Catalysis Letters Vol. 104, Nos. 1–2, October 2005 (© 2005)
DOI: 10.1007/s10562-005-7436-z

Methanol steam reforming over NiAl and Ni (M) Al layered double hydroxides (M = Au, Rh, Ir) derived catalysts

Caixia Qi, John C. Amphlett, and Brant A. Peppley*

Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario K7K 7B4, Canada

Received 6 April 2005; accepted 23 June 2005

This paper deals with an experimental investigation concerning steam reforming of methanol at 280, 340 and 380 °C over NiAl and Ni (Au, Rh or Ir)Al layered double hydroxides (LDHs) derived catalysts. Incorporation of noble metal ions into the NiAl-LDH framework was evidenced by XRD, TGA and TEM techniques. High selectivity to H_2 and CO_2 with less than 5% (volume) CO and trace CH_4 was observed over the NiAl-LDH catalyst. Whereas CO and H_2 are major products at lower temperatures after addition of Au, Rh and Ir to the NiAl-LDH system. They are significantly reduced with the concomitant increase in CH_4 and CO_2 as the temperature increased.

KEY WORDS: steam reforming of methanol; hydrogen production; Ni-based catalysts; Au; Rh; Ir; layered double hydroxide.

1. Introduction

Methanol is a primary candidate as a hydrogen carrier for on-board production of hydrogen for fuel-cell generators for portable applications because of its safe handling, low cost, high energy density and easy synthesis from biomass, coal and natural gas [1]. Steam reforming over copper-containing catalysts, especially CuZn or CuZnAl mixed oxides, is a highly effective conversion process ($CH_3OH + H_2O \rightarrow 3H_2 + CO_2, \Delta H^0 = 49.4$ kJ/mol), due to the high selectivity and activity of Cu-based catalysts [2–5]. However, because the Cu-based catalysts are in general very prone to deactivation by thermal sintering, there is a need for the development of new catalysts that are more thermally stable for use in metal integrated membrane steam reformer. Combining a palladium membrane with a methanol reformer shows considerable promise for generating high purity H_2 in terms of energy efficiency, system simplicity, and compactness [6,7]. Desired catalyst characteristics include high activity and stability in the temperature range of 300–400 °C, which is higher than current commercial Cu-based catalysts, can endure.

Layered double hydroxides belong to a class of anionic clays having a hydrotalcite-like structure. The general molecular formula can be presented as: $\{M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2][A^{n-}]x/n \cdot mH_2O$, where M^{2+} and M^{3+} are metal cations which are cross-linked through hydroxide group and A^{n-} is a charge-compensating anion. It is possible to synthesize hydrotalcite-like compounds with more than two metals and two anions [8]. We have recently conducted studies concerning the catalytic steam reforming of methanol using as-synthesized NiAl layered double hydroxide (LDH) catalysts, which have shown relatively higher stability than commercial Cu catalysts at 390 °C [9]. Unfortunately the improved thermal stability is accompanied by a decrease in selectivity resulting in increased levels of CO and CH_4 in the product gas. So far, no reformate with high selectivity to H_2 and CO_2 has been reported in the limited number of publications concerning Ni-LDH [10,11].

In the present study, we extend our investigation of methanol steam reforming over a NiAl-LDH catalyst, which has a different formula with our previous sample used in [9], and its analogues with the partial substitution of Al^{3+} by Au, Rh and Ir cations. The performance of these catalysts was studied at various temperatures and a molar ratio of 1.2 of steam to methanol.

2. Experimental

2.1. Catalyst preparation

A co-precipitation technique was used to prepare the Ni(M)Al LDHs (M = Au, Rh, Ir), in which molar ratios of 9:0.9:0.1 for Ni/Al/M and 0.1 for (Al+M)/(Ni+Al+M) were adopted. The syntheses were performed at room temperature in air under a constant pH of 7. 800 mL of 0.125 M K_2CO_3 aqueous solution and 800 mL of aqueous solution containing 0.125 M Ni nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], 0.0125 M Al nitrate [$(NO_3)_3 \cdot 6H_2O$] and 0.00139 M M^{3+} chloride [$HAuCl_4 \cdot H_2O$, $HIrCl_4 \cdot xH_2O$, $RhCl_3 \cdot xH_2O$, respectively] were simultaneously added drop-wise into 800 mL distilled water under vigorous stirring. After addition of all reagents, the precipitates formed were further aged for 1 h under continuous stirring, then filtered, washed with distilled

---

* To whom correspondence should be addressed.
E-mail: Peppley-b@rmc.ca

water, re-slurried for another hour and then re-filtered, washed and dried at 70 °C for 22 h. Finally, the dried precursor was calcined in air at 400 °C for 5 h to obtain the catalysts.

