

# Influence of hydrogen sulfide adsorption on the catalytic properties of metal oxides

M. Ziolek<sup>a</sup>, J. Kujawa<sup>a</sup>, O. Saur<sup>b</sup>, J.C. Lavalley<sup>b,\*</sup>

<sup>a</sup> Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznan, Poland

<sup>b</sup> Laboratoire Catalyse et Spectrochimie, URA CNRS 414, ISMRA-Université, 14050 Caen-Cedex, France

Received 15 April 1994; accepted 28 November 1994

## Abstract

The effect of sulfidation by H<sub>2</sub>S at 623 K of various metal oxides (MgO, TiO<sub>2</sub> rutile and anatase, ZrO<sub>2</sub>, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) on their catalytic properties towards isopropanol decomposition, cumene decomposition and methanol hydrosulfurization has been studied. The results are discussed according to the H<sub>2</sub>S adsorption modes. H<sub>2</sub>S coordination mainly occurs on TiO<sub>2</sub> samples and generates strong acid sites. The dissociative adsorption of H<sub>2</sub>S on alumina does not significantly influence its acidity. Replacement of O<sup>2-</sup> by S<sup>2-</sup> ions as in the case of MgO, ZrO<sub>2</sub> and CeO<sub>2</sub> mainly affects their basic or redox properties.

*Keywords:* Acidic properties; H<sub>2</sub>S adsorption; Metal oxides

## 1. Introduction

Sulfidation of metal oxide catalysts has been widely applied in the petroleum industry for the catalytic hydrodesulfurization (HDS process) [1,2]. Other reactions such as hydrodenitrogenation of quinoline [3] or disproportionation of toluene [4] are also promoted by the presence of hydrogen sulfide. Recently, the promotive effect of H<sub>2</sub>S adsorption on zeolites, metal oxides or heteropoly acids for hydrocarbon conversion [5] and hydrosulfurization of alcohols [6] has been reported.

The aim of this study was to determine changes in the catalytic properties of various metal oxides on adsorption of hydrogen sulfide. The following reactions were applied: (i) the isopropanol

decomposition, (ii) the cumene decomposition and (iii) the reaction between methanol and hydrogen sulfide. The isopropanol decomposition was used as one of the typical reactions for determination of acid–base properties of solids for a long time [7] since it can proceed via the two reaction pathways: (i) dehydration leading to the formation of propene and water and (ii) dehydrogenation producing acetone. The first pathway has widely been applied to characterization of the acidity of oxides [8], while many authors used the dehydrogenation of isopropanol to acetone as a test reaction on the basicity of catalysts [9,10]. Although a redox mechanism for isopropanol dehydrogenation is proposed by some authors [11,12] and a concerted mechanism involving both acid and basic sites is postulated by others [13], the isopropanol decomposition seems to be a useful reaction for observation of changes in the

\* Corresponding author. Fax. (+33)31452877.

catalytic properties of metal oxides on sulfidation.

The decomposition of cumene can lead to the formation of propene and benzene if the reaction proceeds via the carbocation mechanism or can produce styrene and/or  $\alpha$ -methylstyrene if the radical mechanism occurs [14]. The cumene cracking to propene and benzene is used as a test reaction for the strong Brønsted acidity [15].

The reaction between methanol and hydrogen sulfide involves acid sites (Brønsted and/or Lewis) and basic sites. The reaction proceeds by surface methoxylation on pairs of Lewis acid–base centres in metal oxides [16] or on the Brønsted acid sites in the hydrogen forms of zeolites [17]. Methoxy species react with  $H_2S$  molecules activated on the catalyst surface. The main products in the reaction of methanol with hydrogen sulfide are methanethiol and dimethylsulfide. The acidity of catalysts strongly influences the selectivity of this process. The selectivity towards dimethyl sulfide increases when the acidity of catalysts (Lewis and/or Brønsted) increases [17,18]. If catalysts provoke the dissociation of  $H_2S$  to  $HS^-$  ions the selectivity towards methanethiol appears to be higher.

## 2. Experimental

Metal oxides used in this work are characterized in Table 1.

Before sulfidation, granulated (0.5–1 mm) samples were activated in the helium flow at 673 K for 2 h. The adsorption of hydrogen sulfide (Fluka) was carried out in the dynamic system.

