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Hydrodesulfurization activity of MoS_2 catalysts modified by chemical exfoliation

M. Del Valle [a,b], J. Cruz-Reyes [b], M. Avalos-Borja [c] and S. Fuentes [c,*]

[a] *Programa de Posgrado en Física de Materiales, Centro de Investigación Científica y Educación Superior de Ensenada, Ensenada, B.C., Mexico*
[b] *Facultad de Ciencias Químicas, UABC, Tijuana, B.C., Mexico*
[c] *Centro de Ciencias de la Materia Condensada de la UNAM, Ensenada, B.C., Mexico*

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The surface area of unsupported MoS_2 catalysts prepared by thiosalt decomposition is found to increase after undergoing a treatment known as chemical exfoliation. Rate measurements of dibenzothiophene hydrodesulfurization in a batch reactor show that activity decreases for the chemically modified MoS_2 catalysts, along with the hydrogenation/hydrodesulfurization ratios (HYD/HDS). These results indicate that both basal and edge planes of the layered sulfides are rearranged by the exfoliation treatment, but that other processes must also be involved. Reference crystalline MoS_2 is also discussed in the work.

Keywords: molybdenum disulfide, hydrodesulfurization, exfoliation

1. Introduction

In the mid-eighties, Joensen et al. [1], introduced a chemical method which was reported to separate bulk MoS_2 into platelets in suspension that were one molecule thick. The method was termed "exfoliation" and consists of intercalating MoS_2 powder with lithium, followed by reaction with water. Exfoliation has since been used on other transition metal sulfides, as well as for making interesting new MoS_2 materials [2]. Miremadi and Morrison have employed this technique to prepare catalysts for methanation [3], while Bockrath and Parfitt have described the application of exfoliated MoS_2 in coal liquefaction [4]. The use of exfoliation for creating pillared MoS_2 materials with intercalated organometallic clusters has also been reported [5].

The intercalation chemistry of layered dichalcogenides of the Group 4, 5, and 6 (IVB, VB, and VIB) transition metals has been extensively researched [6]. In the case of MoS_2, reaction with butyllithium yields different products, depending on the reaction time and conditions. The X-ray diffraction patterns of MoS_2, for example, have suggested that a lithium intercalation compound is first formed, which is an intermediate to amorphous products [7].

As described by Joensen, chemical exfoliation implies the dismantling of metal sulfide layers along the (001) direction. This opens the possibility, when applied to sulfide catalysts, of affecting the HDS activity of border planes. Indeed, according to the simple model for the MoS_2 catalyst particles proposed by Daage et al. [8], layer dismantling should lead to changes in both hydrogenation and HDS reactions. Each model particle consists of a stack of disks n layers thick and of diameter d. The top and bottom layers are said to have both rim and edge sites, while the middle layers have only edge sites. The top surface of the disk is a basal plane, which is considered to be catalytically inert. After applying molecular mechanics to minimize inter- and intramolecular interactions in different schemes for the coordination of DBT on MoS_2, Daage has found that hydrogenation reactions occur only on rim sites, while both rim and edge sites are responsible for the HDS activity. According to this rim-edge model and for large molecules like DBT, the selectivity for hydrogenation reactions increases with the increase in stacking layers. The exfoliation treatment has begun to be used on unsupported MoS_2 catalysts as a way to probe the structure-reactivity relationship [9]. This relationship should eventually be related to changes in the ratio of basal/edge planes, in order to supply further insight on the reactivity of MoS_2. In this work, the effect of the exfoliation treatment on the activity of MoS_2 catalysts for the HDS of dibenzothiophene (DBT) was investigated.

2. Experimental

2.1. Sample preparation

All reagents are from Aldrich, except for ammonium heptamolybdate (Mallinckrodt). Fresh ammonium thiomolybdate (ATM) is precipitated from ammonium heptamolybdate in an ammonia solution by bubbling H_2S, according to a known method [10]. Unsupported MoS_2 catalysts were prepared by thermal decomposition of ATM at 673 K for four hours under a 15%(v/v) H_2S/H_2 gas mixture flowing at 40 ml/min. Exfoliation was carried out in a dry glovebox under nitrogen atmosphere, using a slightly modified version of the procedure described by Miremadi and Morrison [11]. Tipically, 3 g of molybdenum sulfide