2.2. Characterization

Elemental composition was determined by neutron activation analysis (NAA) using a SLOWPOKE-2 reactor at half power, which produces a flux of 5×10^{11} neutrons cm^{-2} s^{-1}. After the sample was made radioactive, it was counted on a Perkin–Elmer Ortec high purity germanium detector. BET surface areas were determined by N_2 adsorption–desorption measurements at 77 K using a Quantachrome Autosorb Automated Gas 9Sorption System (Quantachrome Corp., USA). Thermogravimetric Analyses (TGA) was performed on a 2050 Model Thermogravimetric analyser (TA Instruments, USA). Each sample was heated from room temperature to 700 °C at 10 °C/min in flowing N_2 (100 mL/min). X-ray diffraction was conducted with a SCINTAG X_1 diffractometer (USA) using Cu-K_α radiation operated at 40 kV and 45 mA, a step size of 0.02°, and a scan rate of 2° 2θ/min from 2 to 80° 2θ. Transmission electron microscopy was carried out over Philips CM 20 at 200 kV.

2.3. Catalytic activity measurement

Catalytic activity testing was carried out at atmospheric pressure in an isothermal fixed-bed tubular reactor that contained 0.150 g of 20× 30 mesh catalyst. The reactant composition was 1.2:1 mol ratio water to methanol and this deaerated solution was fed to the reactor using a Gilson model 302 HPLC pump at a total flow rate of 3 mL/h. The catalyst was purged with He at 200 °C overnight and then activated *in situ* with the reactant stream at 200 °C for 6 h prior to reaction at 280, 340 and 380 °C, respectively. The product stream was passed through a condenser (chilled to −4 °C) to trap any unreacted water and methanol. The mixture of dry gas was analysed at intervals of 2 h using a GOW-MAC 550P gas chromatograph equipped with a thermal conductivity detector. The carrier gas was 9 (vol.)% H_2 in He that ensured that H_2 peak was completely negative so that an accurate calibration could be obtained. Separation of H_2, CO, CH_4 and CO_2 was accomplished using a Carbosieve-S column.

3. Results and discussion

3.1. Structural properties of the catalysts

The chemical composition and textural properties for the four calcined catalysts are given in Table 1. A$(Al^{3+}+M^{3+})/(Ni^{2+}+Al^{3+}+M^{3+})$ atomic ratio of >0.20 for the four samples is larger than the ratio of 0.1 used in the starting solution and the molar ratio of Ni to (Al + M) in all samples is significantly less than that in the starting solutions, indicating the incomplete precipitation of Ni^{2+} ions. Incomplete precipitation of Ni^{2+} ions may be a consequence of using a pH of 7 during synthesis [12,13]. N_2 adsorption–desorption experiments show that all catalysts are mesoporous materials with high surface area. Smaller pore diameter and pore volume after addition of M^{3+} (M = Au, Rh, Ir) suggests the possible incorporation of M^{3+} into NiAl-LDH framework.

Figure 1 displays TGA data for the four calcined catalysts (solid lines) and their corresponding as-synthesized precursors (dotted lines). For the precursors, the curves show two principal regions where weight loss occurs in the LDHs. The first weight loss occurs below 200 °C and corresponds to removal of interlayer water molecules. The second weight loss occurs at temperatures around 315 °C. It is ascribed to removal of hydroxyl group from the brucite layers as water molecules and the loss of interlayer carbonate anions as carbon dioxide [14]. The calcined catalysts showed only one small weight loss. This occurs at room temperature and is attributed to physisorbed water, indicating the decomposition of the layered double structure after calcination at 400 °C.

