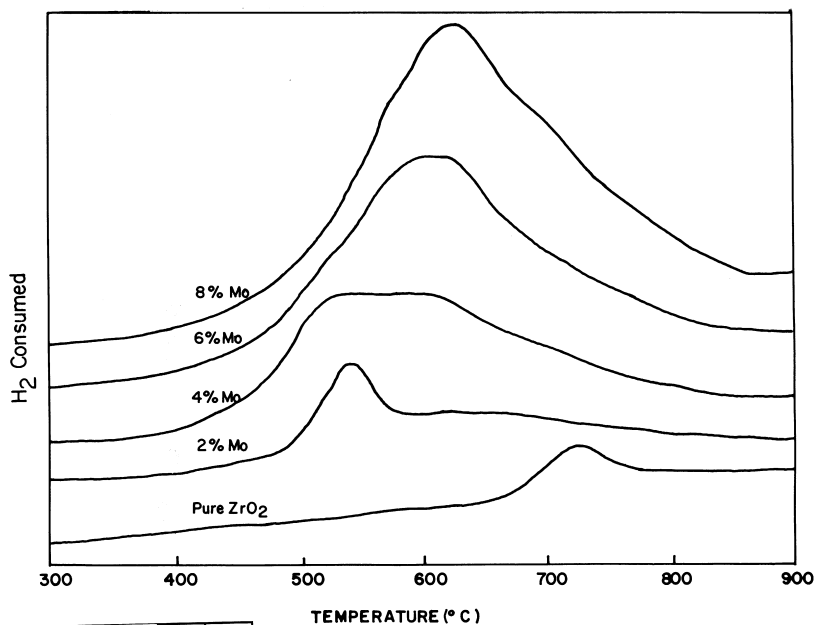


Fig. 2. TPR patterns of Mo/ZrO₂ catalysts at different loadings.

separate band at 878 cm⁻¹ at 10 wt.% Mo-loading. The Mo–O vibrational bands of the tetrahedral species MoO₄²⁻ appear at the 930–830 cm⁻¹ region and those of the octahedral species MoO₆⁶⁻, appear in the 990–930 cm⁻¹ and 860–

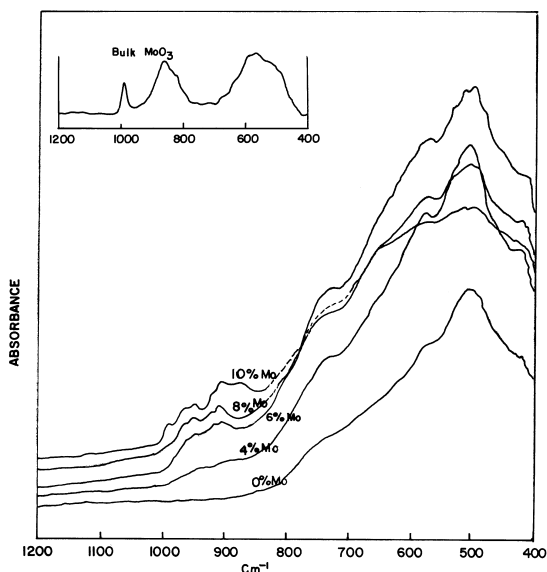


Fig. 3. FTIR spectra of MoO₃/ZrO₂ catalysts at different loadings.

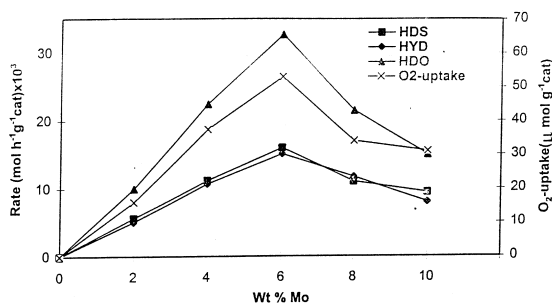
800 cm⁻¹ regions [10]. Hence, it can be concluded from these results that up to 6 wt.% Mo-loading, molybdenum oxide remains as tetrahedral and octahedral polymolybdate species. Above this loading, the concentration of poly-octahedral species increases whereas at 8 wt.% and above, line due to crystalline MoO₃ (~ 992 cm⁻¹) appears. Our results are also in agreement with observations of other workers in this area [11,12].

