



SYNTHESIS OF MnFeO_3 FROM THE OXIDATIVE THERMAL DECOMPOSITION OF $\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$

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Abstract

On the basis of previous studies about the pentacyanonitrosylmetallates whose thermal decomposition generates different type of oxides, the $\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ was used as raw material to give FeMnO_3 . The decomposition was studied by Thermogravimetric (TGA-DTG) and Differential Thermal Analysis (DTA) under air atmosphere, between room temperature and 1200°C. IR spectroscopy and XRPD, refined by Rietveld analysis, were used to follow the process. The XRPD of the sample heated at different temperatures showed the following sequence: MnFe_2O_4 and $(\text{Mn},\text{Fe})_2\text{O}_3$ disordered bixbyite phases, until arriving to the final product, MnFeO_3 . Temperature programmed reduction (TPR) and EDS-EDAX analyses were used for the characterization, as well.

Keywords: pentacyanonitrosylmetallates, spinel, bixbyite, thermal decomposition.

Resumen

En base a estudios previos sobre pentacianonitrosilmetalatos, cuya descomposición térmica genera diferentes tipos de óxidos, el compuesto $\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ fue elegido como materia prima para dar FeMnO_3 . La descomposición en atmósfera de aire, fue seguida por Análisis Termogravimétrico (TG-DTG) y Térmico Diferencial (ATD) hasta 1200°C . Los productos en cada etapa de la descomposición, fueron caracterizados por Espectroscopia Infrarroja (FTIR) y Difracción de Rayos X (DRX) empleando el Método de Rietveld para el ajuste de los datos. El seguimiento por DRX en polvo, a diferentes temperaturas muestra los siguientes productos: MnFe_2O_4 y $(\text{Mn},\text{Fe})_2\text{O}_3$ (desordenada), hasta llegar a MnFeO_3 como único producto final. Para la caracterización de estas fases se utilizaron además, las técnicas de Reducción a temperatura programada (TPR) y espectroscopía de emisión de rayos X (EDS).

Palabras clave: pentacianonitrosilmetalatos, espinela, bixbyta, descomposición térmica.

Introduction

The crystallographic, thermal and vibrational properties of several hydrated and anhydrous alkaline and alkaline-earth pentacyanonitrosylmetallates have been studied in our group [1-13]. An extensive work on pentacyanonitrosylferrate(2-) like $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ including transition metals salts (known as nitroprussides ferrates), $[\text{Mn}(\text{CN})_5\text{NO}]^{3-}$ and $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$, have been previously performed [5,6]. These polymers have a typical face centered cubic unit cell containing $1\frac{1}{3}$ formula units like Prussian blue analogues and the structures are based upon a simple cubic $\text{M}[\text{M}(\text{CN})_5\text{NO}]$ framework. The residues of the thermogravimetric analyses of these compounds, at nearly 600°C , suggested the presence of the mixed oxide with the evolution of the CN and NO related compounds coming from ligands, as showed in the IR spectra. For $[\text{Co}(\text{NH}_3)_5\text{NO}_2][\text{Fe}(\text{CN})_5\text{NO}] \cdot 1.5 \text{H}_2\text{O}$ [11], TGA-DTA under nitrogen atmosphere have been performed and the X-ray pattern of the residue at 500°C showed the presence of the CoFe_2O_4 mixed oxide. Also, the oxidative thermal decomposition of $\text{M}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 4\text{H}_2\text{O}$ $\text{M} = \text{Sr}, \text{Ca}$ generated $\text{MFeO}_{2.5+x}$ ($0 \leq x \leq 0.5$) mixed oxides [12] whereas the Mg salt leads to the MgFe_2O_4 formation [13].

The generation of a mixed oxide at not so high temperature is highly interesting due to the possibility to produce a compound useful for catalytic applications [14].

The crystallographic, spectroscopic and thermogravimetric behavior of $\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ was studied by Aymonino et al [1,4]. In that paper the authors follow the decomposition under nitrogen atmosphere but did not studied the products in details. So, the thermal decomposition under oxidative atmosphere is studied in detail in this paper. The products were analysed by infrared spectroscopy and XRPD analysis, refined by Rietveld Method [15]. The final products were also studied by TPR (temperature programmed reduction) and SEM-EDS-EDAX analyses.