Table 1  
Characteristics of metal oxides used in this work

Metal oxide	Specific surface area, $m^2 g^{-1}$	Preparation method or origin
MgO	70	Prepared from $Mg(OH)_2$
ZrO <sub>2</sub>	80	Prepared from isopropylate
TiO <sub>2</sub> -R (rutile)	28	Tioxide Intern. Ltd
TiO <sub>2</sub> -A (anatase)	85	Tioxide Intern. Ltd
CeO <sub>2</sub>	100	Rhône-Poulenc
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	215	G.F.S. Rhône-Poulenc

A mixture containing  $1 \text{ cm}^3 \text{ min}^{-1}$  of  $H_2S$  and  $35 \text{ cm}^3 \text{ min}^{-1}$  of deoxygenated helium was passed through the catalyst bed (0.2 g) at 623 K for 1 h. The adsorption of  $H_2S$  was followed by the desorption of weaker held species at 623 K for 10 min.

The amount of sulfur deposit on catalysts after sulfidation was measured using elemental analysis.

The pulse technique was applied in studies of the decomposition of isopropanol and cumene. In both processes 0.1 g of catalysts and 3  $\mu$ l of reactants for one pulse were used. The decomposition of isopropanol was carried out at 523 K and that for cumene at 673 K. Both reactions were used as tests for the study of acid sites. It is known that acidic catalysts are easily deactivated upon the transformation of organic compounds. Thus to measure the acidity of the fresh catalysts the pulse technique was applied which allows one to obtain initial reaction data [19].

The continuous flow system was used in studies of the hydrosulfurization of methanol i.e. the reaction between methanol and hydrogen sulfide. A reaction mixture of methanol (1.25 vol.%) and  $H_2S$  (1.25 vol.%) and helium as a carrier gas was used. The flow rate was  $40 \text{ cm}^3 \text{ min}^{-1}$ . The catalyst weight in this reaction was 0.2 g and the reaction temperature 623 K.

The gas chromatographic analyses using FID and FPD (sulfur) detectors were applied for studies of reactant and product concentrations.

The results presented in the tables were obtained in the initial step of the reactions to determine the influence of the  $H_2S$  pretreatment.

## 3. Results

The amount of sulfur deposit (wt%) on various metal oxides after sulfidation with  $H_2S$  at 623 K is shown in Fig. 1. The highest amounts of sulfur are observed on ceria and zirconia as has been already reported by Mauchausse et al. [20].

Table 2 shows the results obtained with the first pulses for the activity and selectivity of pure and

sulfided metal oxides in the decomposition of isopropanol. The activity of pure samples is the lowest for MgO (2% conversion) and the highest for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100% conversion). The increase in the activity of catalysts are in good agreement with the decrease of the number of basic sites on metal oxides calculated in the paper [21]. Propene is the main product in the isopropanol decomposition on all metal oxides used, except CeO<sub>2</sub>. The sulfidation of samples increases isopropanol conversion. This effect was not observed for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the conditions used; the starting Al<sub>2</sub>O<sub>3</sub> sample already presents 100% conversion of alcohol. In two cases, namely on magnesia and zirconia, the selectivity to acetone increases after the sulfidation of oxides. Pure ceria presents a high selectivity to acetone which decreases upon the sulfidation whereas the total activity increases.

The results obtained with the first pulses in cumene cracking on pure and sulfided samples are shown in Table 3. All pure samples with the

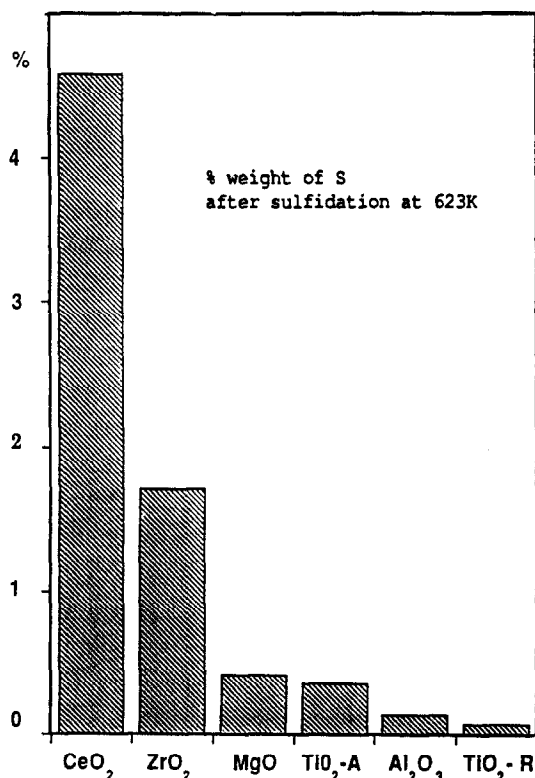


Fig. 1. Amount of sulfur (wt%) on various metal oxides after sulfidation with H<sub>2</sub>S at 623 K.