3.4. Electron spectroscopy for chemical analysis (ESCA)

The binding energies of molybdenum and zirconia are given in Table 1. The binding

Table 1
Results of XPS studies on molybdenum oxide

Mo-loading (wt.%)	Binding energy (eV)				Atomic ratio Mo/Zr
	Zr 3d _{3/2}	Zr 3d _{5/2}	Mo 3d _{3/2}	Mo 3d _{5/2}	
4	184.6	182.3	235.9	232.8	0.20
6	184.6	182.3	235.9	232.8	0.29
8	184.6	182.3	235.9	232.8	0.38

Fig. 4. Variation of rates and O₂ uptake with Mo-loading.

energy of Mo_{3d5/2} in bulk MoO₃ is 233.2 eV [13]. The binding energy of Mo_{3d5/2} in Mo/ZrO₂ catalyst shows an appreciable shift from that of bulk MoO₃. It indicates that electron transfer takes place from support to Mo, which is in agreement with Nag's study [13].

3.5. Oxygen chemisorption

The oxygen uptake values are plotted against Mo-loading and are shown in Fig. 4. The variation of corresponding parameters as a function of Mo-loading is given in Table 2. It is observed that the oxygen uptake increases linearly with Mo-loading up to 6 wt.% Mo and then decreases with further loading. It is possible to calculate equivalent molybdenum sulfide area (EMSA) and dispersion (O/Mo) from oxygen uptake values. It is also possible to calculate the surface coverage by molybdenum and crystallite size of MoS₂. The percentage of dispersion (O/Mo) has been plotted against Mo-loading in Fig. 5. The dispersion is constant up to 6 wt.% Mo-loading and then sharply decreases with

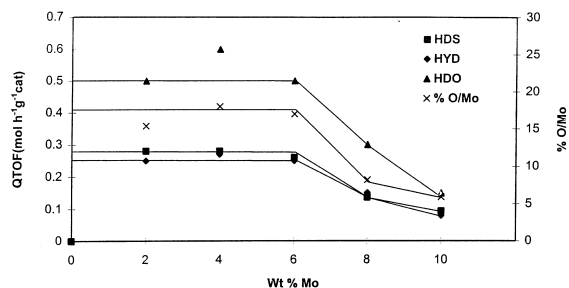


Fig. 5. Variation of QTOF(s) and dispersion with Mo-loading.

further Mo-loading. It is interesting to note that at 6 wt.% Mo-loading, around 94% of the surface is covered by molybdenum atoms. The surface coverage is calculated by dividing EMSA by BET surface area. Due to higher oxygen uptake and low surface area, the surface coverage is high. The crystallite sizes (calculated using EMSA values) did not change appreciably up to 6 wt.% but slow crystal growth can be observed above this loading. Therefore, we can conclude that up to 6 wt.% Mo-loading, molybdenum oxide on zirconia is well dispersed, probably as monolayer and beyond this point molybdenum sulfide crystallites are formed.

3.6. Catalytic activities

All the experiments were conducted in the absence of interpellet and intrapellet diffusional resistances. The rates of HDS, HYD, and HDO reactions for pure ZrO₂ are 11.6×10^{-3} , 10.2×10^{-3} and 12.55×10^{-3} mol h⁻¹ g⁻¹ catalyst, respectively, and proper correction is

Table 2
Results of BET surface area and oxygen chemisorption studies

Mo-loading (wt.%)	BETSA (m ² g ⁻¹)	O ₂ -uptake (μmol g ⁻¹ cat.)	% O/Mo (dispersion)	EMSA (m ² g ⁻¹)	Surface coverage (%)	Crystallite size (Å)
1	41	8.5	16.3	4.8	11.8	21.7
2	39.4	16.0	15.3	9.1	23.5	23.0
4	37.6	37.5	18.0	21.2	58.8	19.6
6	34.0	53.0	16.9	30.0	93.7	20.8
8	33.0	34.0	8.1	19.2	63.4	43.3
10	27.2	31.0	5.9	17.6	71.6	59.3

adopted for this before activity values are plotted against Mo-loading in Fig. 4. All three activities increase linearly with Mo-loading up to 6 wt.% Mo and then slowly decrease with increasing Mo-loading. The quasi turnover frequencies (QTOF) were calculated for all these three reactions and were plotted against Mo-loading in Fig. 5. The QTOFs are almost constant with Mo-loading up to 6 wt.% and then start to decrease at higher loading. It is interesting to recall that the percentage of dispersion (O/Mo) plot also shows a similar trend with Mo-loading. QTOF means the ratio of moles of reactant reacting per hour per gram of molybdenum. In other words, QTOF is equal to the ratio of molecules of reactant reacting per hour per molybdenum. The ratio of surface molybdenum atoms to total number of Mo atoms gives the dispersion of molybdenum. That is why QTOF is proportional to dispersion and hence, shows similar trend with Mo-loading.

