Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 2, 601–606

APPLICATION OF THERMOGRAVIMETRIC ANALYSIS TO THE EVALUATION OF AMINATED SOLID SORBENTS FOR CO_2 CAPTURE

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In this work a series of solid sorbents were synthesized by immobilizing liquid amines on the surface of a mesoporous alumina. The samples were chemically characterized and BET surface areas calculated from the N_2 adsorption isotherms at 77 K. The CO_2 capture performance of the sorbents and their thermal stability was studied by thermogravimetric methods. The effect of amine loading on the CO_2 capture performance of the prepared sorbents was also evaluated. Analysis of TG-DTG curves showed that thermal stabilization of the amines is significantly improved by immobilizing them on an inorganic support. Temperature-programmed CO_2 adsorption tests from 298 K up to 373 K at atmospheric pressure, proved to be a useful technique for assessing the capacity of sorbents for CO_2 capture. Alumina impregnated with diethylenetriamine presented the highest CO_2 adsorption capacities throughout the tested temperature range.

Keywords: *adsorption, CO_2 capture, thermogravimetric analysis*

Introduction

Nowadays global warming is a major concern. The observed increase in average temperatures since the mid-20th century is very likely due to the increase in anthropogenic greenhouse gas (GHG) concentrations, with carbon dioxide being the most important contributor. Moreover, annual fossil carbon dioxide emissions increased from an average of 6.4 GtC per year in the 1990s to 7.2 GtC per year in the period 2000–2005 [1]. The UN Framework Convention on Climate Change, ratified by 186 countries, calls for the stabilization of GHGs, which implies deep reductions in global emissions. Although eventually a new energy scenario must be developed in pro of sustainability, in the short to medium term CO_2 capture and storage (CCS) from large stationary sources, such as power generation plants (post-combustion capture), is a feasible method for cutting down emissions. CCS involves separating CO_2 from other gases, compressing and transporting it to an adequate storage site. At present, the preferred technology for post-combustion capture is amine scrubbing. However, its high energy requirements result in a significant efficiency penalty on the power cycle. Adsorption on porous solids is an emerging alternative that seeks to reduce the costs associated to the capture step.

Porous solids are extensively used for the removal of gaseous contaminants in air, and Pressure Swing Adsorption (PSA) is already the system of choice for the removal of CO_2 from syngas for hydrogen production. The main drawback of adsorption processes in post-combustion CO_2 capture is the necessity of cooling and drying the flue gas. The development of a new generation of materials that would efficiently adsorb CO_2 at moderate temperatures, will undoubtedly enhance the competitiveness of adsorption separation in flue gas applications [2]. Basic alumina can be used directly as an adsorbent for the removal and recovery of CO_2 from power plant flue gases, due to its high resistance to steam and good mechanical and thermal stability properties [3]. However, it would be desirable to improve its capacity for adsorbing CO_2, especially above room temperature. The enhancement of a specific adsorption capacity may be carried out by promoting chemisorption through impregnation with chemicals that react reversibly with CO_2, such as amines. There have been a number of studies on the immobilization of amines for different purposes [4–15]. In this work several compounds were evaluated as potential sources of amine groups for producing high efficiency CO_2 sorbents.

Apart from being energy intensive, one of the main drawbacks of amine scrubbing is the solvent losses associated to the high volatility of amines. Thus, one of the objectives of this work was to study the influence of the support on the thermal stability of amines. However, the main aim was to study the capture performance of the sorbents under different conditions, in order to select the suitable impregnate and operating temperature for the adsorption process. The standardized methods used in sorption measurements are gravimetric and volumetric ones [16]. However, these methods are very time consuming. Simple and

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1388–6150/$20.00

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short experiments in a thermobalance allow rational decisions to be made in a preliminary screening where multiple variables are being considered. In just one experiment, the capacity of an adsorbent can be evaluated over an entire temperature range; likewise, qualitative information about the initial adsorption rates can be obtained. Thermogravimetry, which has been previously applied to the preparation and characterization of adsorbents [17–21], has also proved to be a useful technique for preliminary adsorption capacity assessment.