Table 2

Influence of metal oxide sulfidation on activity and selectivity in isopropanol decomposition at 523 K

Catalyst	Pure		After sulfidation			
	Conv. %	Selectivity %		Conv. %	Selectivity %	
		Propene	Acetone		Propene	Acetone
MgO	2	95	5	10	23	77
TiO <sub>2</sub> (R)	43	ca.	traces	65	100	–
		100				
TiO <sub>2</sub> (A)	81	99	1	100	100	–
ZrO <sub>2</sub>	21	99	1	37	82	18
CeO <sub>2</sub>	11	27	73	87	99	1
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	100	100	–	100	99	1

exception of ceria are inactive or very low active in the cumene cracking. Both titania samples increase their activity in this reaction after sulfidation. The main reaction products on titania are propene and benzene. Pure ceria shows a high activity in the cumene decomposition and a very high selectivity (83%) towards styrene. The activity of ceria significantly decreases after hydrogen sulfide adsorption and the selectivity towards styrene slightly decreases. The other sulfided samples are practically inactive or very low active in the cumene decomposition.

The reaction between methanol and hydrogen sulfide over metal oxides has been studied in our previous work [22]. In this paper we wish to present the influence of the sulfidation of samples on the activity and selectivity in the reaction of CH<sub>3</sub>OH with H<sub>2</sub>S and results obtained after 5 min on stream are reported in Table 4.

The increase in activity on H<sub>2</sub>S adsorption is observed on zirconia and  $\gamma$ -alumina. Ceria activity decreases after sulfidation similarly as was noted for cumene cracking, whereas the activity of neither titania samples changes after sulfidation. However, although the activity of titanias does not change, their selectivity is strongly influenced by the sulfidation, namely the selectivity towards methanethiol decreases and that towards dimethyl sulfide increases on H<sub>2</sub>S preadsorption. The same effect but less evident is observed on zirconia. Sulfided ceria and alumina show higher

Table 3  
Influence of metal oxide sulfidation on activity and selectivity in cumene decomposition at 673 K

Catalyst	Pure				After sulfidation					
	Cumene conv.%		Selectivity %		Cumene conv. %		Selectivity %			
			Propene	Benzene	Styrene	$\alpha$ -methylstyrene	Propene	Benzene	Styrene	$\alpha$ -methylstyrene
MgO	0	–	–	–	0	–	–	–	–	–
TiO <sub>2</sub> (R)	4	29	31	40	10	44	47	9		
TiO <sub>2</sub> (A)	3	51	49	–	13	46	42	12		
ZrO <sub>2</sub>	0	–	–	–	0	–	–	–	–	–
CeO <sub>2</sub>	70	6	11	83	46	8	9	75 <sup>a</sup>		
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1	52	48	–	1	50	50	–		

<sup>a</sup> Additionally 8% selectivity to toluene

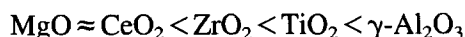
Table 4  
Influence of metal oxide sulfidation on activity and selectivity in hydrosulfurization of methanol at 623 K (H<sub>2</sub>S: CH<sub>3</sub>OH = 1:1)

Catalyst	CH <sub>3</sub> OH conversion, %		CH <sub>3</sub> SH selectivity, %		(CH <sub>3</sub> ) <sub>2</sub> S selectivity, %		CH <sub>4</sub> selectivity, %	
	Pure	Sulfided	Pure	Sulfided	Pure	Sulfided	Pure	Sulfided
	MgO	22	0	ca. 100	–	–	–	–
TiO <sub>2</sub> (R)	27	27	91	81	2	12	7	7
TiO <sub>2</sub> (A)	54	56	53	38	40	53	7	9
ZrO <sub>2</sub>	30	77	99	96	1	3	–	–
CeO <sub>2</sub>	64	54	41	67	2	13	57	20
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	90	100	4	73	95	27	1	–

selectivity towards methanethiol than pure samples. Selectivity towards dimethyl sulfide decreases on sulfided  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and that on sulfided ceria increases. The decrease in the selectivity towards methane is noted on sulfided ceria.

