

Synthesis, characterization and catalytic activity of ruthenium containing aluminum pillared bentonites

Maurizio Lenarda ^{a,*}, Loretta Storaro ^a, Renzo Ganzerla ^a, Renzo Bertocello ^b

^a *Dipartimento di Chimica, Università di Venezia Ca' Foscari, Dorsoduro 2137-30123 Venezia, Italy*

^b *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica and INCM, Università degli Studi di Padova, via Loredan 4, 35131-Padova Italy*

Received 14 July 1998; accepted 2 October 1998

Abstract

Ruthenium containing pillared bentonites were prepared by contacting the clay with an aqueous solution containing aluminum and ruthenium salts or by cation exchange with ruthenium of an aluminum-pillared bentonite. The materials were characterized by chemical analysis, XRD, XPS, H₂-TPR, nitrogen adsorption/desorption. All the prepared samples catalyze after a reductive pretreatment the 1-butene hydrogenation. The catalytic activity is correlated to their chemical and structural properties. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Clays; Pillaring; Ruthenium; 1-Butene; Hydrogenation; Isomerization

1. Introduction

Pillared layered clays (PLCs) are a recently developed class of microporous materials obtained by heat treatment of the intercalation compounds prepared by exchanging the interlayer cations of swellable clays with bulky polyhydroxy metal cations. Polyhydroxy cations of various nuclearities can be obtained by controlled hydrolysis of several multivalent metal salts; however, smectites pillared with polyoxoaluminum cations that are more easily and reproducibly prepared are more extensively studied [1–4]. The details of the pillaring process with Al polyoxocations is still uncertain;

however, it is well established that the Keggin ion $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ is the predominant species in the pillaring solution. Pillared clays can catalyze various reactions and their catalytic properties depend from the nature of the starting clay, the chemical composition of the pillars and from the nature of the cations present in the interlayer space. Both Brønsted- and Lewis-type acid sites have been found in pillared smectites [1,5–8]. The catalytic activity of a clay pillared with hydroxy-aluminum oligomers can be modified by exchanging the residual interlayer alkali cations with other metallic ions, or doping the aluminum pillaring solution with small quantities of metal cations [9–36]. However, only in the case of gallium [9–12] that isomorphous substitution in the Keggin ion was clearly proved, [37,38] while in

* Corresponding author. Tel.: +39-041-2578562; Fax: +39-041-2578517; E-mail: lenarda@unive.it

all the other cases cohydrolysis and copillaring appeared to take place [13–36], leading to the formation of aluminum pillars decorated by the other metal oxide. However, in all cases, more or less relevant modifications of the clay acid–base and redox properties, often related to excellent catalytic activities in a wide range of reactions, were observed [9–36].

In this paper we describe the synthesis and the characterization of a natural bentonite pillared with an aluminum–ruthenium mixed solution. The structural and catalytic properties of this material are compared with those of an aluminum-pillared montmorillonite exchanged with ruthenium cations. The catalytic behaviour, after reductive pretreatment, of both clay samples in the hydrogenation of the olefinic carbon–carbon bonds, is also discussed.

2. Experimental

2.1. Characterization methods

2.1.1. Elemental analyses

Elemental analyses were accomplished by Atomic Adsorption Spectroscopy with a Perkin-Elmer PE 3100 instrument.

2.1.2. Thermogravimetric determinations

Thermogravimetric analyses were carried out on a Simultaneous Thermal Analyzer STA 429 Netzsh using samples weighting about 50 mg. A heating rate of 10 K/min, with air (30 l/min) as purging gas, was used.

2.1.3. Temperature-programmed reduction

Temperature-programmed reduction (TPR) was performed in a conventional U-shaped quartz microreactor (bore = 6 mm, length = 200 mm) using a 5% H₂/Ar mixture flowing at 35 l min⁻¹ (STP). The temperature range was 293–900 K and the heating rate 10 K min⁻¹. The reduction of CuO to metallic copper was used to calibrate the TPR apparatus for H₂ consumption.