Experimental

Materials

A commercial activated alumina, here referred to as A, was selected as the starting material. This partially hydroxylated aluminium oxide has a pore system consisting mainly of meso- and macropores, which has proved to be highly suitable for impregnation purposes. The textural characterization of A showed a mesoporous volume of 0.327 mL g^{-1} calculated by the density functional theory (DFT) method from the N_2 adsorption isotherm at 77 K [22].

A series of sorbents were obtained by loading A with the following compounds: diethylenetriamine (DETA), diisopropanolamine (DIPA), triethanolamine (TEA), 2-amino-2-methyl-1,3-propanediol (AMPD), pentaethylenehexamine (PEHA), and polyethyleneimine (PEI). These compounds were selected due to their different composition and structure: DIPA is a commercially used alkanolamine, AMPD a sterically hindered alkanolamine and TEA is a tertiary alkanolamine. DETA, PEHA and PEI are alkylamines that present a mixture of primary and secondary amine groups and differ mostly in their molecular mass. The amines were immobilized through a wet impregnation method adapted from Xu *et al.* [23]. The impregnated samples were denoted as *A–X*, where *X* represents the type of amine loaded. For series *A–X* the initial amount of amine was always 40% mass/mass with respect to the support.

The samples obtained were characterized in terms of elemental composition, surface chemistry, texture, thermal stability and CO_2 capture performance.

Methods

Chemical characterization

The prepared sorbents were subjected to proximate and ultimate analyses to quantify the degree of impregnation achieved from the increase in volatile matter and nitrogen content. In order to study the influence of impregnation on the acid-base properties of the carbon surfaces, the point of zero charge (pH_{PZC}) was estimated by a mass titration method adapted from Noh and Schwarz [24].

Textural characterization

Textural characterization of the prepared sorbents was carried out by N_2 adsorption isotherms at 77 K in a Micromeritics TriStar 3000. Prior to the measurements the samples were outgassed at room temperature under vacuum for 24 h. The apparent surface area was evaluated from the N_2 adsorption isotherm by the BET equation in the linear form proposed by Parra *et al.* [25].

Thermogravimetric study

Thermal stability tests were carried out in a thermogravimetric analyzer Setaram TGA 92 coupled to a Nicolet Nexus FTIR analyzer through a TG interface. The gas line was heated to prevent condensation of the evolved gases. These experiments involved heating the sample at a rate of 15 K min^{-1} up to 1273 K under a flow rate of 50 mL min^{-1} of Ar. Thermogravimetric analysis combined with FTIR spectroscopy provides information regarding mass changes in a sample and allows the qualitative identification of the gases evolved during thermal degradation [26].

CO_2 sorption measurements

The CO_2 adsorption and desorption performance of the sorbents was also evaluated by thermogravimetric analysis. The CO_2 capture capacity of the sorbents was determined by measuring the mass uptake of the sample when exposed to pure CO_2. Capacity was expressed as mass percentage of dry sorbent. Typically, one sphere of alumina (ca. 200 mg) was placed in a platinum crucible and suspended in the thermobalance. Prior to the adsorption measurements, the sample was dried at 373 K in 50 mL min^{-1} of Ar for 1 h, and then allowed to cool to 298 K. The flow was then changed to 50 mL min^{-1} of pure CO_2 and the temperature was maintained at 298 K for 6 h. The mass uptake during this stage was interpreted as the CO_2 capture capacity of the sample at 298 K. Afterwards, the temperature was increased at a rate of 0.2 K min^{-1} up to 373 K and the mass change was recorded to evaluate the influence of temperature upon the CO_2 adsorption capacity of the sample. Finally, the sample was kept at 373 K and then the flow was changed again to Ar to regenerate the sample.

Results and discussion

From the chemical analysis of the samples, shown in Table 1, it can be seen that impregnation greatly increased the nitrogen and carbon contents of the samples due to the contribution of the immobilized amines. The results also evidence the effectiveness of the impregnation method performed. The oxygen content of the samples impregnated with the alkanolamines (A-DIPA, A-AMPD, A-TEA) doubled that of the ones impregnated with alkylamines (A-DETA, A-PEHA, A-PEI), due to the presence of hydroxyl groups in the structure of the amines. The volatile matter (ca. 8 mass%, db) of the alumina support, A, is assigned to chemically combined water, as will be discussed below. In the case of the impregnated samples, *A–X*, the higher volatile matter content is due to the incorporation of the different types of amines.

