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# ANALYSIS OF THERMALLY INDUCED SOLID-SOLID INTERACTIONS IN VANADIA-ALUMINA SYSTEM

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## Abstract

$V_2O_5/Al_2O_3$ solids of varying compositions were prepared, dried at 100°C and calcined in air at 400–1000°C. The solid–solid interactions between the mixed oxides were investigated by means of DTA, TG and XRD techniques.

The results revealed that ammonium metavanadate and aluminium hydroxide decomposed at 260 and 290°C, respectively, to yield an ammonium vanadium intermediate compound and $Al_2O_3$ as solids. The intermediate compound readily decomposed at 360°C to give $V_2O_5$.

Solid $V_2O_5$ generally catalyses the crystallization of $Al_2O_3$ to an extent proportional to its amount present. The solid–solid interactions between $Al_2O_3$ and $V_2O_3$ to produce $AlV_2O_4$ and $AlVO_4$ took place at 750 and 900°C. These solids decomposed entirely at 1000°C, producing $V_2O_5$ and alpha-corundum. The pure $Al_2O_3$ samples employed existed as amorphous solids even when heated in air at 750°C, but in the presence of $V_2O_5$ (7–18 wt.%) they crystallized to theta-alumina at 600°C. The pure solid alumina crystallized at 1000°C to a mixture of theta and kappa-alumina. In the presence of $V_2O_5$, alpha-corundum together with kappa and theta phases was obtained on heating at 900°C.

**Keywords:** vanadia-alumina system

## Introduction

Vanadium-containing catalysts are commonly employed in the partial or total oxidation of a large number of substrates [1]. The unloaded solid $V_2O_5$, although having excellent activity, is liable to a very rapid drop in activity on enhanced sintering. A suitable support should be employed to increase its durability. Alumina is the most convenient support for the catalysts employed in oxidation-reduction reactions [2–4].

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The nature of these reactions depends on the history of the solids, the calcination conditions, the extent of loading and doping with certain foreign cations [5–9].

The present investigation was devoted to a study of the effects of the extent of loading and the calcination temperature on the mutual solid–solid interactions between $V_2O_5$ and its support. The techniques employed were DTA, TG and XRD.

## Experimental details

### *Materials*

Pure $Al(OH)_3$ was prepared by precipitation from $Al(NO_3)_3$ solution, using 0.2 *M* $NH_4OH$ at 70°C and a *pH* of about 8. The gel obtained was washed with bidistilled water, dried at 100°C to constant weight, then heated in air at 400–1000°C for 6 h. Four specimens of mixed vanadium/aluminium solids with different compositions were prepared by impregnating a finely-powdered $Al(OH)_3$ with solutions containing different proportions of $NH_4VO_3$. The employed chemicals were of analytical grade, supplied by Prolabo. The nominal molar compositions of the solids roasted at 400°C were $0.04V_2O_5:Al_2O_3$, $0.0625V_2O_5:Al_2O_3$, $0.125V_2O_5:Al_2O_3$ and $0.25V_2O_5:Al_2O_3$. These solids are designated VAl-I, VAl-II, VAl-III and VAl-IV, respectively.

### *Techniques*

DTA and TG analyses of the impregnated solids were carried out with a Netzsch-Gerätebau thermal analysis apparatus (STA 405, type 6.223). The rate of heating was 10°C $min^{-1}$. A 50 mg sample was used in each case.

An X-ray investigation of the thermal products of the various solids was carried out with a Philips diffractometer (type PW 1390). The patterns were run with iron-filtered cobalt radiation ($\lambda = 1.7902$ Å) at 36 kV and 16 mA with a scanning speed of 2° in $2\theta$ $min^{-1}$.

## Results and discussion

The thermogravimetry of pure $Al(OH)_3$ indicated a total loss of 46% on heating at 500°C. The loss on heating up to 150°C amounted to 2%; this means that the percentage loss accompanying the decomposition of $Al(OH)_3$ is 44%. This suggests the formula $Al(OH)_3 \cdot 0.7H_2O$ for the prepared hydroxide. Three endothermic peaks were detected. The lowest, below 150°C, corresponds to the removal of physisorbed water. The endotherm at 295°C corresponds to the decomposition to $Al_2O_3$. The third, located between 450 and 500°C is attributed the departure of OH groups strongly bound to the alumina surface [10].