Table 1
Chemical composition and surface areas of the four calcined catalysts

Catalyst[a]	Metal composition (atom.%)[b]			x[c]	Ni/(Al + M)	N_2 adsorption–desorption measurements[d]		
	M[e]	Ni	Al			A_{BET} (m^2/g)	Rp (Å)	Vp (cm^3/g)
NiAl	–	76.5	23.5	0.23	3.3	201.6	50.8	0.48
NiAl-Au	1.2	79.5	19.3	0.20	3.9	195.0	39.5	0.41
NiAl-Rh	2.4	76.2	21.3	0.24	3.2	213.2	37.2	0.38
NiAl-Ir	2.4	74.8	23.1	0.23	3.1	215.8	37.2	0.39

[a] All catalysts were obtained by calcination of as-prepared precursors in air at 400 °C for 5 h.
[b] Determined by Neutron Activation Analysis (NAA).
[c] x: atomic ratio of (Al + M)/(Al + Ni + M).
[d] The pore structure analysis was based on BJH method [22], applied on the desorption branch of the isotherms.
[e] M: noble metal Au, Rh and Ir.

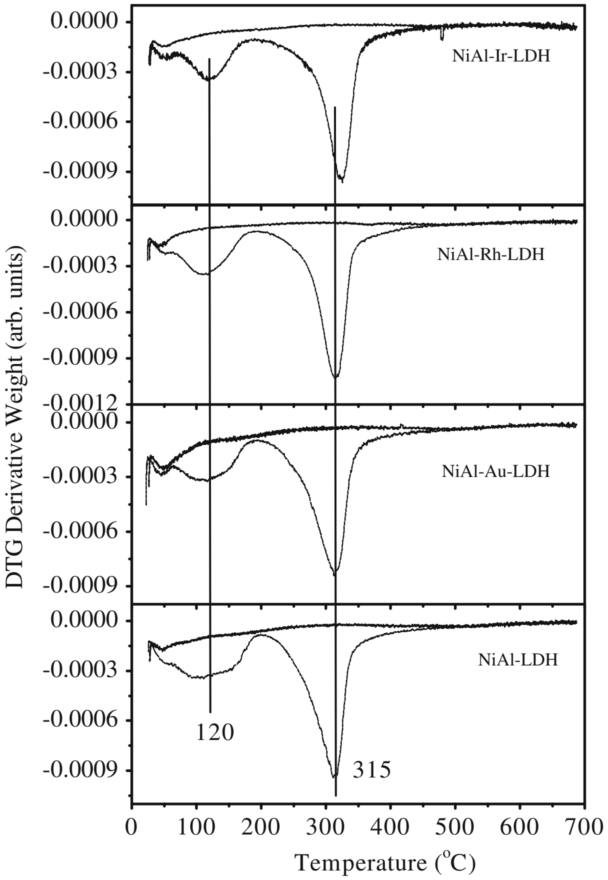

Figure 1. TGA data for the four calcined catalysts (solid lines) and their as-synthesized precursors (dotted lines).

The XRD patterns of all four catalysts and their precursors are displayed in figure 2. For all precursors, there are six peaks for (003), (006), (012), (015), (018) and (110)/(113) reflections, indicating the presence of a single phase of hydrotalcite-like layered double hydroxide (JCPDS file no. 15–87) [15]. The doublet peaks corresponding to (110) and (113) reflections did not separate clearly in our case. All calcined catalysts show a poorly crystalline NiO, evidenced by three peaks at 2θ of 37.2, 43.3 and 62.9 with respect to (101), (012) and (110) reflections (JCPDS file no. 44–1159), respectively. Another broad and asymmetric peak observed at 2θ of 11.7 corresponds to the (003) reflections, the most intense peak for the LDHs, indicating the partial retention of the LDH structure in the calcined sample. It has been reported that the calcination at 350–550 °C of the NiAl-LDH precursor leads to the complete disappearance of the XRD patterns of the LDH structure and to the appearance of the characteristic patterns of mixed oxides of NiO-type [16–19]. In our case, the appearance of (003) reflections could be a consequence of the partial reconstruction of the calcined samples because the samples were taken out of furnace at high temperature. Reconstruction of Ni-containing mixed oxides obtained by calcination under hydrothermal conditions has been proven and the ease of reconstruction depends on calcination temperature [13,18,19].