Experimental

$\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ was prepared by direct reaction between sodium nitroprusside and manganese nitrate aqueous solutions, as previously reported [1]. The brown solid formed was separated by filtration, washed with distilled water, ethanol and kept in a desiccators over CaCl_2 . Then, the sample was heated in the furnace under air atmosphere at $350, 805$ and 1075°C in order to compare with the thermogravimetric results. The crystalline phases were characterized by X-rays powder diffraction using a Goniometer Philips 3020 with a controller PW 3710 with $\text{Cu-K}\alpha$ radiation, Ni filter, 40 kw-20 mA between 10° and 85° , steps of 0.02° and

counting time of 2 seconds. Si elementary attached to the samples like internal pattern was used. The net parameters were refined using the Rietveld Method [16,17].

The simultaneous thermogravimetric (TGA) and differential thermal analyses (DTA) were performed with a NETZSCH STA 409c units, using α - Al_2O_3 like reference with a heating rate of $10^\circ/min$ under air atmosphere. The FTIR spectra were carried out with an EQUINOX 55 spectrophotometer, from 4000 to 400 cm^{-1} . The samples were prepared in form of pills with KBr.

Temperature programmed reduction, TPR, experiments were carried out with the conventional equipment. The TPR was performed using 10% hydrogen in nitrogen (flow rate $20\text{ cm}^3\text{ min}^{-1}$) with a heating rate of $10^\circ\text{C}/\text{min}$ up to 700°C . The sample loaded was 20 mg.

Studies by electron microscopy were performed in a SEM Philips equipment provided with a EDS-EDAX analyzer.

Results and discussion

TGA and DTA data for $Mn[Fe(CN)_5NO]\cdot 2H_2O$ are shown in Figure 1. Three main steps are observed in the TGA for the decomposition process. The first one, with a weight loss of 11.24%, corresponds to the dehydration process (theoretical value 11.74%) identified in the DTA by an endothermic signal at 157°C . The second TGA step, which finishes at 360°C , has a weight loss of 35.40%. This process involves the oxidative decomposition of the complex with the formation of a solid oxide system. The extremely large exothermic signal observed in DTA at 295°C corresponds to the oxidation of the CN and NO groups. The third step evolve a very weak endothermic peak, observed at 1095°C , is associated to 1.50 % weight loss.

The total weight loss observed in TGA is 48.14 %. This value is in agreement with the theoretical one (48.40 %), expected for $MnFeO_3$ as final product.

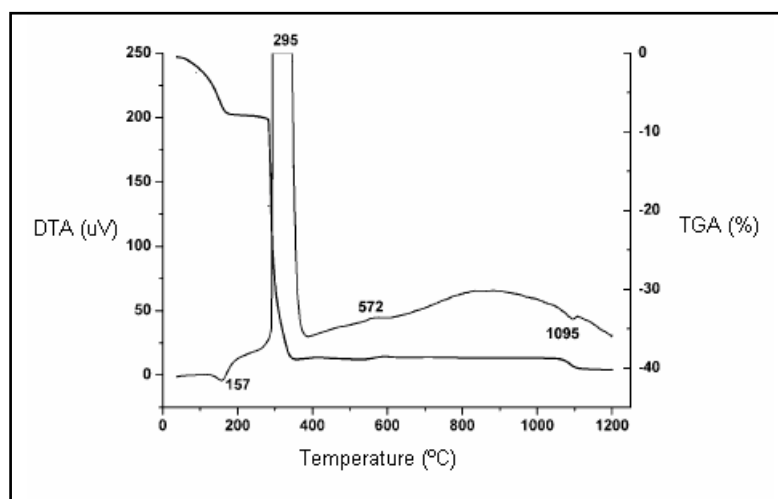


Figure 1. TGA and DTA diagrams of $Mn[Fe(CN)_5NO]\cdot 2H_2O$ in air atmosphere between 25 and 1200°C .