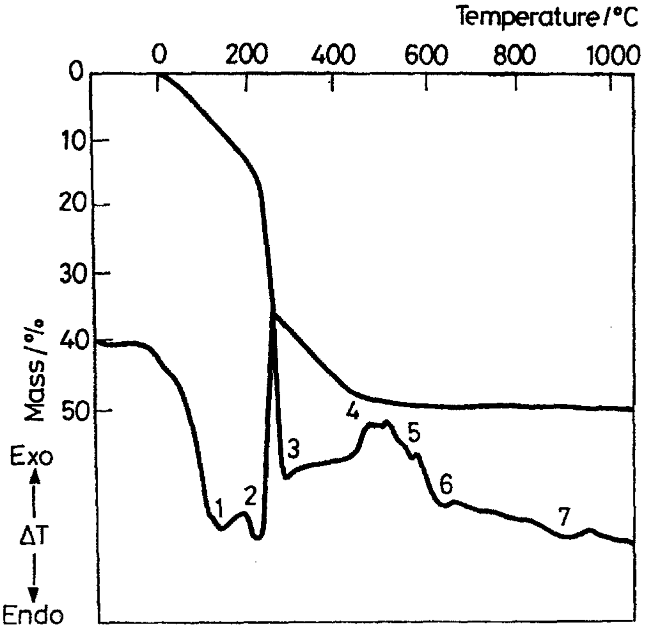

Fig. 1 DTA and TG curves of $0.04NH_4VO_3:Al(OH)_3{\cdot}0.7H_2O$

## *Thermal decomposition of ammonium metavanadate supported on alumina*

Figure 1 presents TG and DTA curves of $0.04NH_4VO_3:Al(OH)_3{\cdot}0.7H_2O$. Seven endothermic peaks are observed: the first and second are very strong and the other peaks are relatively weak. The maxima of these peaks are located at 135, 230, 300, 550, 580, 640 and 910°C and are associated with mass losses of 7.9, 5.9, 20.6, 13.8, 0.9, 0 and 0%, respectively. The last two peaks might characterize solid–solid interactions and/or phase transformation processes. However, one can distinguish three independent stages in the TG curve of this sample. the first stage extends between room temperature and 230°C, the second stage between 230 and 290°C, and the last between 290 and 600°C; these stages are accompanied by mass losses of 13.7, 20.6 and 17.9%, respectively.

Figure 2 presents TG and DTA curves of $0.25NH_4VO_3:Al(OH)_3{\cdot}0.7H_2O$. Four endothermic peaks are observed in the DTA curve: the first peak is very strong and sharp, the second is very strong and relatively broad, and the last two peaks are relatively weak but sharp. The maxima of these peaks are located at 225, 380, 650 and 910°C, respectively. The first peak is accompanied by a mass loss of 30.5% and the second peak by a mass loss of 9.5%. Thermogravimetry indicated three successive stages of mass loss. The first stage ex-

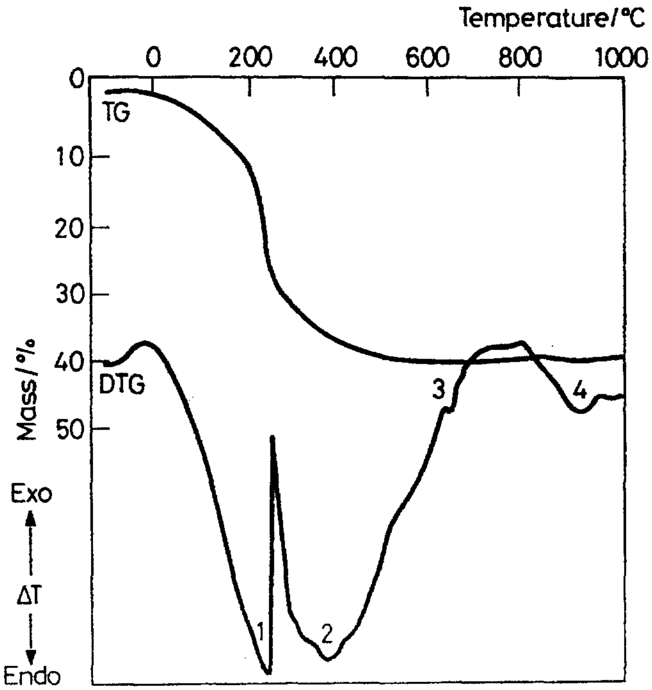

Fig. 2 DTA and TG curves of $0.25NH_4VO_3:Al(OH)_3 \cdot 0.7H_2O$

tends between room temperature and 250°C and is associated with a mass loss of 13.5%. The second stage, with the same mass loss, lies between 250 and 310°C, and the last stage extends between 310–600°C, with a mass loss of 13.7%.