#### 4. Discussion

In a previous study we established the order of the Lewis acid site strength of the metal oxides used [22]:



As for the number of basic sites measured by SO<sub>2</sub> adsorption [21], it increases in the following order:



Considering the results concerning isopropanol decomposition (Table 2), it appears that the activ-

ity of metal oxides selective to propene formation follows the strength of their Lewis acid sites. The two basic oxides, MgO and CeO<sub>2</sub>, present lower activity and a reverse selectivity. Only ceria shows a high selectivity to acetone; this can be related to the redox character of CeO<sub>2</sub> [23] rather than to its basicity in agreement with [12].

Cumene cracking needs strong acid sites. The results of Table 3 show that all the materials are unreactive or weakly active in the formation of benzene and propene except CeO<sub>2</sub>. Only titania samples present an observable activity. This can be related to their Brønsted acidity measured by 2,6-dimethyl pyridine adsorption [24]: among the oxides used, only TiO<sub>2</sub> samples are able to protonate 2,6-lutidine at room temperature. CeO<sub>2</sub> is highly active in cumene decomposition to styrene and  $\alpha$ -methylstyrene which shows that a radical mechanism occurs on ceria. It is related to the well known redox properties of CeO<sub>2</sub> [23].

As shown in a previous paper [22], the most acidic oxides, namely  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ , give rise to a high activity and high selectivity towards dimethylsulfide from methanol reaction with  $\text{H}_2\text{S}$ .  $\text{CeO}_2$  presents a high activity towards this reaction but the main product formed is methane, certainly via a side-reaction, still unknown.

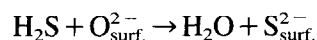
Three possible sulfidation pathways can be considered when  $\text{H}_2\text{S}$  is adsorbed on metal oxides:

- (i) exchange of oxygen from metal oxide to sulfur
- (ii) dissociation of  $\text{H}_2\text{S}$  towards  $\text{HS}^-$  and  $\text{H}^+$ , the latest forming hydroxyl groups on the catalyst surface
- (iii) coordinatively bonded hydrogen sulfide which can be a source of Brønsted acidity [5].

On the basis of the literature data concerning  $\text{H}_2\text{S}$  adsorption on metal oxides and the test reactions studied in this work one can discuss the changes in metal oxides properties resulting from sulfidation.

#### 4.1. $\text{MgO}$

The adsorption of  $\text{H}_2\text{S}$  on magnesia leads to the exchange of some of the surface oxygen ions by sulfur according to the reaction [25]:



Under the sulfidation conditions used in this work the amount of sulfur species on magnesia is not very high ( $1.1 \text{ mol nm}^{-2}$ ). The increase in the sulfided magnesia activity in isopropanol decomposition and high selectivity to acetone indicate that the replacement of oxygen by sulfur in the sample would increase the basic and/or redox character of the catalyst. Brønsted acid sites are not generated when  $\text{H}_2\text{S}$  is adsorbed on magnesia as in cumene cracking and hydrosulfurization of methanol, sulfided magnesia is inactive.

#### 4.2. $\text{TiO}_2$

According to the literature [26,27] hydrogen sulfide is mainly reversibly adsorbed undissocia-

tively on both titania samples, anatase and rutile, giving a coordinatively bonded species.  $\text{H}_2\text{S}$  adsorption on rutile gives additionally irreversibly adsorbed state resulting in either, (i) donation of hydrogen to lattice oxygen to form hydroxyls or water or, (ii) formation of  $\text{H}_2$ . Water was observed when  $\text{H}_2\text{S}$  was adsorbed on rutile used in this work [28].

The increase of the activity of both sulfided titania samples in the decomposition of isopropanol and cumene suggests that, for both rutile and anatase, undissociatively adsorbed  $\text{H}_2\text{S}$  causes the changes in their catalytic activity. Because the increase in the cumene conversion was observed on sulfided titania, one can state that on  $\text{H}_2\text{S}$  adsorption strong Brønsted acid sites are generated. In the reaction between methanol and hydrogen sulfide the increase in the selectivity towards dimethylsulfide resulting in the sulfidation of both titania catalysts also proves the formation of acid sites upon adsorption of  $\text{H}_2\text{S}$ .