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[*] To whom correspondence should be addressed. CECIMAC, PO Box 439036, San Ysidro, CA 92143, USA.

were first soaked in 20 ml of hexane (99+), and stirred in an ultrasound bath for five days. A 50% mol excess of n-butyllithium (1.6 M in hexane) was then added and the mixture stirred in the ultrasound bath for four days. The intercalated solid was recovered by filtration and washed five times with hexane to eliminate excess reagents. After placing the solid in a beaker, 20 ml of water were added and the mixture stirred in the ultrasound bath for eight days. The product was recovered by filtration and left to dry in the glovebox. Reference crystalline MoS_2 (99%) was from Aldrich.

2.2. Surface area analysis

Multipoint BET surface areas were measured with a Micromeritics Gemini 2060 surface analyzer, using nitrogen as adsorbate. Samples were degassed at 473 K under argon for two hours prior to analysis. The precision of the measurements was within ±5%.

2.3. X-ray difraction

X-ray diffraction patterns of the samples were obtained with a Philips X-Pert MPD analytical diffractometer, using Cu Kα radiation. Crystalline phases were identified by comparison with reference patterns from the ICDD Powder Diffraction Files. Peak broadening analysis using the Scherrer equation was applied to the (002) diffraction peak to calculate the average stacking height of each sample. Acceptable estimates by this method are limited to stacking heights from 5 to 300 nm.

2.4. Catalytic activity

Reactions were run in a Parr high pressure batch reactor, which was loaded with 8.8 g of DBT (Acros, 99%) in 200 ml of decaline (Aldrich, 98%), and 0.5–1.0 g of catalyst. The system was purged, then pressurized with H_2 and heated to 3376 kPa (490 psi) and 623 K. The stirring speed was 1725 r.p.m. Reaction rates were calculated as a function of DBT conversion, which was followed by gas chromatography for at least five hours. The reaction products were separated in a $1/8$ inch diameter, 9 ft long analytical column packed with 3% OV-17 on 80/100 Supelcoport. The precision of the reaction rate measurements was within ±5%.

3. Results

The BET surface area measurements are reported in table 1. Crystalline MoS_2 subjected to the exfoliation treatment increased its surface area by 30%. The poorly crystalline MoS_2 samples showed an increase in specific surface area after the chemical treatment, indicating that the effect of said treatment is more efficient on these highly defective materials. Surface area also varied during the reaction tests, most noticeably in the catalyst samples and less so in the crystalline material, reflecting the higher instability of the poorly crystalline structure under the reaction environment [12].

Table 1
Surface area measurements for different sulfide materials, before and after the HDS of DBT.

Sample	BET area (m^2/g) before	BET area (m^2/g) after	BET area increase (m^2/g)
Crystalline MoS_2	4.8	6.5	1.8
Crystalline MoS_2 after exfoliation	6.2	9.7	3.5
MoS_2 catalyst	23.4	5.0	−18.4
MoS_2 catalyst after exfoliation	55.2	14.8	−40.4

Table 2
Reaction rates of different sulfide materials for the HDS of DBT.

Sample	Reaction rate (10^{-7} mol s^{-1} g^{-1})
Crystalline MoS_2	2.7
Crystalline MoS_2 after exfoliation	1.9
MoS_2 catalyst	6.7
MoS_2 catalyst after exfoliation	4.7