The TG and DTA curves of the other prepared mixed solids, $0.06NH_4VO_3:Al(OH)_3 \cdot 0.7H_2O$ and $0.125NH_4VO_3:Al(OH)_3 \cdot 0.7H_2O$, are not illustrated. The thermogravimetry of these solids revealed three stages of mass loss. The first stage, between 240 and 260°C, indicated a mass loss of 16% for VAl-II and of 11.4% for VAl-III. The second stage (240–285°C) indicated a mass loss of 17.7% for VAl-II and of 19.3% for VAl-III. The last stage, which extends to 600°C, reveals a mass loss of 15% for VAl-II and of 13.8% for VAl-III.

Five endothermic peaks are observed in the DTA curve of VAl-II, while only four endothermic effects are exhibited by VAl-III.

The differences in the number and location of the DTA peaks may be attributed to the changes in chemical composition of the investigated mixed solids.

The first endothermic peaks observed in the DTA curves of various mixed vanadium–aluminium solids (Figs 1 and 2), with maxima at 230–260°C, might characterize two spontaneous processes.

The first process indicates the departure of water of crystallization linked to solid $Al(OH)_3$, which amounts to 0.7 mole $H_2O$ per mole $Al(OH)_3$. The second process corresponds to the thermal decomposition of $NH_4VO_3$ (11–13) via the formation of $(NH_4)_2V_6O_{16}$ as an intermediate:

$$6NH_4VO_3 \xrightarrow{230\text{–}250^\circ C} (NH_4)_2V_6O_{16} + 4NH_3 + H_2O \qquad (1)$$

$$(NH_4)_2V_6O_{16} \xrightarrow{335\text{–}360^\circ C} 3V_2O_5 + 2NH_3 + H_2O \qquad (2)$$

The theoretical losses of the supported solids VAl-I, VAl-II, VAl-III and VAl-IV after the departure of water of crystallization and formation of the intermediate ammonium vanadate are 13.9, 13.9, 14.03 and 14.13%, respectively. The observed losses in mass of these four solids, determined from the first stage in their TG curves, are 13.7, 16, 13.7 and 13.5%, respectively. These values are very close to the values calculated on the assumption of the removal of the water of crystallization of $Al(OH)_3$ and the formation of ammonium vanadate as intermediate.

The second endothermic peaks observed in the DTA curves of the various mixed solids (Figs 1 and 2), with their maxima at 300, 350 and 385°C for VAl-I, VAl-II, VAl-III and VAl-IV, respectively, correspond to the thermal decomposition of $Al(OH)_3$ and the intermediate compound.

The theoretical losses accompanying the thermal decomposition of $Al(OH)_3$ and $(NH_4)_2V_6O_{16}$ to yield $V_2O_5/Al_2O_3$ are 35.5, 35.1, 31.1 and 28.4% for VAl-I, VAl-II, VAl-III and VAl-IV, respectively. The actual losses accompanying the second and third stages in the TG curves of the investigated solids are 38, 31, 33 and 27.2%, respectively.

These values are very close to those calculated theoretically. These findings are confirmed by the results of the XRD study presented below.

### *XRD investigation of thermal products of pure aluminium hydroxide and of aluminium hydroxide treated with different proportions of ammonium metavanadate*

The XRD patterns of the thermal products of $Al(OH)_3{\cdot}0.7H_2O$ precalcined in air at 750–1000°C were measured. The patterns (not given in the text) revealed the amorphous nature of the solid preheated at 750°C, with the formation of a poorly-crystalline gamma-$Al_2O_3$ at 900°C and a mixture of theta and kappa-aluminas at 1000°C.