The main crystalline phase observed in the XRPD pattern of the sample heated at 350°C , refined by Rietveld Method, coincides with that of an mixed oxide $Mn_xFe_{3-x}O_4$ type with a cubic cell parameter close to $8,44\text{ \AA}$ due to the relatively low resolution of the pattern. In this structural type it is expected that the manganese and iron metals are present with II and III oxidation states.

The Figure 2 shows the infrared spectra of the complex at room temperature and that of heated at 350°C. This last spectrum confirms the evolution of the CN and NO ligands (absence of the characteristic bands at 2175 and 1947 cm^{-1} , respectively). The spectrum shows only bands in the range from 800 to 400 cm^{-1} typical of the vibrations of metallic oxides.

It is necessary to note that the synthesis of mixed oxide systems at low temperature is highly desired. In fact, traditional methods require much time of thermal treatment at very high temperature and extremely high oxygen pressures [18]. XRPD measure of the sample heated up to 500°C did not show appreciable differences with that of 350°C.

In Figure 3 the powder X-ray pattern of the sample heated at 805°C is presented. The use of the Rietveld Method lead to the MnFe_2O_4 spinel cubic parameter ($a = 8.506 \text{ \AA}$). The MnFe_2O_4 PDF10-0319, used as reference, presents a value of 8.499 \AA with the most intense lines at 2-theta= 34.98, 56.19 and 61.66° respectively. Therefore, peaks of very weak intensity assignable to a bixbyite phase (PDF 80-0100, 2theta=32.90, 55.40 and 66.12°) were observed. On the other hand, very weak XRPD lines were observed, which can be associated to Fe_3C iron carbide [19].

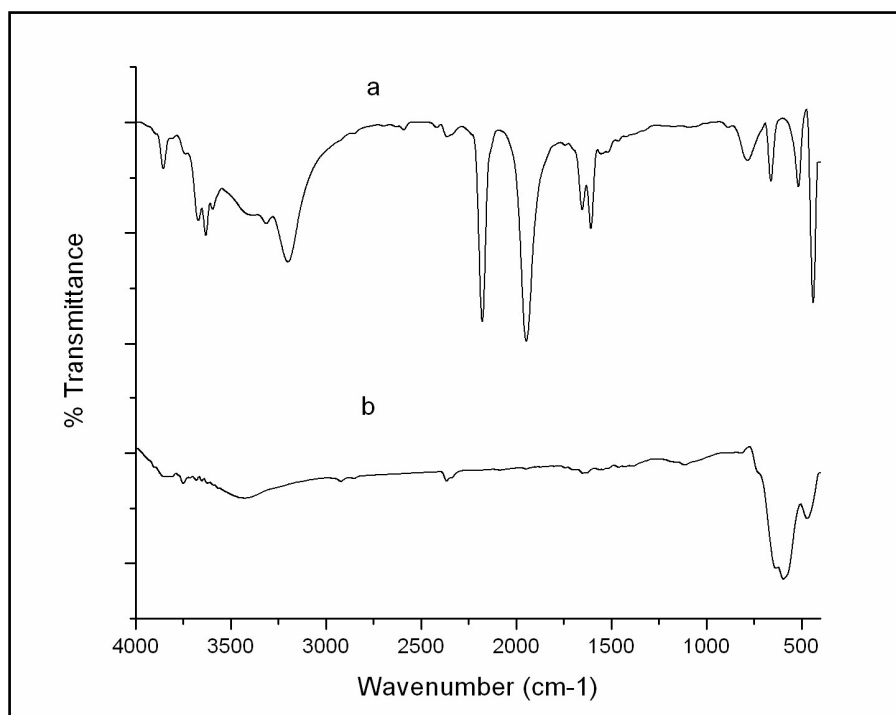


Figure 2. Infrared spectra of $\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ a) at room temperature and b) at 350 °C.

The X ray pattern of the sample heated at 1075°C shows only the MnFeO_3 bixbyite phase with $a = 9,410 \text{ \AA}$ (PDF 0800010 $a = 9.384 \text{ \AA}$) as it is observed in Figure 4. This final product is in good agreement with the total weight loss (48.14%), observed in TGA (theoretical value 48.40 %).