2.1.4. X-ray photoelectron spectroscopy (XPS)

A Perkin-Elmer PHI 5600ci spectrometer with monochromatized AlK α radiation (1486.6 eV) and non-monochromatized MgK α radiation (1253.6 eV) was used for the XPS analyses. The working pressure was less than 2×10^{-7} Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f_{7/2} line at 83.9 eV with respect to the Fermi level. As an internal reference for the peak positions, the C 1s peak of hydrocarbon contamination has been assumed at 284.8 eV [39]. Survey scans (187.85 eV pass energy; 1 eV step; 0.5 s/step dwell time) were obtained in the BE range between 0 and 1350 eV with the Al K α radiation. Detailed scans were recorded at 5.85 eV pass energy, 0.1 eV step; 1.0 s/step dwell time for the Ru (3d_{5/2+3/2} and 3p_{3/2+1/2} lines), Si (2p_{3/2+1/2} line), Al (2p_{3/2+1/2} line), O 1s and C 1s lines. The standard deviation in the BE values of the XPS lines is 0.10 eV. After a Shirley-type background subtraction [40], the raw spectra were fitted using a nonlinear least-square fitting program adopting Gaussian–Lorentzian peak shapes for all the peaks [41]. The atomic compositions were evaluated using sensitivity factors as determined from theoretical photoionization cross-sections and asymmetry parameters calculated within the Hartree–Fock–Slater one-electron central potential model [42].

2.1.5. Nitrogen adsorption / desorption

Adsorption/desorption experiments using N₂ were carried out at 77 K on a C. Erba Sorptomatic 1900. Prior to each measurement the samples were outgassed at 423 K and 1.33×10^{-3} Pa for 6 h. The N₂ isotherms were used to determine the specific surface areas (SA) and the mesopore surface area (S_{meso}), the micropore volume (V_{micro}). Surface areas were obtained using the full BET equation. The α -plot method was used to calculate the surface area of the mesopores and the micropores volume. The starting clay was used as reference material [43,44].

2.1.6. X-ray diffraction (XRD)

X-ray diffraction spectra were measured with a Philips diffractometer using the Cu K α radiation Fig. 1. The samples were disc shaped pressed powders. The samples were treated at the desired temperature (353 K or 673 K) in a ventilated oven.

2.1.7. Carbon monoxide and hydrogen chemisorption

Chemisorption experiments were conducted on a Micromeritics ASAP 2010 at 313 K at a final hydrogen or carbon monoxide pressure of 100 Torr. Before the measurement the hydrogen reduced catalyst was thermally treated at 473 K in He for 4 h, while the catalyst reduced with NaBH₄ was pretreated at 353 K.

2.2. Materials

Detercal P1™ is a natural calcium-rich bentonite (montmorillonite 97%) of North African origin (Nador, Morocco), factory-dried, ground and sieved, which was obtained from Industria Chimica Carlo Laviosa S.p.A. (Leghorn, Italy). (CEC = 84 meq/100 g). Chlorhydrol™, a commercial 5/6 basic aluminum chloride salt pro-

duced by Reheis was kindly given by Eigenmann and Veronelli (Milan). All the chemicals were reagent grade and used without further purification. Acetone 99% was a technical grade reagent from Janssen Chimica.

2.2.1. Pillared clays preparation

The aluminum pillared bentonite (APA) was prepared as previously described [19].

2.2.1.1. Preparation of Al–Ru pillared bentonite (ARUP). The clay was prepared slightly modifying a previously described procedure [19]. Fifty grams of bentonite were suspended in acetone (50% w/w). The suspension was aged 17 h at room temperature. An aqueous solution containing AlCl₃ + RuCl₃ · 3H₂O (Al/Ru = 20) was treated with NaOH until the ratio OH/(Al + Ru) = 2.4 was reached. The solution was aged for 24 h and was added dropwise under stirring to the slurried clay at room temperature. The suspension was aged for 17 h at room temperature, centrifuged and washed several times with a total of 5 l of water. A thin film of the resulting pillared clay was air-dried at 60°C, finely ground (> 40 mesh) and calcined for a minimum of 18 h at 673 K in a ventilated oven.

2.2.1.2. Preparation of an Ru-exchanged aluminum pillared clay (APRU). A solution of RuCl₃ · 3H₂O (0.3 meq/g) was added to an aqueous suspension of 5 g of aluminum-pillared bentonite APA. The suspension was shaken in a high-speed orbital shaker for 17 h at room temperature, centrifuged and washed until free of chloride ion (AgNO₃ test). The resulting ruthenium exchanged pillared clay was air-dried at 60°C.