The changes in pH_{PZC} reflect variations in the ratio between the acidic and basic surface groups of the samples. The estimated value of pH_{PZC} for A (Table 1) is in good accordance with the values found in the literature [24, 27]. Impregnation caused a slight shift in the pH_{PZC} of the sorbents towards higher values due to the immobilization of basic amine groups. The basic nature of the sorbents is expected to be favourable for their application in the adsorption of an acidic gas, such as CO_2.

However, impregnation had a negative effect on the texture of the resultant sorbents, as shown by the significant decrease in the BET surface areas presented in Table 1. This decrease is a consequence of pore blockage by the amine film.

Temperature-programmed desorption (TPD) tests were carried out on the prepared sorbents, and also on the initial amines, to check their thermal stability. Free amines decomposed in a single step below 673 K (Fig. 1a), DETA being the least stable of the tested amines and PEI the thermally most stable. The DTG curves for the support, A, and the impregnated samples are presented in Fig. 1b. The alumina support, A, showed a continuous mass loss between 373 and 1273 K with a maximum at 873 K. This is attributed to the evolution of physically adsorbed water at low temperatures, while at temperatures above 473 K it is ascribed to chemically combined water that comes from the hydroxylated nature of the aluminum oxide. For the impregnated samples the DTG curves present two main peaks followed by a shoulder around 873 K attributed to the alumina support. The first peaks appeared above 473 K and are mostly ascribed to methanol evolution, as this is the solvent used in the wet impregnation procedure. The second peaks (ca. 773 K) correspond to NH_3 evolved from the decomposition of the immobilized amine groups. In addition, the higher decomposition temperatures of

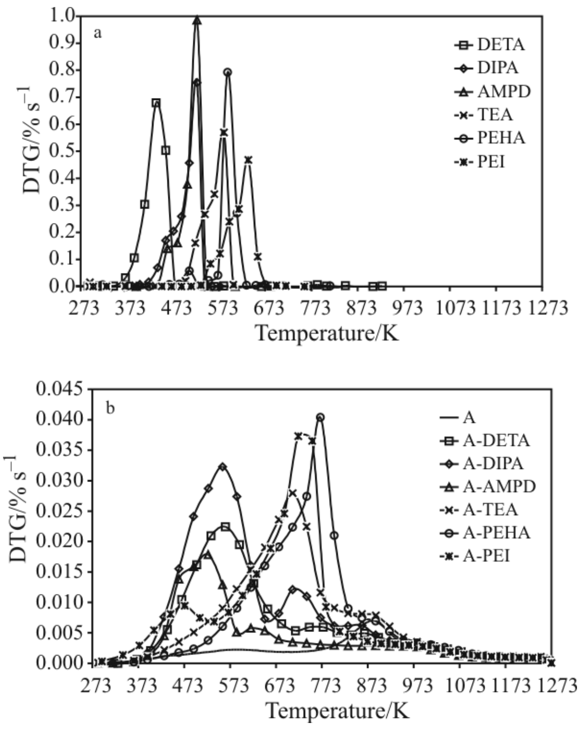

Fig. 1 Thermal stability of the amines studied: a – as-received, b – immobilized on the alumina support

Table 1 Chemical composition, point of zero charge (pH_{PZC}) and BET surface area of the samples

Sample	Proximate analysis/mass%			Ultimate analysis/mass%, db				pH_{PZC}	S_{BET}/ $m^2\ g^{-1}$
	Moisture	Ash/db	VM/db	C	H	N	O[a]		
A	7.5	83.4	7.8	0.3	1.2	0.0	15.1	9.1	271
A-DETA	5.1	80.6	19.5	7.8	2.6	6.7	2.3	10.2	60
A-DIPA	3.3	72.1	29.4	12.5	3.5	2.4	9.5	10.5	37
A-AMPD	2.4	82.9	17.1	5.5	2.0	1.5	8.1	10.2	149
A-TEA	2.5	73.3	28.4	11.1	2.9	2.1	10.6	9.6	58
A-PEHA	2.2	70.0	32.2	13.4	3.7	8.5	4.4	11.1	24
A-PEI	4.7	74.3	27.5	11.5	3.2	6.8	4.2	11.0	58