#### 4.3. $\text{ZrO}_2$

The amount of  $\text{H}_2\text{S}$  adsorbed on zirconia is very high ( $4 \text{ mol nm}^{-2}$ ) to compare with other samples except  $\text{CeO}_2$  (Fig. 1). Hydrogen sulfide adsorbed on  $\text{ZrO}_2$  leads to the formation of OH groups (IR band at  $3645 \text{ cm}^{-1}$  stable after evacuation at room temperature) [29]. That indicates the dissociative adsorption of  $\text{H}_2\text{S}$ . The absence of IR bands in SH region suggests that the second step of  $\text{H}_2\text{S}$  dissociation occurs ( $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$ ) which can lead to the replacement of oxygen by sulfur [30]. This result is in agreement with the unchanged selectivity to dimethylsulfide in methanol hydrosulfurization. The higher activity of sulfided zirconia for that reaction could be due to factors other than acidity, such as for instance thermal stability of methoxy species [22]. The only clearly explainable result seems relative to the change of acetone selectivity in isopropanol decomposition: its increase after  $\text{ZrO}_2$  sulfidation can be related to an increase of the basic or redox properties of  $\text{ZrO}_2$ .

#### 4.4. $Al_2O_3$

Various types of  $H_2S$  adsorbed species on alumina have been described in the literature [31–35] namely: (i) dissociatively adsorbed species stable to 573 K, (ii) coordinatively bonded  $H_2S$  on strong Lewis sites and (iii) possible replacement of oxygen on alumina by sulfur accompanied by the formation of water.

Pure alumina showed 100% conversion of isopropanol under the conditions adopted, so the influence of sulfidation is not observable. However, the results obtained for cracking of cumene indicate that even if adsorption of  $H_2S$  produces new hydroxyl groups they do not present a strong acidic character. The other proof that the acidity of alumina does not increase on sulfidation is the selectivity in the reaction between methanol and hydrogen sulfide. The selectivity towards dimethyl sulfide decreases after  $H_2S$  adsorption on alumina and that for methanethiol increases.

#### 4.5. $CeO_2$

The sulfur amount on ceria was the highest of all the samples (Fig. 1). It is very probably due to the labile character of oxygen ions in ceria which make them easily exchanged by sulfur upon  $H_2S$  adsorption.

Ceria showed a high activity in electron transfer reactions [36]. In the studies presented, ceria showed high selectivity to styrene in the cumene decomposition and high selectivity towards acetone in isopropanol decomposition. That means that a radical mechanism for the first reaction and a redox for the latter are preferred on  $CeO_2$ . The behaviour of sulfided  $CeO_2$  towards isopropanol decomposition is close to that of other acidic oxides ( $TiO_2$ ,  $Al_2O_3$ ), suggesting that sulfidation has decreased the redox properties of  $CeO_2$ , and increased its acidity. This is not in contradiction with results of cumene decomposition since the main effect of sulfidation is a decrease of the activity of ceria. As for methanol and  $H_2S$  reaction, the main effect of sulfidation is a decrease of  $CH_4$  formation. The concomitant increase of  $CH_3SH$

and  $(CH_3)_2S$  selectivity would be in agreement with an increase of  $CeO_2$  acidity.

### 5. Conclusion

- Brønsted acid sites formed via dissociatively adsorbed hydrogen sulfide ( $H_2S \rightleftharpoons HS^- + H^+$ ) do not induce strong acid character ( $Al_2O_3$ ).
- Coordinatively adsorbed hydrogen sulfide as on titania (anatase and rutile) is a source of strong Brønsted acidity. The same was stated for a NaY zeolite [5].
- Sulfidation of ceria poisons its radical and/or redox centres and seems to increase its acidity.
- The replacement of oxygen by sulfur ions upon  $H_2S$  adsorption on MgO and  $ZrO_2$  seems to increase their basicity or redox properties. An increase of basicity was expected taking into account the lower electronegativity of  $S^{2-}$  compared with  $O^{2-}$ .

### Acknowledgements

The authors acknowledge the KBN for partial support of this work by the grant No. 0977/P3/93/04.

### References

- [1] B.C. Gates, J.R. Katzer and G.C.A. Schuit, *Chemistry of Catalytic Properties*, McGraw-Hill, New York, 1979.
- [2] O. Weisser and O. Landa, *Sulfide Catalysts. Their Properties and Applications*, Pergamon, Oxford, 1973.
- [3] C.N. Satterfield, M. Model and J.M. Mayer, *AIChE J.*, 21 (1975) 100.
- [4] S. Hidaka, A. Iino, N. Gotho, N. Ishikawa, T. Mibuchi and K. Nita, *Appl. Catal.*, 43 (1988) 571.
- [5] M. Sugioka, T. Nakayama, Y. Uemichi and T. Kanazuka, *React. Kinet. Catal. Lett.*, 41 (1990) 345.
- [6] M. Ziolek, K. Nowinska and K. Leksowska, *Zeolites*, 12 (1992) 710.
- [7] K. Tanabe, M. Misono, Y. Ono and H. Hattori, *Stud. Surf. Sci. Catal.*, 51 (1989) 1.
- [8] M. Ai, *J. Catal.*, 40 (1975) 327.
- [9] M. Ai, *Bull. Soc. Chem. Jpn.*, 49 (1976) 1328.