2.2.2. Catalysts pretreatment

2.2.2.1. ARUP was reduced by treatment in H₂ flow (20 ml min⁻¹) at 503 K for 2 h (ARUP RED-H). The sample of APRU was reduced: (1) in H₂ (20 ml min⁻¹) flow at 503 K for 2 h

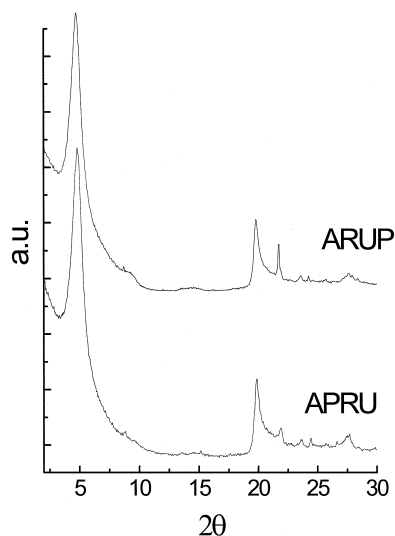


Fig. 1. X-ray diffraction spectra of ARUP- and APRU-pillared bentonites.

(APRU RED-H) or (2) in water at 273 K with NaBH_4 (APRU-Na RED-BH).

2.2.3. Acid sites poisoning by K^+ exchange

The protonic acid centers of the catalyst ARUP RED-H were progressively exchanged shaking the catalysts for one week with a KCl 0.1 N or 1 N solution to give ARUP (K0.1 RED-H), ARUP (K1 RED-H).

2.3. Catalytic measurements

2.3.1. Hydrogenation and isomerization of 1-butene

Catalytic experiments were performed in a tubular glass flow microreactor. Catalyst samples (250 mg) were pretreated for 2 h in H_2 (20 ml min^{-1}) flow at 503 K.

Experiments were performed at $F = 35 \text{ ml min}^{-1}$ ($\text{H}_2/\text{N}_2/\text{olefin} = 25/9/1$), space velocity = 8400 h^{-1} .

3. Results and discussion

3.1. Analytical data

The APRU clay, prepared pillaring a natural bentonite with a Al/Ru mixed solution and the ARUP clay, prepared introducing by cation exchange ruthenium cations in an aluminum pillared bentonite were analyzed by Atomic Adsorption and the structural formulas are reported in Table 1. The ruthenium content resulted 0.8% w/w in both pillared clays.

Table 2

Basal spacings (d_{001}), specific surface areas (S.A.), micropore volumes ($V_{\mu\text{p}}$) and mesopore surface areas (S_{mp}) of the pillared smectites.

Sample	d_{001} (nm)	S.A. (m^2/g)	$V_{\mu\text{p}}$ (m^3/g)	S_{mp} (m^2/g)
ARUP	1.84	340.0	0.13	22.8
APA	1.84	310.1	0.14	14.9
APRU	1.80	278.4	0.11	22.2

3.2. Structural data

The structural characteristics of the mixed pillared clay APRU were determined by XRD and nitrogen adsorption desorption and the data are shown in Table 2 together with those of the ruthenium exchanged ARUP sample. The structural data of the aluminum pillared clay APA [19] are added for comparison.

Both the interlayer distance and the pores distribution are very similar in both the samples APA and ARUP. On the other hand, a slight decrease of the interlayer spacing, surface area and microporosity was observed in the ruthenium exchanged sample APRU. This is not surprising because a decrease of the basal spacing was often observed in pillared clays after cation exchange with trivalent cations. The microporosity decrease is most probably also caused by the presence of the transition metal cations in the interlayer space.