4. Discussion

The commercial zirconia used for this purpose had moderate surface area which further decreases with the addition of MoO₃. This decrease in surface area may be due to the blockage of pore mouth with the addition of molybdenum oxide during preparation. The X-ray diffractograms indicate no evidence for crystalline MoO₃ up to 6 wt.% Mo-loading (14.34 μmol m⁻²). Beyond this, the peak due to crystalline MoO₃ is observed and the intensity of this peak increases with increasing Mo-concentration. It is also observed that Mo induces monoclinic to tetrahedral phase transformation of ZrO₂. Rijnten [14] and Afanaiev et al. [4] also observed monoclinic to tetragonal phase transformation of ZrO₂ with the impregnation of molybdenum oxide. The TPR and FTIR results indicate the presence of tetrahedral molybdenum species at lower loading, whereas, octahedral polymolybdate species are found in higher loadings. Ono et al. [15] reported the presence

of polymolybdate species on monoclinic zirconia. They also showed evidences for the presence of tetrahedral molybdate at lower loading. The decrease in surface coverage beyond monolayer suggests that some of the molybdenum species, which are used to form monolayer, are used in the formation of big MoO₃ crystals. The formation of monolayer depends on the support surface area and preparation method. These findings are in line with the results obtained by others. Reddy et al. [2] obtained monolayer coverage at 3.5 wt.% Mo on a low surface ZrO₂. While on a higher surface area ZrO₂ (130 m² g⁻¹), Duchet et al. [16] found the formation of monolayer at 10 wt.%. Afanaiev et al. [4] observed monolayer formation at still higher loading because they prepared high surface area ZrO₂ by molten salt method. Molybdenum anchors on the surface by interacting with surface hydroxyl groups. On the ZrO₂ surface, two types of hydroxyl groups are characterized by IR, one at 3775 cm⁻¹ and another at 3673 cm⁻¹ [13]. The high frequency peak corresponds to more basic hydroxyl groups and these groups are consumed by initial amount of molybdenum. Stoppek-Longner et al. [17] clearly showed the decrease of intensity of 3775 cm⁻¹ peak down to 1 wt.% molybdenum loading. Therefore, large number of hydroxyl groups can accommodate a large amount of molybdenum up to monolayer level.

The oxygen uptake on MoS₂/ZrO₂ at monolayer level is to 1.21 μmol m⁻² (≡ 53 μmol g⁻¹ cat.), whereas it is 0.13 μmol m⁻² for MoS₂/Al₂O₃ (data related to Al₂O₃ supported catalyst has been taken from Ref. [18]). This indicates the increased density of sites in the

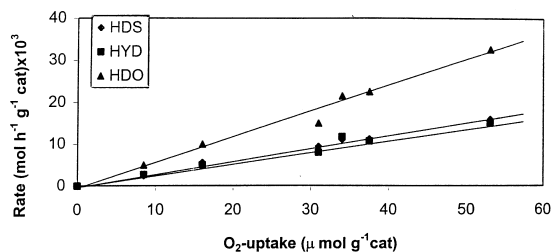


Fig. 6. Correlation between activity and O₂ uptake.

case of ZrO_2 support. The oxygen chemisorbs on anion vacancies that are formed during sulfidation/reduction. The higher surface site density means easy reduction/sulfidation of Mo/ZrO_2 catalysts and this may be due to electron transfer from support to MoO_3 . Sedlacek et al. [5] also observed that 50–65% molybdenum oxide species were reduced to Mo^{4+} on ZrO_2 support, whereas it was only 30% in the case of Al_2O_3 support.

The HDS activity of MoS_2/ZrO_2 catalysts have been found to be better compared to that of MoS_2/Al_2O_3 catalysts, whereas the HYD activity is lower for ZrO_2 supported catalysts. Similar results are also reported by others [19,20]. Hamon et al. [21] reported more HYD activity for ZrO_2 supported catalyst compared to that of Al_2O_3 supported catalyst. It may be due to high surface area ZrO_2 , prepared by molten salt method. There are very good correlations between oxygen uptake and activities (Fig. 6). This suggests that there is proportionality between oxygen chemisorption and all the three catalytic functionalities. Similar correlations were also observed for our other studies [22,23]. However, since there is a strong evidence for different sites for HDS and HYD [24], oxygen chemisorption cannot distinguish them and therefore it is not specific to any one of these functionalities and it may be measuring some parameters related to dispersion.