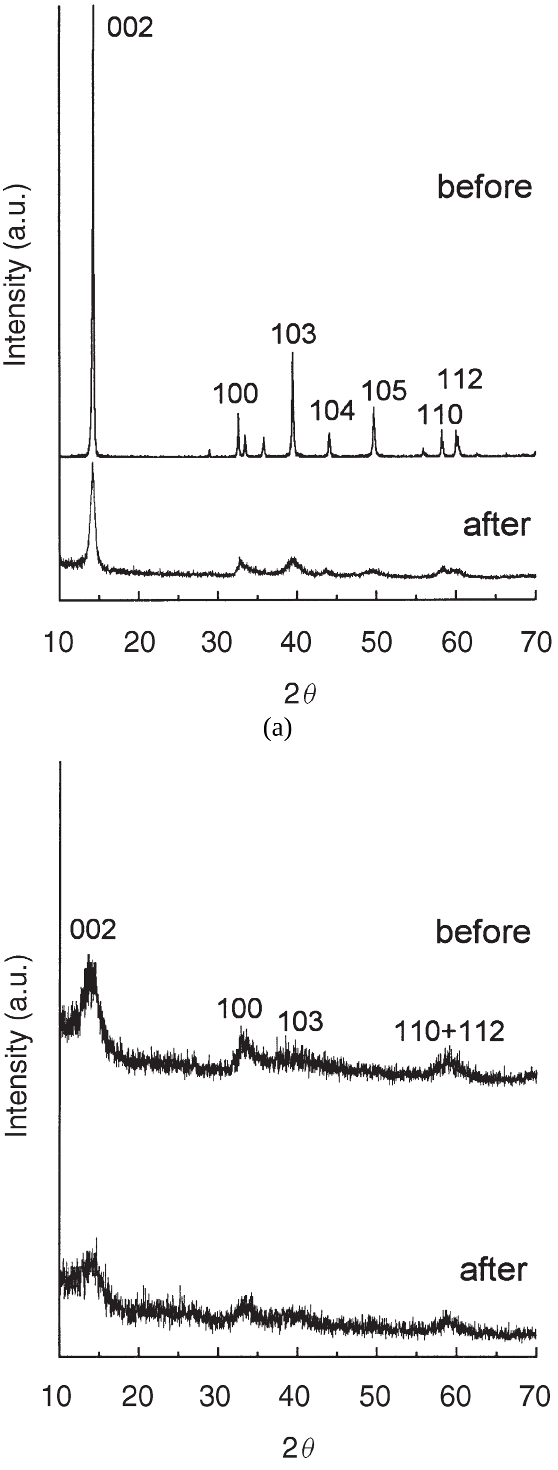
The X-ray powder diffraction patterns of MoS_2 samples before and after the exfoliation treatment are shown in figure 1. In general, the diffraction peaks of the sulfide samples became broader after undergoing the exfoliation treatment. For crystalline MoS_2 the average crystallite size, as measured by X-ray peak broadening analysis of the (002) reflection, decreased from 126 to 14 nm after exfoliation.

The plots of % DBT conversion as a function of time for the various sulfides are nearly linear and agree with earlier statements recognizing pseudo-zero-order kinetics for the HDS of DBT [13]; typical DBT conversion was 15–30% after six hours. Reaction rate constants, in units of mol s^{-1}, were calculated from these plots using the integrated equation for the zero-order rate law

$$X_{\mathrm{DBT}} = (1 - n_{\mathrm{DBT}}/n_{\mathrm{DBT,0}}) = (k/n_{\mathrm{DBT,0}})t, \qquad (1)$$

where X_{DBT} is the conversion fraction of DBT at time t, and $k/n_{\mathrm{DBT,0}}$ is the slope of the plot. Division by the corresponding gram weight of each sulfide charge gives the specific reaction rate constants reported in table 2. The exfoliation treatment was found to reduce the reaction rate of MoS_2 catalysts.

The four main products of the reaction were biphenyl, cyclohexylbenzene, bicyclohexyl, and benzene. Biphenyl (BIP) may be considered to be the true HDS product, whereas cyclohexylbenzene (CHB) and bicyclohexane (BCH) are hydrogenation (HYD) products, and benzene (BZN) is a cracking product. Plots of selectivity as a function of time for the varied sulfides differed in behavior, as shown in figure 2. Thus, the plot for crystalline MoS_2 in



(a)

(b)

Figure 1. X-ray diffraction patterns of (a) crystalline MoS_2, (b) MoS_2 catalyst, before and after the exfoliation treatment.

figure 2(a) shows that the cracking product BZN was preferred during the first minutes of reaction, followed by a steep increase in BIP selectivity during the first half hour of reaction; afterwards, BIP selectivity fell only slightly in favor of CHB. In contrast, the plot for crystalline MoS_2 after the exfoliation treatment, as shown in figure 2(b), gave only BIP during the first hour; thereafter, the plot shows BIP selectivity decreasing in favor of BCH. According to figure 2 (c) and (d), the MoS_2 catalyst had a high selectivity for BZN at the outset, which rapidly decreased to a steady 5%; selectivity for BIP in untreated and exfoliated MoS_2 catalyst samples decreased by $1/3$ or better after 90 min of reaction, with BCH as the main hydrogenation product.