3.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was used to determine the oxidation state of ruthenium in the mixed pillared sample ARUP. Only the Ru $3\text{p}_{3/2}$ peak was available for the evaluation of

Table 1

Unit cell formulae of the pillared materials and of the starting clay samples

Clay	Structural formulae
Detercal P1	$\text{Na}_{0.43}\text{Ca}_{0.13}\text{K}_{0.15}(\text{Si}_{7.56}\text{Al}_{0.44})_2(\text{Al}_{3.23}\text{Fe}_{0.22}\text{Mg}_{0.54})_2\text{O}_{20}(\text{OH})_4$
APRU	$\text{Ru}_{0.08}[\text{Al}_{1.48}(\text{Si}_{7.56}\text{Al}_{0.44})_2(\text{Al}_{3.22}\text{Fe}_{0.24}\text{Mg}_{0.54})_2\text{O}_{20}(\text{OH})_4]$
ARUP	$\text{Al}_{1.69}\text{Ru}_{0.08}(\text{Si}_{7.56}\text{Al}_{0.44})_2(\text{Al}_{3.17}\text{Fe}_{0.27}\text{Mg}_{0.55})_2\text{O}_{20}(\text{OH})_4$

the Ru species oxidation state, because the more intense Ru $3d_{(5/2+3/2)}$ peaks (BE = 280–284 eV) resulted totally masked by the C 1s peak of the contaminating carbon. This is also due to the very low Ru concentration. The ARUP spectrum showed a broad Ru $3p_{3/2}$ peak at 462.3 ± 0.2 eV. Literature data relative to Ru $3p_{3/2}$ binding energies are not available, therefore the attribution of the signal to a Ru(IV) species (the presence of Ru(VI) species cannot be excluded) was made by comparison with the position and the shape of the bands of authentic samples of Ru (0), Ru(III) and Ru(IV) species (the signal of RuO₂ was found at 462.7 ± 0.2 eV) [45,46].

3.4. Temperature-programmed reduction (TPR)

Temperature-programmed reduction is a technique widely used to characterize solid materials, in particular heterogeneous catalysts based on noble metals supported on refractory oxides [47]. Information can be obtained from the TPR profiles on the supported metal species oxidation states, metallic particles dimensions and shape and on metal–support interactions [47]. TPR measurements have been used to obtain true mixed metal pillars in Al/Fe-pillared clays [17].

TPR experiments were carried out on the mixed metals pillared ARUP clay and on the Ru(III) exchanged aluminum-pillared clay APRU, both pretreated in N₂ or in air flow at 673 K. The TPR profiles are shown in Fig. 2.

The TPR profile of ARUP showed a sharp peak centered at 487 K (Curve A) attributable to the Ru(IV)–Ru(0) reduction process [47]. The sample was then reduced in 5% H₂/Ar mixture at 870 K and reoxidized at 673 K in air. After this treatment, the reduction peak was found at 456 K (Profile B). The structure of an aluminum-pillared clay is known to collapse above 700 K, therefore, this curve represents the reduction profile of an oxidized ruthenium species on the pillared clay degraded surface.

The TPR profile of the ruthenium exchanged APRU resulted quite different. The as-prepared

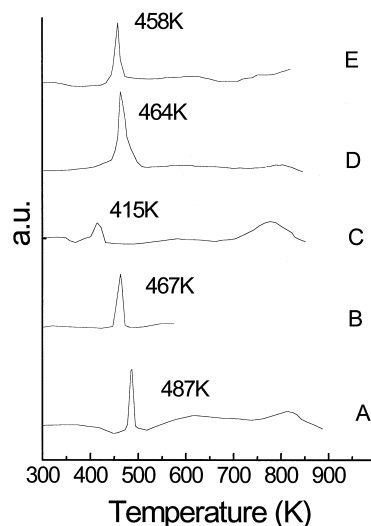


Fig. 2. TPR profiles of (A) ARUP sample; (B) ARUP after reduction in H₂ at 870 K and reoxidation at 673 K in air; (C) APRU sample (D) APRU after oxidation at 673 K; (E) physical mixture of RuO₂ and APA.

sample showed a small reduction peak centered at 415 K (Profile C), attributable to the reduction of the Ru(III) cations to Ru(0) species, while the same sample after oxidation at 673 K showed a Ru(IV)–Ru(0) reduction peak at 464 K (Profile D). A sample was prepared mixing RuO₂ with the aluminum-pillared APA clay and it showed a reduction curve with the maximum centered at 458 K (Profile E).