[a]calculated by difference; db: dry basis

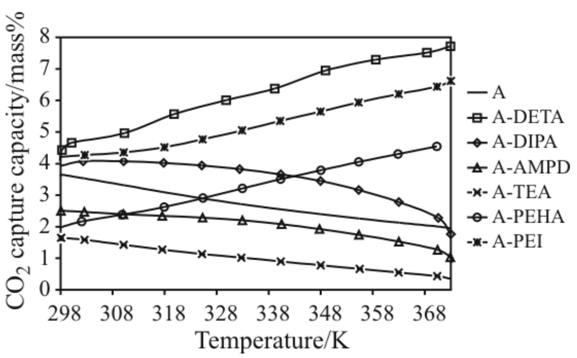

Fig. 2 Effect of temperature on the CO_2 capture capacity of the commercial alumina, A, and the immobilized amines

the supported amines compared to those of the initial liquid amines revealed that the amine groups were effectively stabilized on the alumina support by interaction forces between the amine film and the solid support.

The CO_2 adsorption and desorption potential of the prepared adsorbents was assessed using a thermogravimetric analyzer. Figure 2 displays the CO_2 capture capacities of the studied samples *vs.* temperature during the non-isothermal stage between 298 and 373 K. The alumina support, A, and the alkanolamine-impregnated samples (A-TEA, A-AMPD and A-DIPA) showed a decrease in CO_2 adsorption with increasing temperature while the alkylamine-impregnated samples (A-DETA, A-PEHA and A-PEI) presented an increase in CO_2 capture capacity from 298 to 373 K. For the raw support, A, CO_2 capture could only be due to physisorption occurring within its pore structure. However, the impregnated samples include amine type functionalities that may also contribute to the overall capture capacity. Due to the absence of water in the system, the only possible reaction between amines and CO_2 would be the formation of carbamates:

$$R_2NH+CO_2 \underset{\text{heat}}{\overset{\text{low temperature}}{\rightleftarrows}} R_2NCOO^- + R_2NH_2^+ \quad (1)$$

Carbamates can be formed only by primary and secondary amines but not by tertiary amines, such as TEA [28, 29]. Hence CO_2 adsorption on A-TEA occurs only by physisorption, showing a similar behaviour to that of the alumina support, A, although with a lower overall capacity due to the lower surface area of A-TEA (i.e., 58 *vs.* 271 $m^2 g^{-1}$ for A-TEA and A, respectively). A-AMPD also exhibited a poor performance towards CO_2 capture –CO_2 capture capacities lower than A-. This is most probably due to steric hindrance, as AMPD is by structural definition a sterically hindered amine, with a primary amine group attached to a tertiary carbon [30]. Therefore, for A-AMPD, CO_2 adsorption would proceed again mainly through physisorption in the pores. The alkylamine-impregnated samples (A-DETA, A-PEHA and A-PEI) and A-DIPA presented better performance for CO_2 capture than the alumina support, demonstrating the favourable contribution of the surface chemistry introduced by the amine immobilization.

As carbamate formation is an exothermic reaction, it might be expected that an increase in temperature would reduce the capture capacity of the impregnated samples as happens with A-DIPA. However, the contrary was observed for A-DETA, A-PEHA and A-PEI. In an analysis of the structure of these three impregnates it was found that the common factor between them is the presence of more than one amino group (primary and secondary amines) in their structure. Therefore, a possible explanation for this behaviour could be an improvement of CO_2 diffusivity through the amine film with temperature, as this would allow more amine groups to react, as previously suggested by other authors [31]. Mass transfer would be the rate limiting step for CO_2 capture in these samples, leading to a linear behaviour of CO_2 capacity with respect to temperature, as diffusivity is directly proportional to temperature. In fact, from 323 K A-DETA, A-PEHA and A-PEI showed an increase in CO_2 uptake with nearly the same slope, suggesting that this behaviour is not influenced by the type of impregnate.

Of all the prepared adsorbents A-DETA showed the highest capture capacity over the entire temperature range studied. The possibility of capturing CO_2 at temperatures such as 373 K would be an attractive advantage for the subsequent application of these sorbents, as this would reduce the need to cool the flue gases in the post combustion capture systems installed in power stations.