No changes were observed in TGA-DTA studies between 350 and 1080°C. At 1095°C a small endothermic peak with a weight loss of 1.5% was detected, although no changes in the XRPD pattern was observed. This thermal signal can be probably attributed to the evolution of phases formed during the thermal process (carbides?)

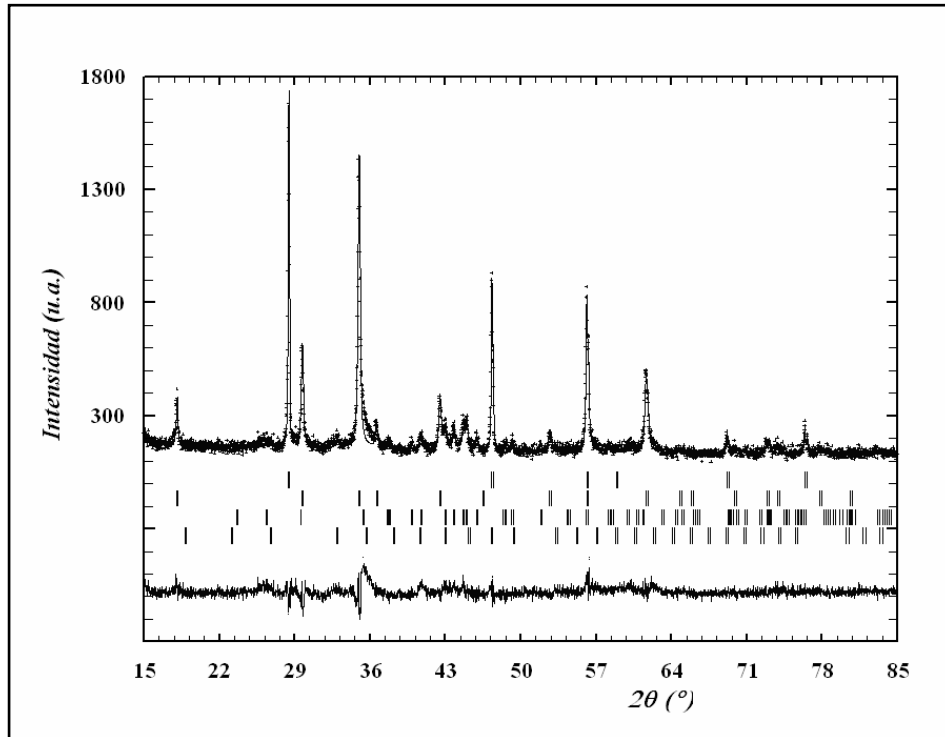


Figure 3. X-ray diffractogram refined by Rietveld of the sample after thermal treatment in air at 805°C . The phases are: (up) Si^0 , type $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$, Fe_3C and $(\text{Mn,Fe})_2\text{O}_3$ (below).