The TPR behaviour of a physical mixture of ruthenium dioxide and an aluminum pillared clay (Curve E) is similar to that of an air oxidized ruthenium exchanged aluminum pillared clay (Curve D) and of a mixed metal Ru/Al pillared clay structurally degraded by the thermal treatment at 870 K (Curve B). On the other hand the Al/Ru mixed pillared clay ARUP appeared to be structurally different and the reduction peak (Profile A) at higher temperature evidences an intimate contact between the oxides that form the pillars.

3.5. Catalytic activity

The catalytic activity of the ruthenium containing clays ARUP and APRU was tested in

Table 3
Gas phase 1-butene hydrogenation at 313 K on pillared clays

Catalyst	Total conversion (mole %)	<i>n</i> -Butane (mole %)	2-Butenes (mole %)	Ruthenium dispersion ^a (%)
ARUP (H-RED)	63.4	27.3	36.1	0.65
ARUP (K0.1 RED-H)	73.0	50.9	22.1	
ARUP (K1 RED-H)	81.1	61.5	19.6	
APRU (RED-H)	100	100		13.2
APRU (NA RED-BH)	100	100		30.6

$F = 35 \text{ ml} \times \text{min}^{-1}$, ($\text{H}_2/\text{N}_2/\text{olefin} = 25/9/1$), space velocity = 8400 h^{-1} .

^aThe ruthenium dispersion was determined by CO and/or H_2 chemisorption.

the 1-butene hydrogenation and isomerization after a reductive pretreatment.

ARUP was reduced in H_2 flow (20 ml min^{-1}) at 503 K for 2 h (ARUP RED-H). The sample of APRU was reduced in two ways: (1) in H_2 (20 ml min^{-1}) flow at 503 K for 2 h (APRU RED-H) or (2) in water at 273 K with NaBH_4 (APRU-Na RED-BH).

The products distribution obtained on all the catalysts in hydrogenation conditions at 313 K is reported in Table 3.

Both hydrogenation and double bond migration products (*n*-butane, 2-butene) were observed when ARUP (H-RED) was used as catalyst, with a total conversion of 63%. Olefins isomerization is known to be catalyzed by medium strength protonic acid centers, but usually it accompanies olefin hydrogenation catalyzed by transition metals [48]. Therefore, after the exchange of the surface protons with potassium ions the isomerization activity was only slightly reduced, but not suppressed.

When the ruthenium exchanged hydrogen reduced catalyst APRU (RED-H) was used, the complete transformation of 1-butene in butane was observed. The same occurred when the catalyst was pre-reduced by treatment with sodium tetrahydroborate at room temperature.

The catalysts activity was tested also in the absence of hydrogen at 313 K and the data are reported in Table 4.

ARUP (H-RED) produced in this case only 2-butenes with a total conversion of 52.4%. The catalytic activity is attributable to the protonic acid centers of the interlayer space as demon-

strated by its almost total suppression after potassium exchange. This is confirmed by the very low activity of APRU (NA RED-BH) catalyst, the protons of which were substituted by the sodium ions of the reducing agent during the pretreatment. Interestingly, the double bond migration activity of the mixed pillared clay ARUP (RED-H) is very similar to that of the aluminum pillared sample APA, suggesting that, in both cases, the pillaring process generates an analogous number of protonic acid sites. Nevertheless, these protons slowly migrate, by a well known phenomenon, inside the clay octahedral layer, where they are quite unaccessible for the incoming olefin molecules, justifying the low isomerization activity of ARUP and APA. The metal dispersion of ARUP (H-RED) was determined by hydrogen and CO chemisorption and resulted very low (Table 3) giving an explanation of the low hydrogenation activity of the catalyst. The very low ruthenium dispersion could be explained by the presence of extremely

Table 4
Gas phase 1-butene isomerization at 313 K

Catalyst	2-butenes (mole %)
ARUP (H-RED)	52.4
ARUP (K 0.1 RED-H)	31.7
ARUP (K1 RED-H)	3.39
APRU (RED-H)	100
APRU (NA RED-BH)	9.7
APA	54.0

$F = 35 \text{ ml} \times \text{min}^{-1}$ ($\text{He}/\text{N}_2/\text{olefin} = 25/9/1$), space velocity = 8400 h^{-1} .