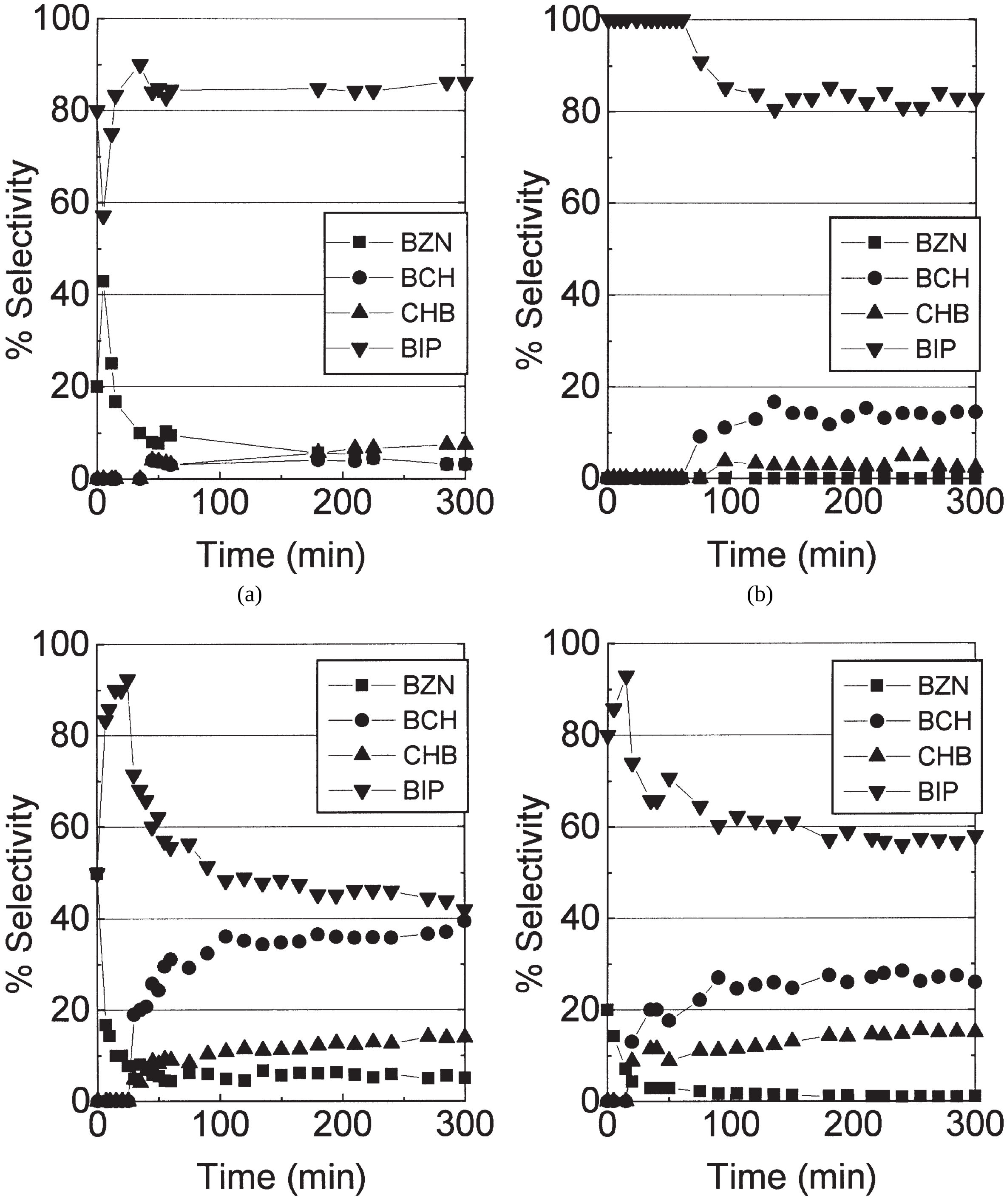
4. Discussion

The working hypothesis on the effects of chemical exfoliation on MoS_2 catalysts, posed at the outset of this work, is as follows: exfoliation of catalytic materials is similar to exfoliation of crystalline sulfides, with layer dismantling taking place preferentially along the $(00l)$ direction, and is expected to (1) expose mainly basal planes, increasing surface area while reducing the stacking of (002) planes in MoS_2 microcrystals, (2) have no effect on the number of edge plane active sites for HDS and, therefore, catalytic activity should not change; (3) increase the selectivity ratio HYD/HDS, which according to Daage et al. [8] is related to the rim/edge ratio of MoS_2 crystallites and depends on the average stacking of basal planes in the crystallites.