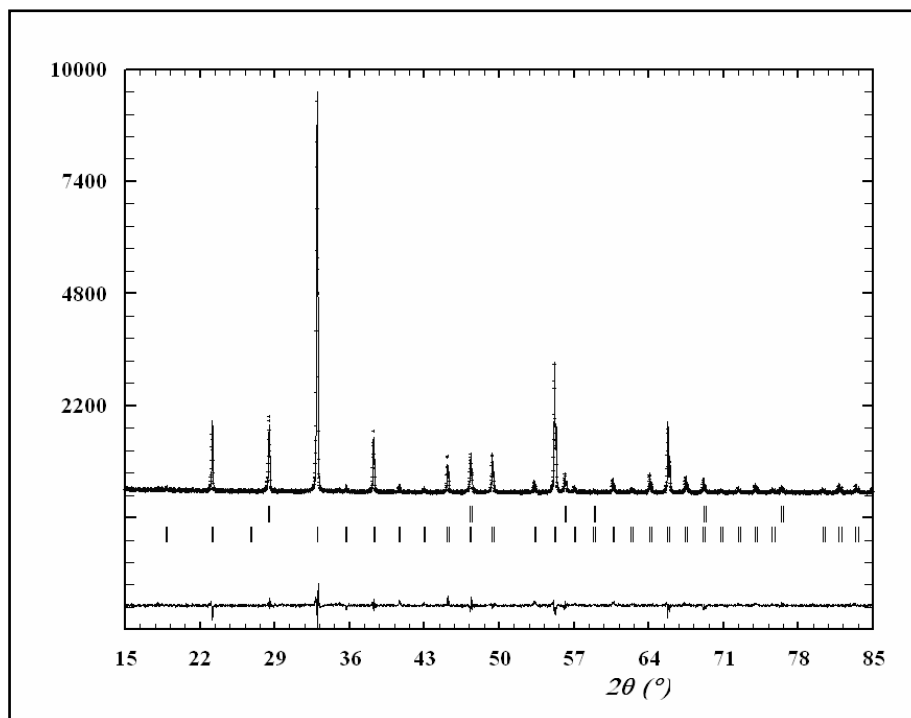


Figure 4. X-ray diffractogram refined by Rietveld of the sample after thermal treatment in air at 1075°C . The phases are (up) Si^0 and MnFeO_3 (below).

In order to better understanding the redox behaviour of the system, the temperature-programmed reduction (TPR) with hydrogen was performed. The TPR profiles for the samples heated at 805 °C and 1075°C are shown in Figure 5.

As it is known, the reduction process of MnO_2 to Mn_2O_3 pure oxide occurs between 150 and 350°C [20]. From Figure 5 it can be noted that no hydrogen consumption is observed in this range, indicating that there are no pure Mn-oxide segregated phases. Likewise, the reduction of pure hematite Fe_2O_3 to Fe^0 occurs in three steps [20]. The first one involves a Fe_2O_3 to Fe_3O_4 partial reduction (between 200 and 400°C) while the second one is associated to the Fe_3O_4 to FeO transition (between 400 to 750°C). Finally, the FeO to Fe^0 reduction occurs at temperatures higher than 750 °C [20], depending on the experimental conditions. No peaks attributed to the reduction of the segregated pure iron oxides are observed in the TPR diagrams.

The studied sample heated at 805 °C shows a very weak peak at 570°C (curve a) while the TPR profile of the sample heated at 1075 °C exhibits an intense and well defined peak centered at 630 °C (curve b). These differences allow us to attribute the intense TPR signal to the bixbyte reduction. The lower temperature observed in (a) can be associated to crystal structural characteristic (lattice order, size particle, etc.). In this range of temperature the spinel phase reduction is not expected.

The EDS-EDAX surface analyses of the sample heated at 1075 °C (50.3 % for Mn and 49.7 % Fe) are in accordance with the bulk Mn:Fe ratio for the MnFeO_3 .

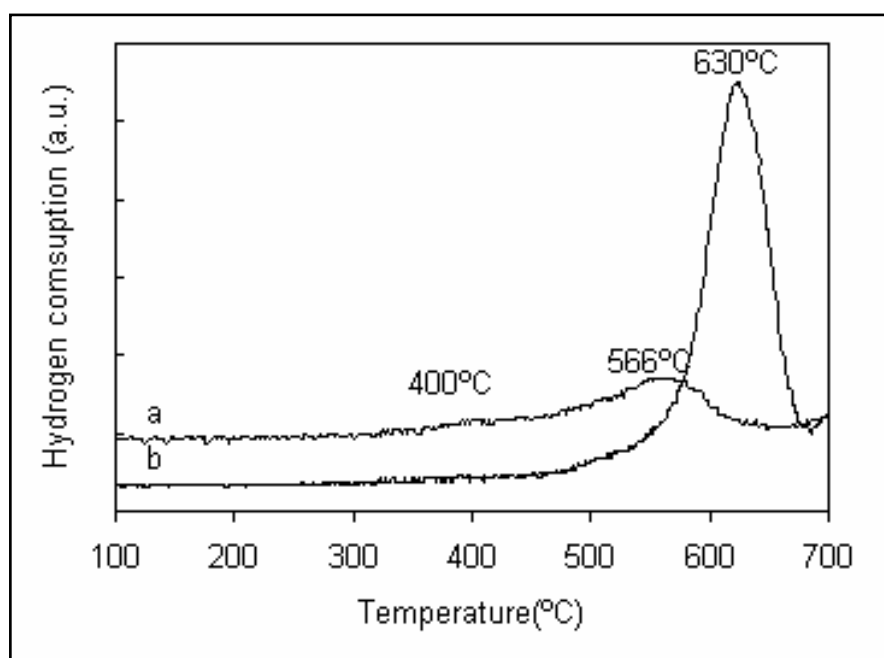


Figure 5. TPR profiles of samples after heat treatment in air (a) at 805 and (b) at 1075°C.