APA is an aluminum pillared bentonite [19].

large metallic particles, but this seems quite unrealistic, in our experimental conditions. Therefore, we prefer to suppose that the reduction of the intimate mixture of aluminum and ruthenium oxides constituting the pillars leads to ruthenium crystallites in part covered by an aluminum oxide layer. Consequently, only a small fraction of the metallic ruthenium emerges from the surface and is available for reagents chemisorption, giving a justification of the very low value of metal dispersion obtained.

4. Conclusions

Cation exchange with ruthenium of an aluminum pillared clay and pillaring with an Al/Ru solution leads, after reduction, to quite different catalytic materials. Cation exchange followed by reduction in hydrogen leads to the formation of relatively large metallic crystallites most probably located on the clay external surface.

Reduction of the mixed pillared derivative gives origin to smaller crystallites that most probably remain in the interlayer space, but that are mostly covered by an aluminum oxide layer with a consequent drastic reduction of the catalytic activity. Reduction of the exchanged sample APRU with sodium tetrahydroborate gives smaller crystallites and the total suppression of the protonic surface acidity.

Acknowledgements

The financial support of the MURST is acknowledged. The authors thank A. Talon for the analytical determinations and T. Finotto for the XRD spectra.

References

- [1] T.J. Pinnavaia, *Science* 220 (1983) 365.
- [2] F. Figueras, *Catal. Rev. Sci. Eng. Sci.* 30 (1988) 457.
- [3] D.E.W. Vaughan, *Catal. Today* 2 (1988) 187.
- [4] J.R. Butruille, T.J. Pinnavaia, in: J.L. Atwood et al. (Eds.), in *Comprehensive Supramolecular Chemistry*, Vol. 7, Pergamon, Oxford, 1996, p. 219.
- [5] M.L. Occelli, R.M. Tindwa, *Clays and Clay Miner.* 31 (1983) 22.
- [6] M.L. Occelli, J.E. Lester, *Ind. Eng. Chem. Prod. Res. Dev.* 24 (1985) 27.
- [7] D. Tichit, F. Fajula, F. Figureas, J. Bousquet, C. Gueguen, in: B. Imelik, C. Naccache, G. Coudurier, Y.T. Ben Taarit, J.C. Vedrine (Eds.), *Catalysis by Acids and Bases*, Elsevier, Amsterdam, 1985, p. 351.
- [8] H. Auer, H. Hofmann, *Appl. Catal. A, General* 97 (1993) 23.
- [9] F. González, C. Pesquera, I. Benito, S. Mendioroz, *J. Chem. Soc. Chem. Commun.* (1991) 587.
- [10] X. Tang, W.-Q. Xu, Y-F. Shen, S.L. Suib, *Chem. Mater.* 7 (1995) 102.
- [11] S.A. Bagshaw, R.P. Cooney, *Chem. Mater.* 7 (1995) 1384.
- [12] M.J. Hernando, C. Pesquera, C. Blanco, I. Benito, F. González, *Chem. Mater.* 8 (1996) 76.
- [13] J. Barrault, C. Zivkov, F. Bergaya, L. Gataineau, N. Hassoun, H. Van Damme, D. Mari, *J. Chem. Soc. Chem. Commun.* (1988) 1403.
- [14] F. Bergaya, N. Hassoun, J. Barrault, in: I.V. Mitchell (Ed.), *Pillared Layered Structures*, Elsevier Applied Science, London, 1990, p. 167.
- [15] M.L. Occelli, J.M. Stencel, S.L. Suib, *J. Mol. Catal.* 64 (1991) 221.
- [16] J. Barrault, L. Gataineau, N. Hassoun, F. Bergaya, *Energy and Fuels* 6 (1992) 760.
- [17] F. Bergaya, N. Hassoun, J. Barrault, L. Gataineau, *Clay Min.* 28 (1993) 109.
- [18] D. Zhao, G. Wang, Y. Yang, X. Guo, Q. Wang, J. Ren, *Clays and Clay Min.* 41 (1998) 317.
- [19] L. Storaro, M. Lenarda, R. Ganzerla, A. Rinaldi, *Microporous Mater.* 6 (1996) 55.
- [20] S. Perathoner, A. Vaccari, *Clay Minerals* 32 (1997) 119.
- [21] D. Zhao, Y. Yang, X. Guo, *Zeolites* 15 (1995) 58.
- [22] R. Toranzo, M.A. Vicente, M.A. Bañares-Muñoz, *Chem. Mater.* 9 (1997) 1829.
- [23] N.D. Skoularikis, R.W. Coughlin, A. Kostapapas, K. Carrado, S.L. Suib, *Appl. Catal.* 39 (1988) 61.
- [24] M. Lenarda, R. Ganzerla, L. Storaro, S. Enzo, R. Zaroni, *J. Mol. Catal.* 92 (1994) 201.
- [25] L. Storaro, R. Ganzerla, M. Lenarda, R. Zaroni, *J. Mol. Catal.* 97 (1995) 139.
- [26] I. Pálinkó, Á. Molnár, J.B. Nagy, J-C. Bertrand, K. Lázár, J. Vályon, I. Kiricsi, *J. Chem. Soc., Faraday Trans.* 93 (1997) 1591.
- [27] L. Storaro, R. Ganzerla, M. Lenarda, R. Zaroni, A. Jiménez López, P. Olivera-Pastor, E. Rodríguez Castellón, *J. Mol. Catal. A* 115 (1997) 329.
- [28] K. Bahrnowsky, E. Serwicka, *Geol. Carpath., -Ser. Clays* 44 (1993) 17.
- [29] F. Gonzales, C. Pesquera, I. Benito, S. Mendioroz, G. Poncet, *J. Chem. Soc. Chem. Commun.* (1992) 491.
- [30] A. Geatti, M. Lenarda, L. Storaro, R. Ganzerla, M. Perissinotto, *J. Mol. Catal.* 121 (1997) 111.
- [31] Kukkadapu, L. Kevan, *J. Phys. Chem.* 92 (1988) 6073.
- [32] V.N. Parulekar, J.W. Hightower, *Appl. Catal.* 35 (1987) 249.