The effect of amine loading was also studied by preparing a series of samples impregnated with DETA. The samples were denoted as A-DETA3, A-DETA7 and A-DETA12 where the number represents their nitrogen content after impregnation (dry basis). Figure 3 shows the N_2 adsorption isotherms of

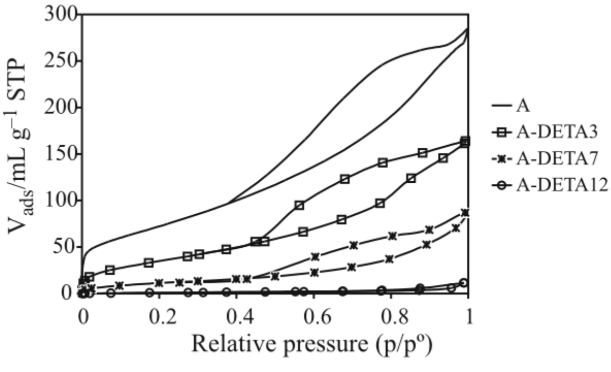

Fig. 3 N_2 adsorption isotherms measured at 77 K for the A-DETA series

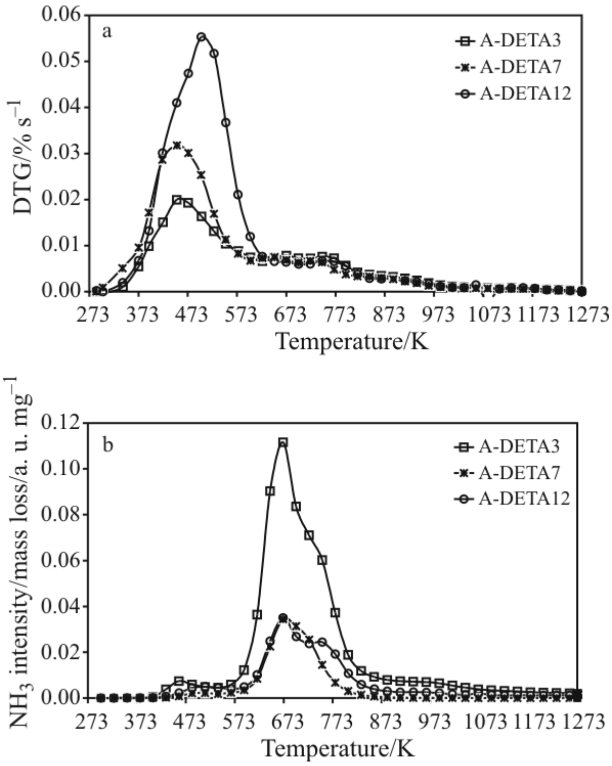

Fig. 4 Thermal stability tests for the A-DETA series: a – DTG profiles; b – NH_3 emission analyzed by FTIR

the as-prepared samples. It can be observed that a higher amine loading reduces the textural properties of the support significantly, as the amine film partially or totally fills the pore system depending on the load of amine used. A-DETA12 exhibits the maximum loading as almost all the pore system of the support is completely filled or blocked by DETA.

Thermal stability tests were also carried out for the A-DETA series, and the evolved gases were analyzed by FTIR. Figure 4 presents the DTG curves and the resulting profiles of the evolved NH_3. As the loading increases, so does the rate of mass loss. The DTG curves present two characteristic decomposition intervals: a sharp peak ca. 473 K and a softer band at around 673–773 K. The first DTG peak can be mainly assigned to water and methanol, while the latter represents mostly ammonia and ethane, from the decomposition of DETA. The evolution of NH_3 starts at 573 K and reaches a maximum at around 673 K. The aim of impregnation is to immobilize the amine on the support. However, during this process, water and methanol are thought to be trapped by the amine film in the porous system of the alumina, their contribution to mass loss being more significant for higher loadings of amine, as shown by the greater area below the first DTG peak. Thus, to evaluate the yield of the impregnation (i.e., amount of immobilized amine per total loading) the NH_3 intensities were corrected in accordance with the amount of mass loss during the TPD tests (40 mg for A-DETA3, 65 mg for A-DETA7 and 123 mg for A-DETA12). As previously mentioned, this mass loss corresponds not only to the immobilized amine but also to other volatiles, fundamentally water and methanol. A-DETA3 showed the highest NH_3 intensity per milligram of mass loss, suggesting that it was the most effective load.