The surface area and XRD results confirm the first effect of the hypothesis. The increase in the surface area of reference crystalline MoS_2 due to the exfoliation treatment is similar to that observed by Bockrath and Parfitt [4] in comparably exfoliated and dried crystalline MoS_2 samples. The larger increase in surface area for MoS_2 catalysts can be attributed to a more profuse intercalation process. Although intercalation of lithium into highly defective structures is usually more difficult than into perfect structures, in the case of poorly crystalline MoS_2, however, the small stacking height of the material (which X-ray peak broadening analysis would place at around 4 nm) may well offset this difficulty and even favor a higher extent of intercalation.

With regard to layer stacking, the diffraction patterns of crystalline MoS_2 show that the reflection peaks are generally broader after the chemical exfoliation treatment. As discussed by Joensen et al. [1], layer dismantling along the $(00l)$ axis reduces particle size in that direction, which causes the broadening of the (002) peak, while other peaks also broaden as sliding and/or rotation of basal planes reduces the long range order of the corresponding family of planes. For crystalline MoS_2 the average stacking height, as measured by X-ray peak broadening analysis of the (002) reflection, decreases from 126 to 14 nm after exfoliation. The average number of stacking planes, calculated from the average particle size and $d = 0.61$ nm, decreases from over 200 layers to 23 layers. Dismantling of layers is clearly the cause of the reduction in stacking height due to the exfoliation process.

In the case of MoS_2 catalysts obtained by decomposition of thiosalts, the XRD patterns before exfoliation are characteristic of the “poorly crystalline” phase reported in the literature. According to the modelling study by Liang et al. [14], this phase is consistent with a highly defective structure containing rotated and shifted (002) planes. The XRD



(a) (b) (c) (d)

Figure 2. HDS selectivity plots of (a) crystalline MoS_2, (b) crystalline MoS_2 after exfoliation, (c) MoS_2 catalyst, and (d) MoS_2 catalyst after exfoliation.

patterns of the catalysts after exfoliation are quite similar to those of the untreated materials. Stacking height by peak broadening analysis is around 4 nm for both, although estimates below 5 nm by this method are not as sensitive and stacking height may well be smaller for the treated catalysts, as the surface area measurements demonstrate.

A significant decrease in the catalytic activities of both crystalline and catalyst MoS_2 samples occurs as a result of the exfoliation treatment, which is inconsistent with the second effect of the hypothesis. This suggests that the changes due to the exfoliation treatment are not limited to the primary process of separation of layers – as shown by XRD and BET surface area – but rather imply others as well. A second process may involve the formation of LiS_2, which would allow some amount of lithium to remain in the sample [7]. Given the very high electron donor character of Li, it may then deactivate coordinatively unsaturated Mo sites or react with –SH groups located on the surface, thus

Table 3
Selectivity and selectivity ratios of different sulfide materials for the HDS of DBT.

Sample	Conversion (%)	Selectivity (%)				Selectivity ratio (HYD/HDS)
		BIF	CHB	BCH	BZN	
Crystalline MoS_2	3.2	84.4	3.1	3.1	9.4	0.07
Crystalline MoS_2 after exfoliation	4.2	83.0	2.4	14.6	0	0.20
MoS_2 catalyst	4.4	56.9	9.1	29.5	4.5	0.68
MoS_2 catalyst after exfoliation	4.5	64.5	11.1	22.2	2.2	0.52

reducing the activity of the MoS_2 samples after chemical treatment. Crystal sintering along edge planes could also explain the drop in catalytic activity.