The results of XRD investigation of solids VAl-I and VAl-IV preheated in air at 400, 600, 750 and 1000°C are shown as diffractograms in Figs 3 and 4. The diffractograms of VAl-II and VAl-III are not illustrated. VAl-I and VAl-II preheated in air at 400°C were found to be amorphous, while VAl-III and VAl-IV calcined at the same temperature consisted of amorphous alumina and $V_2O_5$ phases with low crystallinity. The absence of all diffraction lines of the $V_2O_5$ phase in the mixed solids VAl-I and VAl-II might be attributed to the dispersion effect of alumina and/or the location of vanadium species in octahedral and tetrahedral sites of the $Al_2O_3$ lattice, forming a two-dimensional vanadium-aluminium compound [13, 14–16]. The four solid mixed oxides heated at 600°C consisted of amorphous solids, theta-alumina, gamma-alumina and a mixture of theta-alumina and $V_2O_5$ phases in the cases of VAl-I, VAl-II, VAl-III and VAl-IV, respectively. These results indicate that elevation of the calcination temperature from 400 to 600°C resulted in the complete disappearance of the $V_2O_5$ lines in the case of VAl-III and the crystallization of amorphous alumina into theta and gamma phases.

The disappearance of the $V_2O_5$ phase from VAl-III at 600°C might be attributed to the formation of amorphous vanadium–aluminium compound(s) and/or the transformation of $V_2O_5$ into finely dispersed crystallites that can not be detected by XRD measurements.

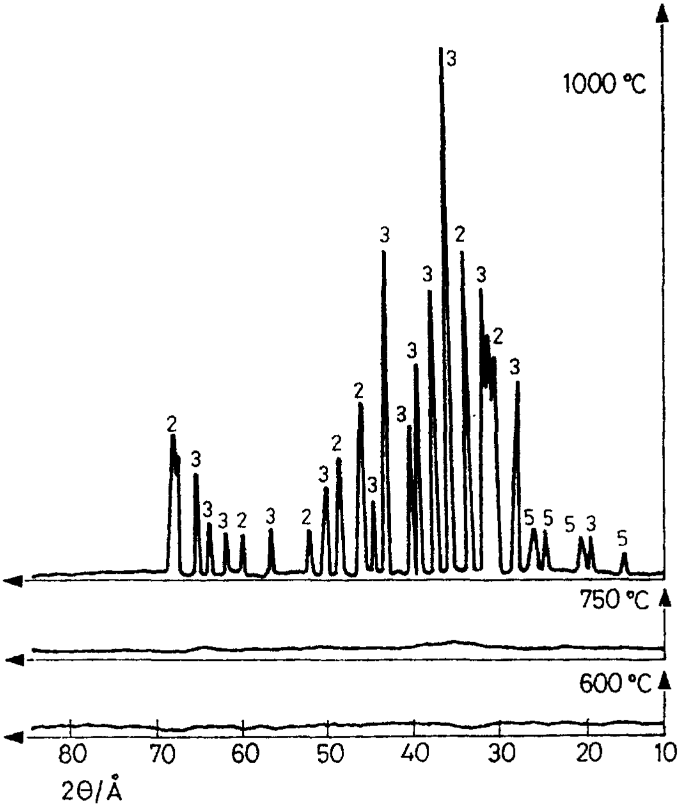

Fig. 3 X-ray diffractograms of $0.04NH_4VO_3{:}Al(OH)_3 \cdot 0.7H_2O$ calcined in air at 600, 750, and 1000°C, lines (2) $\theta$-$Al_2O_3$, (3) $\kappa$-$Al_2O_3$