- [10] P.E. Hathway, *J. Catal.*, 35 (1974) 218.
- [11] H. Orita, T. Hayakawa, M. Shimizu and K. Takemira, *Appl. Catal.*, 77 (1991) 133.
- [12] C. Lahousse, J. Bachelier, J.C. Lavalley, H. Lauron-Pernot and A.M. Le Govic, *J. Mol. Catal.*, 87 (1994) 329.
- [13] A. Gervasini and A. Auroux, *J. Catal.*, 131 (1991) 190.
- [14] P.A. Jacobs, *Carboniogenic Activity of Zeolites*, Elsevier, Amsterdam, 1977, p. 113.
- [15] M. Guisnet, *Stud. Surf. Sci. Catal.*, 20 (1985) 283.
- [16] V. Yu Mashkin, *Appl. Catal. A*, 109 (1994) 45.
- [17] M. Ziolk and I. Bresinska, *Zeolites*, 5 (1985) 245.
- [18] A.V. Mashkina, E.A. Paukshtis, V.N. Yakovleva and G.V. Timofieeva, *Kinet. Catal.*, 30 (1989) 1239.
- [19] G. Marcelin, *Catalysis*, 10 (1993) 83.
- [20] C. Mauchausse, H. Mozzanega, P. Turlier and I.A. Dalmon, *Proc. 9th Int. Congr. Catal.*, Calgary, Vol. 2, 1988, p. 775.
- [21] M. Waqif, A. Mohammed Saad, M. Bensitel, J. Bachelier, O. Saur and J.C. Lavalley, *J. Chem. Soc., Faraday Trans.*, 88 (1992) 2931.
- [22] M. Ziolk, J. Kujawa, O. Saur and J.C. Lavalley, *J. Phys. Chem.*, 97 (1993) 9761.
- [23] A. Laachir, V. Perrichon, A. Badri, J. Lamotte, E. Catherine, J.C. Lavalley, J. El Fallah, L. Hilaire, F. Lenormand, E. Quemere, G.N. Sauvion and O. Touret, *J. Chem. Soc., Faraday Trans. I*, 87 (1991) 1601.
- [24] C. Lahousse, A. Aboulayt, F. Maugé, J. Bachelier and J.C. Lavalley, *J. Mol. Catal.*, 84 (1993) 283.
- [25] A.M. Deane, D.L. Griffiths, J.A. Lewis, J.A. Winter and A.J. Tench, *J. Chem. Soc., Faraday Trans. I*, 71 (1975) 1005.
- [26] H. Saussey, O. Saur and J.C. Lavalley, *J. Chim. Phys.*, 81 (1984) 261.
- [27] D.D. Beck, J.M. White and C.T. Ratcliffe, *J. Phys. Chem.*, 90 (1986) 3123.
- [28] D. Dudko, MSc Thesis, Caen–Poznan, 1993.
- [29] M. Ziolk, O. Saur, J. Lamotte and J.C. Lavalley, *J. Chem. Soc., Faraday Trans.*, 90 (1994) 1029.
- [30] M. Bensitel, PhD Thesis, El Jadida, Morocco, 1993.
- [31] T. Slager and C. Amberg, *Can. J. Chem.*, 50 (1972) 3416.
- [32] A.V. Deo and I.G. Dalla Lana, *J. Catal.*, 21 (1971) 270.
- [33] O. Saur, T. Chevreau, J. Lamotte, J. Travert and J.C. Lavalley, *J. Chem. Soc., Faraday Trans. I*, 77 (1981) 427.
- [34] Y. Okamoto, M. Oh Hara, A. Maezawa, T. Imanaka and S. Teranishi, *J. Phys. Chem.*, 90 (1986) 2396.
- [35] A. Datta and R.G. Cavell, *J. Phys. Chem.*, 89 (1985) 450.
- [36] A. Jadi, PhD Thesis, Caen, 1990.