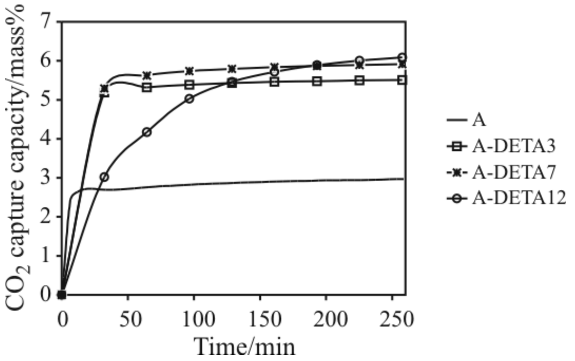

Fig. 5 Influence of amine loading on the CO_2 sorption rate of the A-DETA series at 298 K

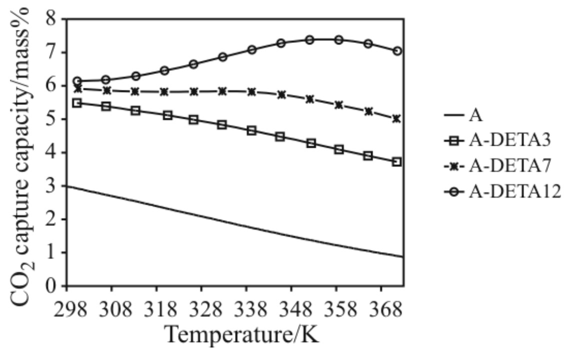

Fig. 6 Effect of temperature on the CO_2 capture capacity of the A-DETA series

The capture tests carried out on the A-DETA series (Fig. 5) showed that the CO_2 capture capacity of the raw support at 298 K was doubled by impregnation with different amounts of DETA. However, it was also observed that increasing impregnation loadings slow down the initial adsorption rate, due to resistance to mass transfer through the amine film. While A reaches its maximum capture capacity in only 17 min, A-DETA3 and A-DETA7 require 60 min, and A-DETA12 takes ca. 200 min.

Figure 6 displays the influence of temperature on the CO_2 capture capacity of the A-DETA samples. Lower loadings (A-DETA3) resulted in a sorption rate-controlled process where an increase in temperature diminished CO_2 capture capacity. As DETA load was increased, a gradual change in the rate-limiting step was observed. For A-DETA7 a stable CO_2 uptake was observed up to 343 K, while for the highest loading (A-DETA12), mass transfer seems to be the limiting step up to 363 K as shown by the promoting effect of temperature on capacity.

Conclusions

Six different amines were successfully immobilized on an alumina support through a wet impregnation method, resulting in improved thermal stability compared to that of the initial liquid amines. Furthermore, the results showed the potential of impregnating alumina with amines for CO_2 capture purposes. The sample impregnated with DETA presented the highest CO_2 capture capacity throughout the studied temperature range (298–373 K). A-DETA doubled the CO_2 capture capacity of the raw alumina at 298 K (i.e. 6 *vs.* 3 mass%). Moreover, A-DETA presented ca. 8 mass% CO_2 uptake at 373 K, whilst the raw alumina only achieved 1 mass% of CO_2 capture at the same temperature. The high CO_2 capacities achieved by the adsorbents at 373 K, and the important consequences of using them for CO_2 capture in flue gases must also be pointed out.

CO_2 adsorption on amine-impregnated alumina cannot be explained by a single process, as it can be controlled by physical/chemical sorption or by mass transfer. Therefore, the type and load of amine used to impregnate the support and the temperature of the process need to be optimized. Moreover, to produce an effective CO_2 solid sorbent a compromise between maximum capture capacity at the desired temperature and the kinetics of CO_2 adsorption (i.e., CO_2 capture rate) may be required.

Acknowledgements

This work was carried out with financial support from the Spanish MEC (Project CTM2005-03075/TECNO). M.G.P. and C.P. acknowledge the support received from the CSIC I3P Program co-financed by the European Social Fund.

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Received: March 29, 2007
Accepted: May 10, 2007

DOI: 10.1007/s10973-007-8493-x