It can be seen from the XRD patterns that the intensity/sharpness of all diffraction peaks is reduced upon the

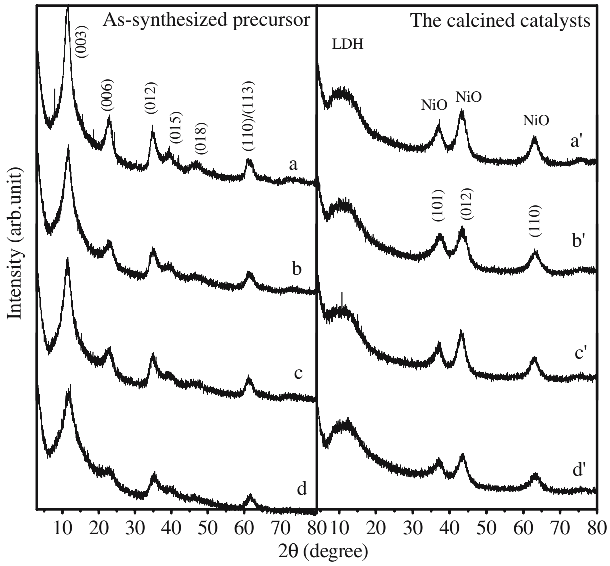

Figure 2. XRD patterns for (a/a′), NiAl; (b/b′) NiAl-Au; (c/c′), NiAl-Rh; and (d/d′), NiAl-Ir layered double hydroxide precursors and the calcined catalysts.

addition of Au, Rh and Ir for both precursors and the calcined catalysts. This is consistent with many observations when a cation is substituted by another isovalent cation having similar ionic radii [14], indicating that the M^{3+} (M = Au, Rh, Ir) isomorphously substitute the Al^{3+} in the LDH framework (ionic radii of Ni^{2+}, Al^{3+}, Au^{3+}, Rh^{3+} and Ir^{3+} in their octahedral coordination are 0.83, 0.68, 0.99, 0.81 and 0.82, respectively [20]).

TEM images of the four calcined catalysts are displayed in figure 3. For the calcined NiAl sample (figure 3a), aggregates of fibrous particles, characteristic of hydrotalcite-like compounds [16,21], were detected. This suggests the retention of the general crystal morphology of the precursor after calcination, in agreement with previous observations [13,16,18]. The morphology of noble-metal modified catalysts (figure 3b, c, d) was markedly different, showing aggregates of small, irregular crystallites. Au, Rh and Ir particles are homogeneously dispersed in the NiAl mixed oxides. This further confirms the introduction of noble metals into the NiAl-LDH system.

3.2. Catalytic activity

Table 2 summarizes the catalytic performance of four Ni-based LDH-derived catalysts in the steam reforming reaction. It was found that NiAl-LDH catalyst was inactive at temperature of 280 °C. However, the catalytic activity increased and showed high selectivity to H_2 and CO_2 from 340 to 380 *°C*. These results compare well with those reported by Segal *et al.* [10 and Velu *et al.* 11]. While our results show similar conversions of methanol to their catalysts, the selectivity of our catalyst is far superior, with no CH_4 and much lower contents of CO in the product stream. On the other side, the noble-metal modified catalysts are more active than NiAl-LDH one, indicated by higher conversion rates of methanol. However, these catalysts displayed dramatic differences in terms of product composition. CO and hydrogen are primary products at low temperatures (such as 280 °C). A ratio of H_2 production rate/CH_3OH conversion rate of around 2 suggests that methanol decomposition is the major reaction. As temperature increased, significant amounts of CH_4 are formed, resulting in the virtual disappearance of CO and appreciable reduction in H_2 generation. The methanol conversions were also appreciately enhanced. The reaction of $CO + 3H_2 \rightarrow CH_4 + H_2O$ $\Delta H^0 = -206.4$ kJ/mol) is probably the source of methane production. Obvious increases in CO_2 selectivity as temperatutre increased suggested that the steam reforming of methanol was accerlerated significantly at high reaction