Acknowledgements

Our sincere thanks to Dr. V.K. Kausik (IPCL, Baroda) for the ESCA analysis and Dr. O.S. Tyagi for IR analysis. We are grateful to Dr. V.V.D.N. Prasad and Dr. Ramakrishna for their constant help.

References

- [1] K.C. Pratt, J.V. Sanders, V. Chritov, *J. Catal.* 124 (1990) 416.
- [2] B.M. Reddy, K.V.R. Chary, B. Rama Rao, V.S. Subrahmanyam, C.S. Sunandana, N.K. Nag, *Polyhedron* 5 (12) (1986) 191.
- [3] K.S. Rao, H. Ramakrishna, G. Murali Dhar, *J. Catal.* 133 (1992) 146.
- [4] P. Afanaiev, F. Geantet, M. Breyse, *J. Catal.* 153 (1995) 17.
- [5] J. Sedlacek, Z. Vit, *Collect. Czech. Chem. Commun.* 54 (1989) 2064.
- [6] M. Breyse, J.L. Portefaix, M. Vrinat, *Catal. Today* 10 (1991) 489.
- [7] S.W. Oliver, T.D. Smith, J.R. Pilbrow, K.C. Pratt, V. Chritov, *J. Catal.* 111 (1988) 88.
- [8] G.C. Bond, S. Flamerz, L. Van Wijk, *Catal. Today* 1 (1987) 229.
- [9] C. Li, Q. Xin, K.L. Wang, X. Guo, *Appl. Spectrosc.* 45 (5) (1991) 874.
- [10] F. Prinetto, G. Cerrato, G. Ghiottand, A. Chiorino, *J. Phys. Chem.* 99 (1995) 5556.
- [11] F. Mauge, J.C. Duchet, J.C. Lavally, S. Houssenbay, E. Payen, J. Grimbot, S. Kasztelan, *Catal. Today* 10 (1991) 561.
- [12] E. Payen, L. Gengembre, F. Mauge, J.C. Duchet, J.C. Lavally, *Catal. Today* 10 (1991) 521.
- [13] N.K. Nag, *J. Phys. Chem.* 91 (1987) 2324.
- [14] H.Th. Rijten, PhD Thesis, Delft Technical University, 1971.
- [15] T. Ono, H. Kamisuki, H. Hisashiand, H. Miyata, *J. Catal.* 116 (1989) 303.
- [16] J.C. Duchet, M.J. Tilliette, D. Cornet, L. Vivier, G. Perot, L. Bekakra, C. Moreauand, G. Szabo, *Catal. Today* 10 (1991) 579.
- [17] K. Stoppek-Longner, J. Goldwasser, M. Houalla, D.M. Hercules, *Catal. Lett.* 32 (3) (1995) .
- [18] H. Ramakrishna, *Catalytic Functionalities of Supported Sulfides*, PhD Thesis, 1991.
- [19] C. Mauchausse, H. Mozzanega, P. Turlier, J.A. Dalmon, *Proc. of 9th ICC* 775 (2) (1988) .
- [20] M. Vrinat, D. Hamon, M. Breyse, *Catal. Today* 20 (1994) 273.
- [21] D. Hamon, M. Vrinat, M. Breyse, B. Durand, M. Jebrouni, M. Roubin, P. Magnoux, T. des Courieres, *Catal. Today* 10 (1991) 613.
- [22] B.N. Srinivas, S.K. Maity, V.V.D.N. Prasad, M.S. Rana, M. Kumar, G. Murali Dhar, T.S.R. Prasada Rao, *Stud. Surf. Sci. Catal.* 113 (1998) 497.
- [23] S.K. Maity, B.N. Srinivas, V.V.D.N. Prasad, A. Singh, G. Murali Dhar, T.S.R. Prasada Rao, *Stud. Surf. Sci. Catal.* 113 (1998) 579.
- [24] G. Murali Dhar, H. Ramakrishna, T.S.R. Prasada Rao, *Catal. Lett.* 22 (1993) 351.