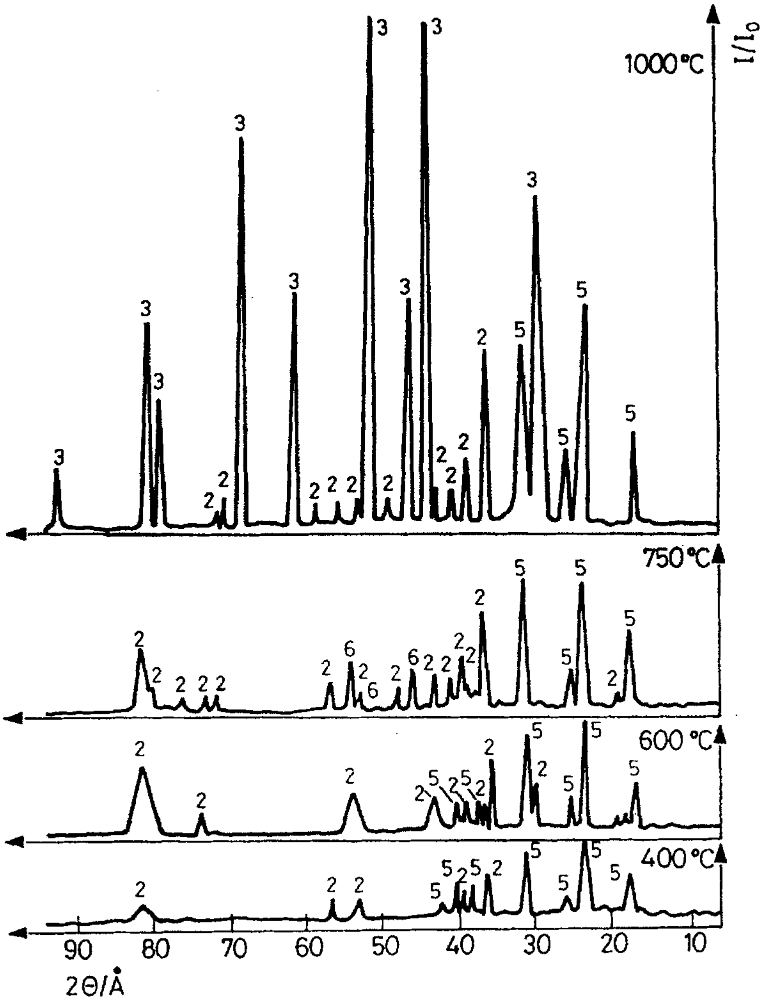

Fig. 4 X-ray diffractograms of $0.25NH_4VO_3$:$Al(OH)_3 \cdot 0.7H_2O$ calcined at 400, 600, 750, and 1000°C, lines (2) θ-$Al_2O_3$, (3) α-$Al_2O_3$, (5) $V_2O_5$, (6) $AlV_2O_4$

The coexistence of crystalline $V_2O_5$ and the theta-alumina phase in VAl-IV at 600°C indicates that the amount of $V_2O_5$ in this particular sample exceeded the amount corresponding to the mono-layer dispersion capacity of alumina towards $V_2O_5$ crystallites [17]. Increase of the temperature of calcination of the mixed solids up to 750°C led to the formation of a mixture of a well-crystallized theta-alumina, $AlV_2O_4$, $AlVO_4$ and $V_2O_5$ in the samples VAl-II, VAl-III and VAl-IV, while VAl-I at 750°C remained in the amorphous state. The formation of mixed aluminium-vanadium solids takes place according to:

The formation of solid $AlVO_4$ from alumina and $V_2O_5$ is not accompanied by any change in mass, but the formation of $AlV_2O_4$, which requires the presence

$$Al_2O_3 + V_2O_5 \xrightarrow{750°C} 2AlVO_4 \tag{3}$$

$$Al_2O_3 + 2V_2O_5 \xrightarrow{750°C} 2AlV_2O_4 + 5/2O_2\ (g) \tag{4}$$

of excess $V_2O_5$, is accompanied by a loss in mass of about 10.3%, assuming the presence of $V_2O_5$:$Al_2O_3$ in a molar ratio of 2:1.

It is plausible to argue that the endothermic peak with maximum at 650°C in the DTA curves of VAl-II, VAl-III and VAl-IV indicates the solid–solid interactions between alumina and $V_2O_5$ to form $AlVO_4$.

Increase of the temperature of calcination of VAl-II up to 900°C led to the formation of kappa, alpha and theta-alumina, together with high-temperature $AlV_2O_4$ [20]. The disappearance of free $V_2O_5$ from this particular solid clearly indicates its complete transformation into aluminium vanadate. Increase of the calcination temperature of the different mixed solids up to 1000°C led to the decomposition of aluminium vanadate, with subsequent formation of $V_2O_5$ and a mixture of different amounts of kappa, theta and alpha-aluminas. The relative abundances of the alumina phases produced were calculated by comparing the