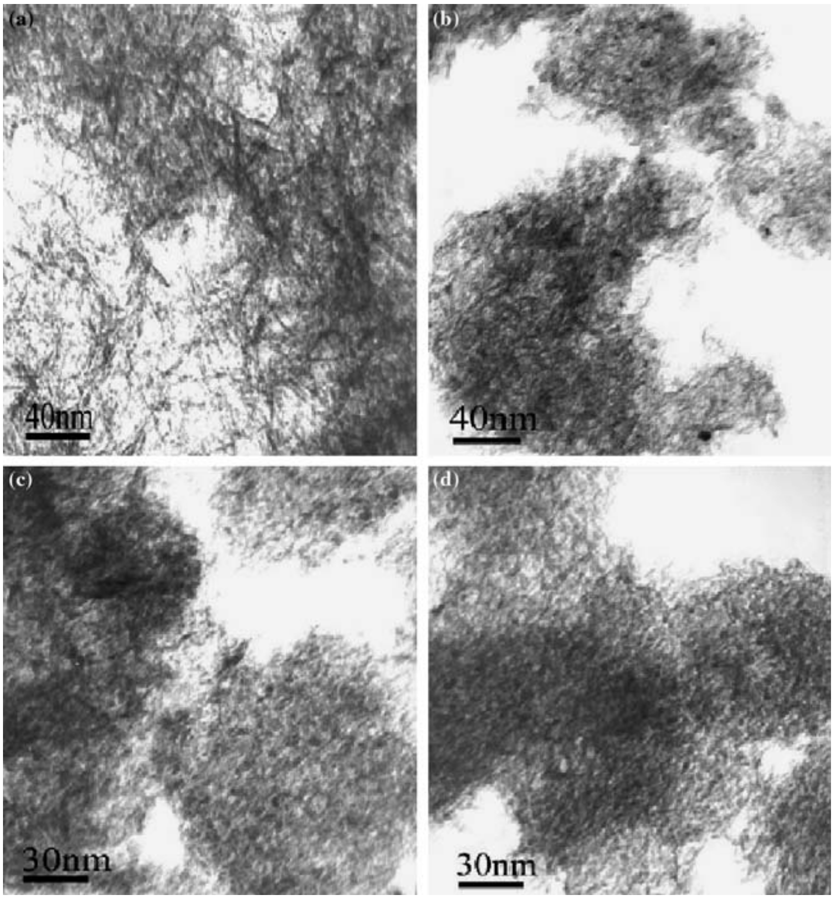

Figure 3. TEM images of (a), NiAl; (b), NiAl-Au; (c), NiAl-Rh; and (d), NiAl-Ir LDH-derived catalysts.

Table 2
The catalytic performance of four catalysts in steam reforming of methanol

Catalyst	Reaction temperature (°C)	MeOH conversion		H_2 prod. rate/mmol kg^{-1} s^{-1}	H_2 prod. rate/CH_3OH conv. rate	H_2O Conv. Mol.%	Selectivity of gaseous products (Mol. %)			
		Mol. %	Rate/mmol kg^{-1} s^{-1}				H_2	CO_2	CO	CH_4
NiAl	280	–	–	–	–	–	–	–	–	–
	340	16.1	15.5	42.7	2.8	12.0	73.4	20.2	6.4	0.0
	380	35.0	33.6	95.0	2.8	28.4	73.6	21.8	4.6	0.0
NiAl-Au	280	27.1	26.0	54.3	2.1	2.3	66.1	5.0	28.9	0.0
	340	82.9	795	128.7	1.6	−6.4	60.5	5.0	29.0	5.5
	380	99.4	95.4	56.9	0.6	−20.7	36.2	26.0	1.6	36.2
NiAl-Rh	280	36.7	35.0	65.8	1.9	−3.2	63.4	0.6	35.4	0.6
	340	80.2	79.9	50.0	0.6	−21.5	37.7	20.0	8.7	33.6
	380	82.6	82.2	40.2	0.5	−22.0	32.2	26.1	0.3	41.4
NiAl-Ir	280	44.6	43.1	77.6	1.8	−5.1	62.5	0.4	35.5	1.6
	340	85.3	82.4	73.0	0.9	−24.5	46.9	9.3	20.9	22.9
	380	92.9	89.7	61.3	0.7	−15.4	40.1	25.7	0.3	33.9

The data were collected after 6 h reaction at each temperature.

temperature, leading to a higher partial pressure of H_2 and further kinetically increasing the rate of the methanation reaction, a thermodynamically unfavorable reaction.