Conclusions

1.- The results of the thermal decomposition of the $\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ in oxidative atmosphere, suggest the formation of different mixed oxides whose compositions depend on the temperature.

2.- The combination of the DTA, TGA, XRPD, FTIR, TPR and EDS techniques is useful for the study of the system.

3.- The decomposition products are MnFe₂O₄ spinel with a low proportion of (Mn,Fe)₂O₃ (disordered) phase at 805°C while at 1075°C only the MnFeO₃ bixbyite phase is observed.

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REFERENCES

- [1] L. A. Gentil, E. J. Baran and P. J. Aymonino, *Inorg. Chim. Acta* **1976**, *20*, 251.
- [2] S. R. Gonzalez, O. E. Piro, and P. J. Aymonino, *J. Chem. Phys.*, **1984**, *81*, 625.
- [3] D. B. Soria, J. I. Amalvy and P. J. Aymonino, *J. Cryst. Spect. Res.* **1987**, *17*, 139.
- [4] A. Benavente, J. A. Morán, O. E. Piro, E. E. Castellano. and P. J. Aymonino, *J. Chem, Cryst.* **1997**, *27*, 335.
- [5] D. B. Soria, L. A. Gentil and P. J. Aymonino, *J. Cryst. Spect. Res.* **1988**, *18*, 133.
- [6] D. B. Soria and P. J. Aymonino, *Spectrochim. Acta A*, **1995**, *51*, 677.
- [7] D. B. Soria, J. I. Amalvy, O. E. Piro, E. E. Castellano and P. J. Aymonino, *J. Cryst. Chemist.*, **1996**, *26*, 5.
- [8] D. B. Soria, O. E. Piro, E.E. Castellano and P. J. Aymonino, *J. Chem. Crystallogr.*, **1999**, *29*, 75.
- [9] D. B. Soria and P. J. Aymonino, *Spectrochim. Acta A*, **1999**, *55*, 1243.
- [10] D. B. Soria, O. E. Piro, E. L. Varetti and P. J. Aymonino, *J. Chem. Crystallogr.*, **2001**, *31*, 471.
- [11] D. B. Soria, M. E. Chacón Villalba, O.E. Piro and P.J., Aymonino, *Polyhedron*, **2002**, *21*, 1767.
- [12] M. I. Gómez, J. A. de Morán, R. E. Carbonio and P. J. Aymonino, *J. Sol. State. Chem.*, **1999**, *142*, 138.
- [13] M. I. Gomez, J. A de Morán, R. Carbonio y P. J. Aymonino, *XXII Congreso Argentino de Química*, setiembre **1998**, La Plata, R. Argentina.
- [14] M. Paulis, M. Martin, D. B. Soria, A. Díaz, J. A. Odriozola, and M. Montes, *Applied Catalysis A*, **1999**, *180*, 411.
- [15] D. B. Soria and A. Mazzoni, SAM 2005, Octubre **2005**, Mar del Plata.
- [16] R. A. Young, *The Rietveld Method*. IUCr, Oxford University Press, New York, 1993.
- [17] Rodríguez-Carvajal, Abstracts of the Satellite Meeting on Powder Diffraction XV of Congress of the IUCr, Toulouse, France, p.12, 1990.
- [18] Infrared Spectra of Ferrites, R. D. Waldron, *Physical Review*, **1955**, *99*, 1727.
- [19] V. B Mohair and A. Howath, *Acta Chem. Scand.* **1967**, *21*, 1462.
- [20] A. Khan, P. G. Smirniotis, *J.Mol. Catal. A*, **2008**, *280*, 43.