- [33] V. Luca, Kukkadapu, L. Kevan, J. Chem. Soc., Faraday Trans. 87 (1991) 3083.
- [34] M. Lenarda, R. Ganzerla, L. Storaro, A. Trovarelli, R. Zaroni, J. Kaspar, J. Mol. Catal. 72 (1992) 75.
- [35] R. Molina, S. Moreno, A. Vieira-Coelho, J.A. Martens, P.A. Jacobs, G. Poncelet, J. Catal. 148 (1994) 304.
- [36] S. Moreno, R. Sun Kou, G. Poncelet, J. Catal. 162 (1996) 208.
- [37] J.B. Nagy, J-C. Bertrand, I. Pálincó, I. Kiricsi, J. Chem. Commun. (1995) 2269.
- [38] W. O'Neil, L. Parker jr., R. Millini, I. Kiricsi, Inorg. Chem. 36 (1997) 779.
- [39] M.P. Seah, G.C. Smith, in: Practical Surface Analysis, D. Briggs, M.P. Seah, (Eds.), Vol. 1, 2nd edn., Appendix 1, Wiley, Chichester, 1990, pp. 543–544.
- [40] D.A. Shirley, Phys. Rev. 55 (1972) 4709.
- [41] J. Vegh, J. Electron Spectr. Rel. Phen. 46 (1988) 411.
- [42] J.J. Yeh, I. Lindau, Atomic Data and Nuclear Data Tables 32 (1985) 1.
- [43] S.J. Gregg, K.S.K. Sing, Adsorption, Surface Area and Porosity, 2nd edn., Academic Press, London, 1982.
- [44] M.S. Baksh, E.S. Kikkinides, R.T. Yang, Ind. Eng. Chem. Res. 31 (1992) 2181.
- [45] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, in: Handbook of X-ray Photoelectron Spectroscopy, J. Chastain (Ed.), Perkin-Elmer, Eden Prairie, MN, USA, 1992.
- [46] X-ray Photoelectron Spectroscopy Database, Version 1.0, National Institute of Standards and Technology, Gaithersburg, MD, USA, 1989.
- [47] A. Jones, B.D. Mc Nicol, Temperature programmed reduction for solid materials characterization, Marcell Dekker, New York, 1986.
- [48] G.A. Olah, A. Molnár, Hydrocarbon Chemistry, Wiley, New York, 1995.