**Table 1** Effect of $V_2O_5$ content on relative abundance of alumina phases present in different mixed solids preheated at 1000°C

| Solid | Vanadium content (expressed as $V_2O_5$ wt.%) | Phase | Relative abundance |
|---|---|---|---|
| $Al_2O_3$ | 0% | α | 0.00 |
| | | θ | 0.35 |
| | | κ | 0.65 |
| VAl-I | 7% | α | 0.05 |
| | | θ | 0.35 |
| | | κ | 0.60 |
| VAl-II | 10% | α | 0.67 |
| | | θ | 0.17 |
| | | κ | 0.16 |
| VAl-III | 18% | α | 0.72 |
| | | θ | 0.28 |
| | | κ | 0.00 |
| VAl-IV | 31% | α | 0.77 |
| | | θ | 0.23 |
| | | κ | 0.00 |

intensities of some diffraction lines with $I/I_o=80\%$ for various alumina phases. The relative abundances obtained are shown in Table 1. The endothermic peak at 910°C in the DTA curve of VAl-I might correspond to the transformation of amorphous $Al_2O_3$ into a mixture of crystalline kappa, theta and alpha-aluminas. Increase of the temperature of calcination of VAl-II, VAl-III and VAl-IV up to 1000°C led to the disappearance of aluminium vanadate, indicating its decomposition into alumina in alpha, theta and kappa forms, together with $V_2O_5$.

A comparison of the diffractograms of VAl-II and VAl-IV precalcined in air at 1000°C revealed that increase of the $NH_4VO_3$ content in the mixed solid from 0.0625 mole to 0.25 mole/mole aluminium hydroxide led to the disappearance of all diffraction lines relative to kappa-alumina. In other words, vanadium oxide might play the role of a catalyst for the crystallization of the kappa into the alpha-$Al_2O_3$ phase. It can be observed from Table 1 that the preheating of pure $Al_2O_3$ at 1000°C led to its crystallization into the kappa and theta phases, and that the presence of a small amount of vanadium species (7% $V_2O_5$) affected the crystallization of alpha-corundum, the extent of which increased on increase of the vanadium oxide content present. Table 1 also shows that the relative abundance of kappa-alumina decreased on increase of the vanadium oxide content, and the presence of 18% $V_2O_5$ was found to be enough to suppress completely the crystallization of alumina into the kappa phase. It can also be concluded that $V_2O_5$ catalyses the crystallization of aluminium oxide into alpha-corundum, and in order to obtain aluminium oxide as pure alpha-corundum it is necessary to increase the amount of $V_2O_5$ present to above 31%.

## References

1 H. Bosch and F. Janssen, Catal. Today, 2 (1988) 369.
2 G. A. El-Shobaky and A. Al-Noaimi, Surf. Technol., 26 (1985) 117, 26 (1985) 235.
3 G. A. El-Shobaky and A. Al-Noaimi, APP. Catal., 29 (1987) 235.
4 G. A. El-Shobaky, G. Fagal, N. Petro and A. Dessouki, Radiat. Phys. Chem., 29 (1987) 39.
5 C. J. Luy and M. J. Parera, Appl. Catal., 26 (1986) 295.
6 P. Sidheswaran, J. N. Fafadia, A.V. Pol, V. S. Kulkarni and M. R. Murthy, Indian J. Technol., 25 (1987) 247.
7 M. E. Ezzo, G. A. El-Shobaky and M. M. Selim, Surf. Technol., 10 (1980) 75.
8 G. A. El-Shobaky, G. Fagal and T. Saber, Bull. Soc. Chim. Fr., 4 (1987) 544; 4 (1987) 547; 4 (1987) 55; 6 (1987) 930.
9 A. Lycourghiotis, C. Defosse and B. Delmon, Rev. Chim. Minerale, 16 (1979) 32.
10 J. Zemlica and C. Barta, Krist. Technol., 7 (1972) 965.
11 T. M. Sas, V. A. Novozhilon and Y. A. Velinkodnyi, Neorg. Zh. Khim, 23 (1978) 3254.
12 R. Gajerski, S. Komornicki, A. Malekcki and A. Podgoreck, Mater. Chem., 4 (1979) 135.
13 G. A. El-Shobaky, K. M. El-Barawy and F. H. A. Abdalla, Thermochim. Acta., 96 (1985) 129.
14 Z. Soblik, R. Kozowski and J. Haber, J. Catal., 127 (1991) 665.
15 G. Bergeret and F. Gallezot, J. Appl. Catalysis, 40 (1988) 191.
16 N. K. Nag and F. E. Massoth, J. Catal., 124 (1990) 127.
17 G. A. El-Shobaky and A. A. Ibrahim, Thermochim. Acta, 147 (1989) 175.