4. Conclusions

Ni-based catalysts derived from NiAl-layered double hydroxides with or without modification of noble metals like Au, Rh, and Ir were synthesized by co-precipitation method and investigated in the steam reforming of methanol at relatively high temperatures. Noble metal ions were evidenced to be incorporated into NiAl-LDH framework, showing the textural features of LDHs as checked by XRD, TGA and TEM technique. The catalyst without modification presented high selectivity to CO_2 and H_2, therefore largely reducing the risk of deterioration in the efficiency and lifetime of metal permeable membranes due to the high amount of CO in the reformate [23,24]. This catalyst shows the potential to be used in the integrated-membrane reactor for the methanol steam reforming in the temperature range 300–400 °C. Partial substitution of Al by Au, Rh or Ir considerably catalyzes the methanation reaction at higher temperatures. Methane is undesirable byproduct in methanol-steam reforming for the purpose of producing H_2, because the production of CH_4 drastically reduces the H_2 yield. These catalysts would likley not be suitable for fuel-cell hydrogen production from methanol.

Acknowledgments

The authors would like to express their sincere gratitude to Bob Whitehead, Jim Irving and Kathleen Fulton for XRD, TGA and BET measurements. Financial support from NSERC and the Canadian Department of National Defence is gratefully acknowledged.

References

[1] Y. Matsumura, K. Tanaka, N. Tode, T. Yazawa and M. Haruta, J. Mol. Catal. A Chem. 152 (2000) 157.

[2] G.C. Shen, S. Fujita, S Matsumoto and N. Takezawa, J. Mol. Catal. A Chem. 124 (1997) 123.

[3] B.A. Peppley, J.C. Amphlett, L.M. Kearns and R.F. Mann, Appl. Catal. A Gen. 179 (1999) 21.

[4] J.P. Breen and J.R.H. Ross, Catal. Today 51 (1999) 521.

[5] M.M. Gunter, T. Ressler, R.E. Jentoft and B. Bems, J. Catal. 203 (2001) 133.

[6] J. Han, I. Kim and K. Choi, J. Power Source 86 (2000) 223.

[7] Y.M. Lin and M.H. Rei, Int. J. Hydrogen Energy 25 (2000) 211.

[8] F. Cavani, F. Trifiró and A. Vaccari, Catal. Today 11 (1991) 173.

[9] J. C. Amphlett, R. F. Mann, B. A. Peppley, H. M. Jensen, D. Akporiaye and H. Fjellvage, in: *Proceedings of the 17th NACS, Toronto, ON. Canada, June 2001.*

[10] R. Segal Scott, B. Anderson Ken, A. Carrado Kathleen and L. Marshall Christopher, Appl. Catal. A Gen. 231 (2002) 215.

[11] S. Velu, K. Suzuki and T. Osaki, Catal. Lett. 69 (2000) 43.

[12] C. Kruissink Edgar, L. van Reijen Louis and R.H. Ross Julian, J. Chem. Soc. Faraday Trans. 1(77) (1981) 649.

[13] F. Prinetto, G. Ghiotti, P. Graffin and D. Tichit, Microporous Mesoporous Mater 39 (2000) 229.

[14] S. Velu, K. Suzuki, M.P. Kapoor, S. Tomura, F. Ohashi and T. Osaki, Chem. Mater. 12 (2000) 719.

[15] S. Kannan, A. Narayanan and C.S. Swamy, J. Mater. Sci. 31 (1996) 2353.

[16] O. Clause, R. Rebours, E. Merlen, F. Trifiro and A. Vaccari, J. Catal. 133 (1992) 231.

[17] F. Trifirò, A. Vaccari and O. Clause, Catal. Today 21 (1994) 185.

[18] F. Prinetto, D. Tichit, R. Teissier and B. Coq, Catal. Today 55 (2000) 103.

[19] Heidi, M. Jansen, *Synthesis, Calcination and Reconstruction of Hydrotalcite-like Compounds, A study of Catalyst Support Materials for Alkane Dehydrogenation*, Ph. D. Dissertation, University of Oslo, Norway, pp. 97–115, 2003.

[20] J.E. Huheey, E.A. Keiter and R.L. Keiter, *Inorganic Chemistry: Principle of structure and Reactivity* 4 ed.(Harper Collins College Publishers, New York, 1993).

[21] F. Thevenot, R. Szymanski and P. Chaumette, Clays Clay Miner. 37 (1989) 396.

[22] E.P. Barret, L.G. Joyner and P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.

[23] J. Chabot, J. Lecomte, C. Grumet and J. Sannier, Fusion Technol. 14 (1988) 614.

[24] S. Hara, K. Sakaki and N. Itoh, Ind. Eng. Chem. Res. 38 (1999) 4913.