The rim-edge model for MoS_2 crystallites, described earlier, assigns both hydrogenation (HYD) and HDS sites to atoms located in rim positions, while atoms located in edges only have HDS sites. Variation in selectivity for HYD and HDS reactions is explained as owing to changes in the average stacking of layers within the microcrystals. MoS_2 crystallites with a high stacking (sharp 002 peak in XRD) should yield mostly HDS products, while single layers of MoS_2, which contain only rim sites, are expected to yield mainly hydrogenation products.

Regarding CHB and BCH as HYD products, and BIP as the formal HDS product, the HYD/HDS ratio discussed by Daage is defined here as

$$\mathrm{HYD/HDS} = \frac{\text{CHB selectivity} + \text{BCH selectivity}}{\text{BIP selectivity}}. \qquad (2)$$

In order to make valid comparisons, the HYD/HDS selectivity ratios for the series of MoS_2 materials are best calculated for the same conversion. Accordingly, the selectivity data for 4% (±1) conversion, along with the calculated HYD/HDS selectivity ratios are listed in table 3. The untreated MoS_2 catalysts have a significantly higher HYD/HDS ratio compared to untreated crystalline MoS_2, in agreement with the difference in their (002) X-ray peak width.

Relating the rim-edge model to the exfoliation process as described in the literature, the HYD/HDS ratio is expected to be higher for all the exfoliated sulfide samples. Yet the third effect of the hypothesis is found to only hold good for crystalline MoS_2, since its HYD/HDS ratio increases significantly after exfoliation; the ratio for the treated MoS_2 catalysts is clearly lower. As with the catalytic activities, the selectivity results indicate that the exfoliation treatment must modify the sulfide structures in other ways not previously reported. For MoS_2 catalysts, the HYD/HDS ratio decreases along with the overall catalytic activity after the exfoliation treatment. Given the poorly crystalline structure of the catalyst samples, the exfoliation treatment may lead to a preferred deactivation of hydrogenation sites due to lithium poisoning, compared to the crystalline reference material after the same treatment.

5. Conclusions

When applied to MoS_2 catalysts, the exfoliation treatment reduces their HDS activity and HYD/HDS ratio. The rim-edge model is found useful for discussing the effects of the treatment on the catalytic activity and selectivity of MoS_2 materials. It is discovered that these effects cannot be explained solely in terms of exfoliation, i.e., basal plane dismantling, as described in the current literature, but require that other pathways also be considered. It remains to be proven if the poisoning or blocking effect of lithium on the active sites, especially rim sites, plays a significant role in the HDS behavior of the treated sulfides.

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References

[1] P. Joensen, R.F. Frindt and S. Morrison, Mater. Res. Bull. 21 (1986) 457.
[2] D. Yang and R. Frindt, Am. Chem. Soc. Dir. Petroleum Chem. Preprints 39 (1994) 612.
[3] B.K. Miremadi and S.R. Morrison, J. Catal. 112 (1988) 418.
[4] B.C. Bockrath and D.S. Parfitt, Catal. Lett. 33 (1995) 201.
[5] J.R. Brenner, C.L. Marshall, J.M. Heising and M.G. Kanatzidis, in: *15th Meeting of the North American Catalysis Society*, Chicago, USA, May 18–22, 1997, paper B-16, p. 60.
[6] M.S. Whittingham and A.J. Jacobson (eds.), *Intercalation Chemistry* (Academic Press, New York, 1982).
[7] M.B. Dines, Mater. Res. Bull. 10 (1975) 287.
[8] M. Daage and R.R. Chianelli, J. Catal. 149 (1994) 414.
[9] M. Del Valle, M. Avalos-Borja, J. Cruz and S. Fuentes, Mater. Res. Soc. Symp. Proc. 351 (1994) 287.
[10] G. Krüss, Ann. 225 (1884) 29.
[11] B.K. Miremadi and S.R. Morrison, J. Appl. Phys. 63 (1988) 4970.
[12] M. Del Valle, M.J. Yáñez, M. Avalos-Borja and S. Fuentes, in: *Hydrotreating Technology for Pollution Control*, eds. M.L. Occeli and R. Chianelli (Dekker, New York, 1996) p. 47.
[13] T.A. Pecoraro and R.R. Chianelli, J. Catal. 67 (1981) 430.
[14] K.S. Liang, R.R. Chianelli, F.Z. Chien and S.C. Moss, J. Non-Cryst. Solids 79 (1986) 251.